Lecture Notes for Chem 110A
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First Part:
Chemical Thermodynamics: Introduction and Summary

The final goals of Chemical Thermodynamics are:

> When several substances mix and/or react, what general rules can we place on their (i) concentrations, and (ii) the amount of energy that can be extracted from their reaction, or, alternately, is needed to derive their reaction.

The whole course and these lecture notes (based mostly on Chapters 1-7, 9, 12 in the book of Ira Levine, *Physical Chemistry*) develop the theory leading to these results, and its interpretation. **(With a few extra lectures on Statistical Mechanics, in the much-shorter 2^{nd} part of these notes.)**

The development must proceed slowly, going from simplified to more complicated systems. We could have gone faster, but then we would be "stamp-collecting", not studying. Do not let the details, however, divert you from the main goals!

In Chapter 1 we establish the basis, by considering equations of state for the simplest system: a single component in a single phase (typically gas). We also develop a mathematical foundation, which will become very important later.

Chapter 2 discusses the implication of the conservation of energy, U. Two form of energy transfer are introduced: work (ordered transfer) w and heat (disordered transfer) q. The conservation of energy law (1^{st} law),

$$U = q + w$$

with $dw_{\text{mech}} = -PdV$, is then elucidated in numerous examples, which have two main purposes: (i) Demonstrate that while energy is a state function (path independent), w and q separately are path-dependent; (ii) and show that one can, using laboratory measurements, extract U and the enthalpy, $H \equiv U + PV$.

The partial derivatives introduced in Chapter 1 are then shown to have physical meanings – the heat capacities, which are the amounts of heat a body absorbs for a 1K (Kelvin) rise in T under different constraints, are shown to be the partial derivatives of H and U.

The conservation of energy is one of the two foundations of thermodynamics. It is supplemented in Chapter 3 by the second law, which generalizes a simple observation: disorder always increases in nature. The disorder is labeled as "entropy", S, which is a state function. We write the second law as

$$dS_{\text{world}} = \frac{dq_{\text{world}}}{T} \geq 0$$

where S_{world} is the total world entropy.

We divide the "world" to system + environment. Only S_{world} must increase or at least non-decrease. Thus, for a given system, the entropy of the system, S, may decrease if $S_{\text{environment}}$ increases sufficiently.

In Chapter 3 we study this law and show how S can be estimated in different circumstances. This will also lead to the understating of the efficiency and performance of engines and air-conditions and heat-pumps.

For example, we'll understand how a heat pump can input 5kW (kilo-Watt) to a room while only taking 1kW from an electrical outlet, by removing 4kW from the cold ground and depositing that to the (hotter) room.

The formal connection between thermodynamics and chemistry is outlined in Chapter 4. A few simple mathematical manipulations convert the second law ($dS_{\text{world}} \geq 0$) to an equation for the system variables only, $dS \geq \frac{dq}{T}$, which yields a rule:

> The Gibbs Free energy, $\boldsymbol{G \equiv H - ST}$, will be at a minimum for systems at constant $\boldsymbol{T}$ and $\boldsymbol{P}$ if no electrical energy is given or taken.

Then we use this rule to derive a very powerful theorem:

> For a fixed T and P, a substance is in equilibrium between two phases (say gas and liquid) if, and only if, the chemical potential of the substance in one phase is the same as in the other phase, $\mu_1 = \mu_2$, where the chemical potential μ is defined in Chapter 4 in terms of the Gibbs Free energy,
>
> $$\mu = \frac{\partial G}{\partial n}.$$

This statement is then extended by a more general statement which is valid for a reacting system in equilibrium, $\sum_J \nu_J \mu_J = 0$, where "J" stands for each product or reactant species, and ν_J are the stoichiometric coefficients (positive for products, negative for reactants).

Together, these two statements conclude the first half of the course, the "physical thermodynamics" part.

In the 2nd part, Chapter 5 and beyond, we study the implications and applications of these rules.

Chapter 5 is essentially a "list of definitions" chapter with a short review of familiar concepts, like enthalpy of reaction and enthalpy of formation, concepts which intimately tie to measurable quantities.

Chapter 6 derives the simple **pressure dependence** of the chemical potential and uses the relation $\sum_J \nu_J \mu_J = 0$, to derive the equilibrium constant for a **reacting ideal gas** (which you learned without proof in first-year chem.). The **temperature dependence** of the chemical potential is then used to derive the corresponding dependence of the equilibrium constant on T.

We'll then understand qualitatively the trends of the partial pressures (and densities) with changing total pressure or changing temperature, using:

> **LeChatelier's principle** – a system partially fights any changes induced externally.

Chapter 7 starts tackling the problem of several **phases** at once.

(i) Based on the concept of chemical potential as introduced in Chapter 4, we find what is the number of "independent variables" that can be changed without changes the number of phases

E.g., when there's equilibrium between vapor and liquid water – such as when we put some water in a closed rigid water bottle with room for vapor – then when we change one variable, e.g., the temperature, the rest (in this case the pressure of the vapor) is automatically changing.

We will elucidate the relation between the number of "intensive variables" (composition in each phase, as well as pressure and temperature) and the number of phases.

(ii) We then turn from the general case to study phase equilibrium for a single species (one-component) system and find the shape of the $P(T)$ **phase boundary line,** for, e.g., the vapor-liquid and liquid-solid separating lines; again, this will be simply based on the equality of the chemical potential.

Chapter 9 continues elucidating the several-phases case, but now we consider the chemically important problem of **mixed liquids.** The mixing increases the disorder, thereby stabilizing the mixture (formally: decreasing the chemical potential).

We also introduce concepts (partial molar volumes) that are important for the next chapter.

Chapter 12 concludes our study of multi-phase systems, in a few parts (presented in a different order from the book):

First, we continue with our discussion from Chapter 9 and derive, for two ideal liquids, the **phase diagram**, with two-phase and single-phase regions. We will also briefly study non-ideal liquids, including partially immiscible liquids. As usual, all our discussion will be obtainable or expressed in terms of the chemical potential.

Then we'll review a part which in the book is in Chapter 9. Specifically, to obtain quantitative results on the **chemical potential**, at least for **ideal liquids**, we do a trick: we first consider mixed liquids in equilibrium with their vapors, then use the chemical potentials of the vapors to infer the chemical potential for the liquids, and then change the pressure so only liquids remain!

Finally we derive, analytically, **colligative properties** (properties that depend only on the presence of a solute and not on its exact identity – beyond some general features); using again the concept of chemical potential, these colligative properties lead to an **increased stability of the liquid** if the solute has a low vapor pressure (e.g., for a solute like salt, or sugar) – e.g., boiling point increase, lower freezing temperature, and osmotic pressure.

To conclude: by the end of this first (and main) part of the course you should be able to understand general laws on how compounds mix and react based on a simple concept, the chemical potential. All of chemistry – organic reactions, biochemistry, geochemistry, etc.– can then be understood based on this basis.

Note: these notes should only **supplement** your reading and class attendance, not replace them!

Chemical Thermodynamics in half a page:

- 1st law: $dU = dq + dw,\qquad dw_{\text{mech}} = -P\,dV$

  State functions vs. path dependent functions.
- 2nd law: disorder increases, $dS_{\text{univ}} \geq 0$. S: state function. Efficiency and coefficient-of performance (c.o.p.)
- $dS_{\text{univ}} \geq 0 = dS - \frac{dq}{T}$ → $G = H - ST$ not-increasing for fixed P, T. Further:

  $$-\Delta G = \text{maximum work out (for fixed } P, T\text{)}.$$
- Substance A in two coexisting phases I, II $\mu_{A,\text{I}} = \mu_{A,\text{II}},\qquad \mu_{A,I} = \frac{\partial G}{\partial n_{A,\text{I}}}$
- $\mu_{\text{gas}} = \mu^o_{gas} + RT\ln\left(\frac{P}{P^o}\right)$ → $K(T) = e^{-\frac{\Delta G^o}{RT}}$
- The phase rule: $f = 2 + c - p$.
- Raul's law: $P_A = x_A(l)P_A^*$ ("*" means pure). Henry's law.
- Solutions $\mu_A = \mu_A^*(T) + RT\ln\frac{P_A}{P_A^*}$ → colligative properties,

$$e^{-\frac{\Delta G^o}{RT}} = \Pi a_i^{\nu_i},\quad a_i = \begin{cases} \dfrac{P_i}{P^o} \quad \text{(gases)} \\ x_i \quad \text{(solute, solvent, ideal solution)} \\ 1 \quad \text{(solids)} \end{cases}$$

(with the caveat that for a *non − ideal* solute the reference G is changed)

Greek letters

α: alpha
β: beta
γ, Γ: gamma
δ, Δ: delta
ϵ, ε : epsilon
$\phi, \varphi,\ \Phi$: phi
η: eta. (do not confuse with n)
κ: kappa.
λ: lambda
μ: mu
ν : nu (do not confuse with v, i.e., v)
ψ, Ψ: psi
o: omicron, used to label°C degree.
π, Π: pi
θ: theta
ω: omega (don't confuse with w)
ξ: xi (do not confuse with ζ).
ζ: zeta (do not confuse with J).

I. Warmup, math

1.1) Preliminaries

Thermodynamics: deals with macroscopic systems in equilibrium or near-equilibrium. A single species in a single phase (gas, liquid, solid) is characterized by

$$P, T, V, \quad n \equiv \frac{N}{N_{\text{Avogadro}}}$$

where

$$N_{\text{Avogadro}} \sim 6 * 10^{23}.$$

Of these:

- P, T are intensive: e.g., when we double the system in size (and double the particle number) then P, T are unchanged.
- V, n are extensive, i.e., proportional to the system size. We therefore often use the molar volume, $V_m \equiv \frac{V}{n}$, an intensive quantity.

1.2) Units

Usually MKS: Joule, m, K, etc. (note that occasionally we'll use cm, and for volume we'll usually use $\text{L} = 10^{-3}\text{m}^3$).

It's useful to know that

$$\boldsymbol{P^0} \equiv \mathbf{1bar} = 10^5 \text{ pascal} = 10^5 \frac{\text{N}}{\text{m}^3} = 10^5 \frac{\text{J}}{\text{m}^3} = \mathbf{100} \frac{\mathbf{J}}{\mathbf{L}}$$

and $\boldsymbol{P^0} \simeq P_{\text{room}}(\text{at sea leavel}) = \mathbf{1\ atm} \simeq \mathbf{1.02bar}$

We'll usually round $\boldsymbol{P^0} \simeq \mathbf{1\ bar}$, i.e., round $\mathbf{1atm} \simeq \mathbf{1\ bar.}$

The temperature T is always measured in Kelvin: $T(\text{K}) = T(°\text{C}) + 273.15$.

Room temperature (25°C=298.15K) will be usually rounded to $\boldsymbol{T_{\text{room}}}$ **≃300K**

1.3) Equation of state

For every specific system there is an **equation of state** relating (in our case) P, T, V and n (or if you prefer: P, T and V_m).

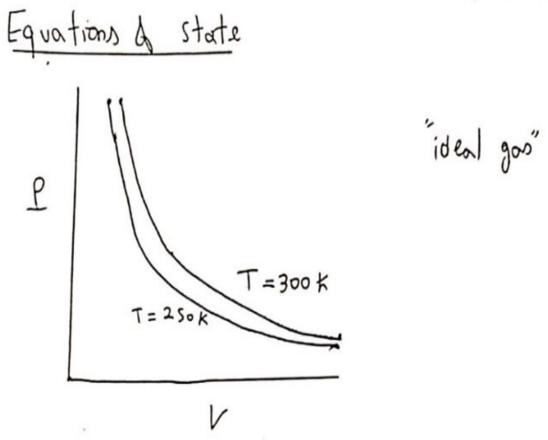
Example: ideal gases law

$$PV = nRT \qquad R \simeq 8.31 \frac{\text{J}}{\text{K mol}}.$$

Note: $PV = nRT$ **is valid only for rarified gases.** This gas law can be derived if we assume that gas particles are very small, and do not interact (and you may have seen the derivation in 14B/20B).

Shortcuts: Henceforth we'll approximate $RT_{\text{room}} = 8.31\frac{\text{J}}{\text{K mol}} \cdot 300\text{K} = 2493\frac{\text{J}}{\text{mol}}$ as

$$\boldsymbol{RT_{\text{room}} = 2500\frac{\text{J}}{\text{mol}}}$$



<u>**Example for using the gas law:**</u> molar volume of air at room pressure and temperature.

Recall that we approximate always room pressure as 1bar=100$\frac{\text{J}}{\text{L}}$.

Therefore, the molar volume of an ideal gas is:

$$V_m = \frac{V}{n} = \frac{RT_{\text{room}}}{P^o} = \frac{2500\frac{\text{J}}{\text{mol}}}{100\frac{\text{J}}{\text{L}}} = \mathbf{25\frac{L}{mol}}$$

So a mole of an ideal gas (i.e., any <u>rarefied</u> gas) occupies 25 Liter at room temperature and pressure, <u>regardless of the gas identity.</u>

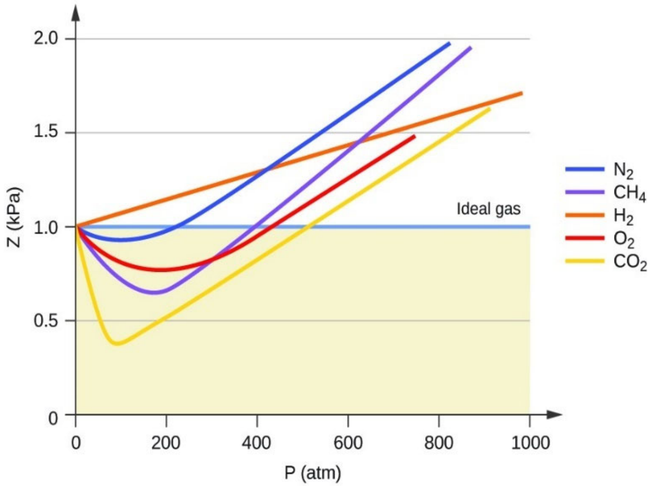
The **molar density** (note that for us <u>density refers to the number of moles per volume, not the mass per volume</u>) is

$$\frac{n}{V} = \frac{1}{V_m} = \frac{1}{25}\frac{\text{mol}}{\text{L}} = 0.04\frac{\text{mol}}{\text{L}} = 40\frac{\text{mol}}{\text{m}^3}$$

One note on ideal gases: a feature of them is that the energy depends only on the temperature, $\boldsymbol{U = U(T)}$ **(for ideal gases),** since it depends only on the velocity and internal energy of each molecule. Whether molecules are closer or further apart does not matter in an ideal gas, since they do not interact.

Word of caution: I reemphasize that **you should never apply the ideal gas law to anything but rarified gases**. It is **not valid for liquids, nor solids,** and is only qualitative, not quantitative, for highly compressed gasses (tens of bars and especially hundreds of bars or more).

1.4) Deviations from Ideal gas behavior



In practice there are small deviations from the ideal gas law already at room pressure for gases. These deviations, as we mentioned, get worse at higher pressures.

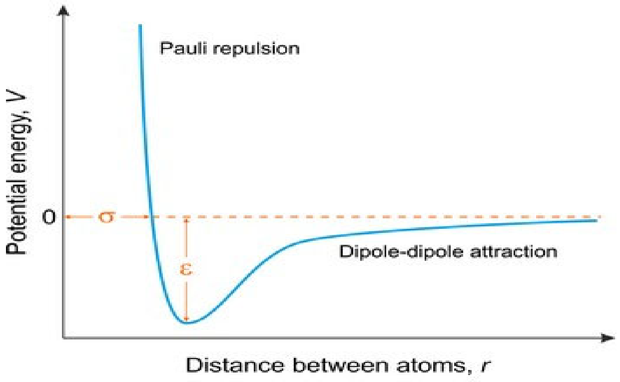
These deviations from the ideal-gas law are often quantified by a quantity labeled Z, defined as

$$Z \equiv \frac{PV}{nRT}.$$

(Word of caution: we don't have enough letters. So in statistical mechanics we use the same symbol, Z, for something completeley different, the partition function).

For an ideal gas, Z would be 1, but in real life it deviates from 1, as the figure here[1] shows – it shows Z for different gases, **all at room temperature,** as a function of pressure.

The behavior of Z relates to two aspects we ignored in the discussion of ideal gas: the **attraction** of molecules when they are fairly close; and their strong **repulsion** if they are "touching", i.e., too close. This is shown in the figure[2]



Back to the plot of Z. Note that for H_2, Z just rises with pressure. This is because there is very little attraction between different H_2 molecules. The dominant effect is repulsion; **and repulsion**

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[1] https://courses.lumenlearning.com/chemistryformajors/chapter/non-ideal-gas-behavior/

[2] https://glossary.periodni.com/glossary.php?en=Lennard-Jones+potential

tends to increase the volume and pressure since molecules want to stay away from each other.

Put differently:

> Pressure is, fundamentally, how much force (per unit area) the molecules exert on a container they are in, so:
>
> The more repulsion there is, the more they will try to move away from each other, i.e., they will try to get to the container walls, i.e., **repulsion increases the pressure.**

On the other hand, consider CO_2. Here, van der Waals attractions are strong. Attractions bring molecule together, reducing the overall volume they occupy; they are less likely to collide strongly with the container walls, so the pressure decreases.

So **attraction reduces Z**. And indeed, at 50-100 bar the pressure in CO_2 is strongly reduced compared with the ideal-gas law, so $Z \sim 0.5$.

Only at pressures of 500 bars and above (for room temperature) are the molecules in CO_2 so close that repulsion dominates, and $Z > 1$.

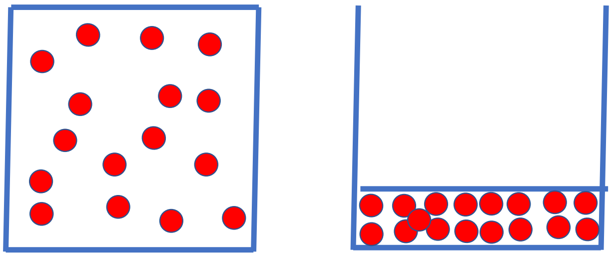
1.5) van-der-Waals (vdW) equation of state.

In the 19th century Johannes Diderik van der Waals (vdW for us) tried to come forward with a mathematical equation that incorporates repulsion and attraction.

His final equation, "derived" below, has some useful features that **are reminiscent of the transition between gases and liquids,** but it also has a non-physical feature which we'll point out (and "correct").

vdW **started** from the ideal gas equation, $P = \frac{nRT}{V} = \frac{RT}{V_m}$. Then he made modifications.

First, gases are really not point particles – they have finite extent. Think of molecules as being "billiard balls", and label the volume of a mole of such "balls" as b. This "b" should essentially be the molar volume of a liquid (see the figure).



Origin of $V_m - b$ in the vdW equation

Left: Molar volume of molecules, V_m. The molecules have a finite size; the molar size, labeled b is essentially the volume of the liquid (right). So in the left picture the **free volume (total minus "red" molecular volume)** is $V_m - b$.

So the first thing vdW did was write

$$P = \frac{RT}{V_m - b} \qquad \text{(first modification, due to repulson)}$$

The second step was that he realized that **the pressure would be reduced by attraction** between gas molecules. At a given molar volume, molecules tend, due to attraction, to cluster together, and not to hit the wall as hard as they would have done without the attraction.

vdW assumed a specific density dependent factor for the reduction of pressure due to attraction: $-\frac{a}{V_m^2}$, where a is a material-specific constant. Obviously for a weakly attracting molecule a will be tiny.

> **Comment:** to understand the form, let's start from the sign. Attraction reduces pressure; therefore the sign is negative.
>
> Now to understand the dependence on V_m^{-2}: the lower the volume, the more the particles will be in the vicinity of each other, and the more the attraction will be important.
>
> Specifically, if we were to reduce the volume by a factor of, say, 3, then the molar density would rise by a factor of 3.
>
> I.e., there will be 3 times as many particles in a volume, and each of them will "collide" and attract 3 times as many particles as before, so the attraction effect will be 3*3=9 times higher – exactly as the $\frac{a}{V_m^2}$ form predicts (since if V_m is 3 times smaller, $\frac{1}{V_m^2}$ is 9 times higher),

So the final vdW equation is

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad \text{(final vdW equation)}$$

which we can write in terms of $V = nV_m$ also as

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}.$$

In practice, for room pressure the a and b corrections are typically tiny. They become important only at high pressures. To see how small they are, consider the following example:

Example:

2 moles of air (essentially N_2) in a closed chamber, at T_{room}, and volume 100L.

Calculate the pressure inside using:

- The ideal gas equation
- The vdW equation, where the parameters for $\boldsymbol{N_2}$ **(don't use these parameters for other molecules!**) are

$$a = 1.4 \text{ bar} \frac{\text{L}^2}{\text{mol}^2}$$
$$b = 0.04 \frac{\text{L}}{\text{mol}}$$

Answer: (note that our answer is not exactly accurate since we use a rounded-number for *R*, but that's OK).

From the ideal gas law, as we derived:

$$P = \frac{RT_{\text{room}}}{V_m} = \frac{2500\,\frac{\text{J}}{\text{mol}}}{\frac{100\text{ L}}{2\text{mol}}} = 50\,\frac{\text{J}}{\text{L}} = 0.5000\text{ bar.}$$

The vdW equation gives

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{2500\,\frac{\text{J}}{\text{mol}}}{50\,\frac{\text{L}}{\text{mol}} - 0.04\,\frac{\text{L}}{\text{mol}}} - \frac{1.4\text{ bar}\,\frac{\text{L}^2}{\text{mol}^2}}{\left(50\,\frac{\text{L}}{\text{mol}}\right)^2}$$

i.e.,

$$P = (50.04 - 0.06)\,\frac{\text{J}}{\text{L}} = 49.98\,\frac{\text{J}}{\text{L}} = 0.4998\text{ bar}$$

Thus the overall vdW correction in this case was only 0.0002bar, i.e., just 0.04% of the total pressure.

Interestingly, the repulsion increased the pressure here by 0.0004 bar but the attraction negated it by 0.0006 bar, leading to the final smaller correction. So the effects of attraction and repulsion almost canceled each other in this case.

Since the vdW corrections are small, for "usual" gases (at room pressure, etc.) we can ignore these corrections and assume that the gases are ideal.

1.6) Plotting the vdW picture – physical and unphysical features.

Below we show a plot[3] of the vdW equation and using parameters for CO_2:

$$a = 3.6\text{ bar}\,\frac{\text{L}^2}{\text{mol}^2}$$
$$b = 0.043\,\frac{\text{L}}{\text{mol}}$$

The plot (next page_ shows **isotherms,** i.e., lines that are each at a (different) fixed temperature. The axes are P vs. V (really V_m).

The first thing to note is the weird blue line, i.e., the isotherm at 10°C. **It has an unphysical region** between about $V_m = 1 * 10^{-4}\text{m}^3$ to about $V_m = 1.8 * 10^{-4}\text{m}^3$ (i.e., $100\frac{\text{cm}^3}{\text{mol}}$ - $400\frac{\text{cm}^3}{\text{mol}}$). **In that range the vdW equation predicts that when the volume decreases the pressure decreases too. And that's unphysical (**consider pushing a balloon – lowering the volume must lead to a higher pressure)

A way to "fix" the incorrect region (devised by the great 19th century British scientist, Maxwell) is to replace a **portion** of the blue line between points A and B, by a straight line (dashed). Then the behavior is physical:

- For 10°C, when we start from very large molar volume, the pressure is low and the material is all gas. The material is then compressed until we get to the volume at point B.

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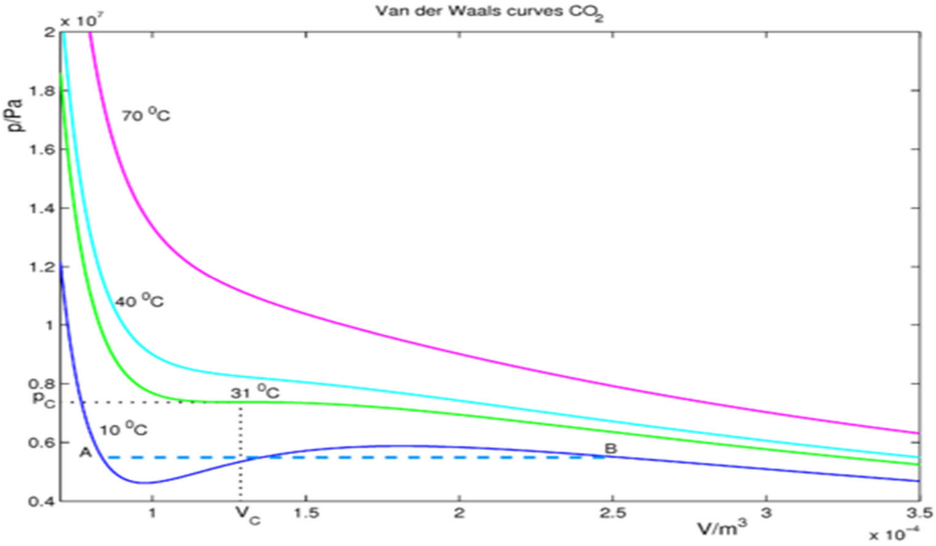
[3] https://www.tau.ac.il/~tsirel/dump/Static/knowino.org/wiki/Van_der_Waals_equation.html

At that point, as we compress the gas even lower, the isotherm goes along the dashed line, i.e., the volume is shrinking but the pressure does not.

> Note: we will see later that that's the correct physical behavior. What happens is that the system will be then, in between points B and A, in a **2-phase region – where a gas (**represented by the volume at point B) coexists with a **liquid** (represented by the volume at point A).



Different isotherms (curves of constant temperature) obeying the van der Waals equation of state, with parameters adjusted to approximately fit CO_2.

- **Above the critical temperature** (31 °C) the behavior of P vs. V is monotonic, like an ideal gas.
- Looking at a lower temperature (10 °C), the dashed line from A to B is drawn to replace the physically incorrect portion of the curve where as V decreases P also decreases. This dashed line represent the liquid-vapor transition.

- As we compress the system even further, the volume reaches that of point A, and the system is then purely a liquid. To reach below that volume we'll need to apply stronger and stronger pressures.

  This 2-phase behavior (same pressure over a range of volumes) is physical, that's what happens in reality, but of course the numbers predicted by the vdW equations, even when we used optimal parameters a, b, will not exactly match experiment – that's since the vdW equation is an approximate one.

- Next, let's talk about the behavior of the pink (magenta) line. That, at a high temperature, looks similar to the ideal-gas equation – it is monotonic, i.e., lowering the volume is accompanied by increased pressure (at fixed T). In that case the transition from "gas" to "liquid" is continuous.

- The most interesting case is then of the green line, which is at 31°C, which is the "critical temperature" for CO_2 for these parameters. It separates the temperatures where there's a liquid-vapor transition, from temperatures where the transition is continuous.

  These a, b parameters that we wrote above were chosen to reproduce the experimental critical temperature of CO_2, which is experimentally indeed 31°C.

- Above the critical temperature the behavior of P vs. V is monotonic (see the light-blue and magenta lines), i.e., the gas turns continuously to liquid and there's no pressure at which the two phases coexist;

  While for all temperatures below the critical temperature there will be a range (like the dashed line drawn here) where liquid and gas coexist.

  For water, the critical temperature is 375°C (647 K). (Much higher than for CO_2, since the attractions in water are much stronger).

  What this means is that as we compress water above that temperature there will never be a pressure where we'll see a dense phase "liquid" and a lesser dense "vapor" coexisting.

  Below that critical temperature we'll see vaporization, e.g., at 1bar for 100 °C, at 2bar for about 120°C, and at about 210bar for temperature just below the critical temperatures, i.e., around 373°C

  We'll cover this in greater detail around chapter 7.

1.7) Summary of the vdW equation of state – it is useful since:

- It shows you that the ideal gas law is just one of many possible eq. of states.
- It is more correct at high P than the ideal gas law, but even though it is still not perfect and not the "truth"
- It shows, once we "correct" for the unphysical wiggle (in which, when P increases, V also increases), that at high densities a liquid may form, so that liquids and gases are really interconnected. We'll discuss this at the end of the quarter.
- It describes qualitatively the liquid-to-gas phase transition (boiling) and the fact that at very high temperatures (above 31°C for CO_2, above 374°C for water) there is no vaporization transition – when raising the pressure the vapor goes continuously to liquid.

1.8) Mathematical prelude

We'll use a few concepts from calculus. A refresher:

Log / Ln:

For us, **log** will mean **ln,** i.e., logarithm in base "e" (while log in base 10 will be denoted as $\log_{10}$)

Integration of simple functions (of one variable)

Indefinite integrals: We'll use

$$\int dx = x, \quad \int x\, dx = \frac{x^2}{2}, \quad \int x^{-2}\, dx = -\frac{1}{x}$$

and in general

$$\int x^n\, dx = \frac{x^{n+1}}{n+1} \qquad \text{for } n \neq -1.$$

Also (generally, γ refers to a constant here)

$$\int \frac{1}{x}\, dx = \ln(x)$$

$$\int e^{\gamma x}\, dx = \frac{1}{\gamma} e^{\gamma x}$$

$$\int \ln x\ dx = x\ln(x) - x.$$

We'll prove below the last relation.

Definite integrals: similar. E.g.,

$$\int_a^b \frac{1}{x} dx = (\ln x)|_a^b = \ln b - \ln a = \ln\left(\frac{b}{a}\right)$$

$$\int_a^b x^2 dx = \left.\frac{x^2}{2}\right|_a^b = \frac{b^2}{2} - \frac{a^2}{2}.$$

Differentiation of one-dimensional functions.

You know that:

$$\frac{d}{dx} x^n = n x^{n-1}$$

$$\frac{d}{dx} e^{\gamma x} = \gamma e^{\gamma x}$$

$$\frac{d}{dx} \ln x = \frac{1}{x}$$

Exercise: what is $\frac{d}{dx}\ln(\gamma x)$, γ const.? Answer: $\frac{1}{x}$.

You need to remember:

$$\frac{d(fg)}{dx} = g\frac{df}{dx} + f\frac{dg}{dx}$$

Example – use this relation to prove the expression for the integral of $\ln x$ above:

$$\frac{d(x\ln x - x)}{dx} = \frac{dx}{dx}\ln x + x\frac{d\ln x}{dx} - \frac{dx}{dx} = 1\cdot\ln x + x\cdot\frac{1}{x} - 1 = \ln x \qquad Q.E.D.$$

Differentials:

Say we have a function of x, labeled $f(x)$. Often we vary the value of x by a little bit (Δx) and want to find out what is the change of the value of f, i.e., what is $\Delta f \equiv f(x + \Delta x) - f(x)$.

If Δx is small we can use

$$\Delta f \simeq \frac{df}{dx}\Delta x$$

where $\frac{df}{dx}$ is the derivative of f, **evaluated at the "original value"** (x) which we often can calculate from other means. If Δx is tiny, this equation above is very accurate; but even if it is just small and not tiny we can still apply it without too much error.

Example: Question – what's the variation of pressure in a piston full of one mole of air, when, at room temperature, the volume is varied by 20% from $V = 25\text{L}$ to $V = 20\text{L}$, i.e., $\Delta V = -5L$.

Exact answer

Just apply the ideal gas law for the pressures: old (labeled P) and new (labeled P_{new}).

$$P = \frac{nRT_{\text{room}}}{V} = \frac{1\text{ mol} \cdot 2500\frac{\text{J}}{\text{mol}}}{25\text{L}} = 100\frac{\text{J}}{\text{L}} = 1\text{bar}$$

$$P_{new} = \frac{1\text{ mol} \cdot 2500\frac{\text{J}}{\text{mol}}}{20\text{L}} = 125\frac{\text{J}}{\text{L}} = 1.25\text{ bar}$$

i.e.,

$$\Delta P = 0.25\text{ bar}$$

Alternate approach: let's use the formula we just learned to get an approximate answer for the change in pressure:

$$\Delta P \simeq \frac{dP}{dV}\Delta V.$$

Now evaluate the derivative, $\frac{dP}{dV}$, from the ideal gas law (remembering that $T = T_{\text{room}}$ is held fixed, so here P is a function of a single variable, V).

$$\frac{dP}{dV} = \frac{d\left(\frac{nRT}{V}\right)}{dV} = nRT\frac{d\left(\frac{1}{V}\right)}{dV} = -\frac{nRT_{\text{room}}}{V^2} = -\frac{2500\text{ J}}{(25\text{L})^2} = -4\frac{\text{J}}{\text{L}^2} = -0.04\frac{\text{bar}}{\text{L}}$$

(where we used $1\frac{\text{J}}{\text{L}} = 0.01\text{ bar}$). Therefore

$$\Delta P \simeq \frac{dP}{dV}\Delta V = 0.04\frac{\text{bar}}{\text{L}} \cdot (-5\text{L}) = 0.2\text{ bar}.$$

This is fairly close to the exact $\Delta P = 0.25\text{bar}$ value. The values are not extremely close since the variation ΔV is here quite large, 20% of the initial volume. If $\frac{\Delta V}{V}$ was smaller then the two ΔP values would have been much closer.

Derivatives of functions of 2 (or more) variables

Very similar to what we had before. Say we have a function of two variables, $z(x, y)$. Then the partial derivative $\left.\frac{\partial z}{\partial x}\right|_y$ is obtained by fixing y, and then differentiating z with respect to x as if y is constant.

Formally:

$$\left.\frac{\partial z}{\partial x}\right|_y = \lim_{\Delta x \to 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x}.$$

Example:

$$z = (x^5 + y^2)^{\frac{3}{2}}.$$

In this case:

$$\left.\frac{\partial z}{\partial x}\right|_y = \frac{3}{2}(x^5 + y^2)^{\frac{1}{2}} \cdot 5x^4$$

$$\left.\frac{\partial z}{\partial y}\right|_x = \frac{3}{2}(x^5 + y^2)^{\frac{1}{2}} \cdot 2y$$

Relations among derivatives

In the example above, we could treat y as a function of x and z.

$$y = \sqrt{z^{\frac{2}{3}} - x^5}$$

or similarly treat x as a function of y, z:

$$x = \left(z^{\frac{2}{3}} - y^2\right)^{\frac{1}{5}}.$$

We can get therefore

$$\left.\frac{\partial y}{\partial z}\right|_x, \quad \left.\frac{\partial y}{\partial x}\right|_z$$

and also

$$\left.\frac{\partial x}{\partial z}\right|_y, \quad \left.\frac{\partial x}{\partial y}\right|_z$$

Thus, there are **6** partial derivatives (for three variables). But only 2 are independent, because of the following relations (**which I presume you have seen in Calculus**):

$$\left.\frac{\partial y}{\partial x}\right|_z = \frac{1}{\left.\frac{\partial x}{\partial y}\right|_z}$$

with two similar relations,

$$\left.\frac{\partial x}{\partial z}\right|_y = \frac{1}{\left.\frac{\partial z}{\partial x}\right|_y}, \qquad \left.\frac{\partial z}{\partial y}\right|_x = \frac{1}{\left.\frac{\partial y}{\partial z}\right|_x}$$

and in addition, the **cyclic chain rule**:

$$\left.\frac{\partial y}{\partial x}\right|_z \left.\frac{\partial x}{\partial z}\right|_y \left.\frac{\partial z}{\partial y}\right|_x = -1.$$

> Note: the factor of -1 is non-intuitive in the last equation, so you need to remember it.

Therefore, there are 4 relations constraining 6 partial derivatives, and therefore **only 2 partial derivatives are independent.**

Exercise: verify that these general relations are fulfilled for the example above.

The relations among the derivatives are very useful when measuring equations of state, say of a one-component one-phase substance $P = P(V, T)$ (we'll fix n for the moment).

Of all 6 possible partial derivatives, only 2 are independent, as mentioned. Traditionally, one measures these two.

First: the thermal expansion coefficient:

$$\text{Thermal expansion coefficient: } \alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P \qquad \text{units: K}^{-1}$$

Formally, α equals the relative change in $\boldsymbol{V}$ per a change of 1K in the temperature $\boldsymbol{T}$ at fixed pressure.

> **Example**, if for some substance V was initially 20 L and changes by 0.04 L when the temperature rises 5K (while the pressure stays fixed), then $\frac{\Delta V}{V} = \frac{0.04\text{L}}{20\text{L}} = 0.002$ (i.e., 0.2%) so
>
> $$\alpha = \frac{\Delta V}{V\Delta T} = \frac{\Delta V}{V} \cdot \frac{1}{\Delta T} = 0.002 \cdot \frac{1}{5\text{K}} = \frac{0.0004}{\text{K}} = \frac{4 \cdot 10^{-4}}{\text{K}}.$$

For an ideal gas, the thermal expansion coefficient is:

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P = \frac{1}{V}\left.\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right|_P = \frac{1}{V}\frac{nR}{P} = \frac{1}{T}$$

So for room temperature $\alpha = \frac{1}{300\text{K}} \sim 0.0033\text{K}^{-1}$ (ideal gas only!). For solids and liquids however, α is very small (our body does not change its volume significantly when we have a fever!)

Second coefficient: compressibility

In addition to the thermal expansion coefficient, there's an analogous coefficient:

$$\text{Compressibility coefficient: } \kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \qquad \text{units: bar}^{-1} \text{ or atm}^{-1} \text{ or } \left(\frac{\text{N}}{\text{m}^3}\right)^{-1}$$

which is minus the relative change in $\boldsymbol{V}$ per a change in pressure, at fixed temperature $\boldsymbol{T}$.

> Note that κ is always positive -- when the pressure rises the volume decreases, so the derivative is negative, so with the minus in front it becomes positive.

For an ideal gas the compressibility is:

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T = -\frac{nRT}{V}\frac{\partial \frac{1}{P}}{\partial P}\Bigg|_T = -\frac{nRT}{V}\left(-\frac{1}{P^2}\right) = \frac{nRT}{VP}\cdot\frac{1}{P} = \frac{1}{P}$$

i.e., for an ideal gas at room pressure:

$$\kappa = \frac{1}{1\ \text{bar}}\quad \text{(ideal gas, room pressure)}$$

while liquids and solids: are hard to compress so the compressibility is much smaller ($\kappa \ll 1\text{bar}^{-1}$).

Example: when we dive into a pool the pressure rises significantly (about 0.1bar per meter). But our volume does not change appreciably!

Example: using the relations between partial derivatives – application for thermodynamics.

Let's exemplify how the relations among derivatives help us to get potentially important quantities that are difficult to measure, in terms of $\boldsymbol{\alpha}, \boldsymbol{\kappa}$ which are fairly easy to measure.

Specifically: **find** $\frac{\partial P}{\partial T}\big|_V$ in terms of α, κ.

Answer: use the **cyclic chain rule** $\frac{\partial y}{\partial x}\big|_z \frac{\partial x}{\partial z}\big|_y \frac{\partial z}{\partial y}\big|_x = -1$. In terms of the three variables here, it reads

$$\frac{\partial P}{\partial T}\bigg|_V \frac{\partial T}{\partial V}\bigg|_P \frac{\partial V}{\partial P}\bigg|_T = -1$$

So the desired derivative is

$$\frac{\partial P}{\partial T}\bigg|_V = -\frac{1}{\frac{\partial T}{\partial V}\Big|_P \frac{\partial V}{\partial P}\Big|_T}$$

And using the first rule of partial derivatives, $\frac{1}{\frac{\partial T}{\partial V}\big|_P} = \frac{\partial V}{\partial T}\big|_P$, gives

$$\frac{\partial P}{\partial T}\bigg|_V = -\frac{\frac{\partial V}{\partial T}\Big|_P}{\frac{\partial V}{\partial P}\Big|_T} = \frac{\frac{1}{V}\frac{\partial V}{\partial T}\Big|_P}{-\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T}$$

where we divided the numerator and denominator by V. Therefore:

$$\frac{\partial P}{\partial T}\bigg|_V = \frac{\alpha}{\kappa}$$

This relation is valid for every equation of state, be it ideal gas, the van der Waals equation of state, or any other equation of state.

Example for the validify of the relation above $\left.\frac{\partial P}{\partial T}\right|_V = \frac{\alpha}{\kappa}$: let's check it for an ideal gas.
In an ideal gas

$$\frac{\alpha}{\kappa} = \frac{\frac{1}{T}}{\frac{1}{P}} = \frac{P}{T} \quad \text{(ideal gas only} - \text{don't apply to other substances)}$$

while

$$\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial\left(\frac{nRT}{V}\right)}{\partial T}\right|_V = \frac{nR}{V} = \frac{P}{T} \quad \text{(ideal gas only)}$$

So the two expressions match, as promised.

Note: in the HW you will be asked to use these relations for a vdW gas

Epilogue: the relation we derived, $\left.\frac{\partial P}{\partial T}\right|_V = \frac{\alpha}{\kappa}$ is highly useful for any substance regardless of whether it is an ideal gas or not. This is because it may be very hard to directly measure $\left.\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{T}}\right|_{\boldsymbol{V}}$ for solids or liquids where it is hard to keep $\boldsymbol{V}$ constant when T changes, while it is easy to measure α and κ.

Differential of a 2-D function

We learned that if x is varied by a small Δx, then the variation in the value of a function $f(x)$ is approximately the derivative of f times the change in x, $\Delta f = \frac{df}{dx}\Delta x$.

Similarly, for a 2D function $z(x, y)$, the differential is defined as

$$\Delta z \equiv z(x + \Delta x, y + \Delta y) - z(x, y),$$

and it is related to the partial derivatives as

$$\Delta z \simeq \left.\frac{\partial z}{\partial x}\right|_y \Delta x + \left.\frac{\partial z}{\partial y}\right|_x \Delta y$$

We are not going to prove it; you probably saw this relation in calculus but if not then just accept it.

This expression is important because often we can determine (or measure) the derivatives, and then when we need to calculate the change in z for an arbitrary (but small) change in x and y we don't have to "remeasure" z.

Example: consider $P(V, T)$, for a fixed amount, $n = 2\text{mol}$ or air – assumed again to be an ideal gas.

- Initially: $V = 25\text{L}$, $T = 300\text{K}$
- Finally: $V_{\text{new}} = 23\text{L}$, $T_{\text{new}} = 310\text{K}$, i.e., $\Delta V = -2\text{L}$, $\Delta T = 10\text{K}$

Question: calculate the change in pressure both exactly (using the ideal gas law) and using the concept of a differential, and compare the results

Answer: First use the differential formula

$$\Delta P \simeq \left.\frac{\partial P}{\partial V}\right|_T \Delta V + \left.\frac{\partial P}{\partial T}\right|_P \Delta T = \left.\frac{\partial \frac{nRT}{V}}{\partial V}\right|_T \Delta V + \left.\frac{\partial \frac{nRT}{V}}{\partial T}\right|_P \Delta T$$

i.e.,

$$\Delta P \simeq -\frac{nRT}{V^2}\Delta V + \frac{nR}{V}\Delta T$$

i.e., using $RT_{room} = 2500\frac{\mathrm{J}}{\mathrm{mol}}$

$$\Delta P \simeq -2\mathrm{mol}\frac{2500\frac{\mathrm{J}}{\mathrm{mol}}}{(25\mathrm{L})^2}(-2\mathrm{L}) + 2\mathrm{mol}\frac{8.31\frac{\mathrm{J}}{\mathrm{K\,mol}}}{25\mathrm{L}}(10\mathrm{K})$$

i.e.,

$$\Delta P \simeq 16\frac{\mathrm{J}}{\mathrm{L}} + 6.7\frac{\mathrm{J}}{\mathrm{L}} = 23.7\frac{\mathrm{J}}{\mathrm{L}} = \mathbf{0.237\ bar}$$

Next, compare this to the exact answer:

$$\Delta P = P_{\mathrm{new}} - P$$

Initially we are at room temperature, so

$$P = \frac{nRT}{V} = 2\mathrm{mol}\frac{2500\frac{\mathrm{J}}{\mathrm{Kmol}}}{25\mathrm{L}} = 200\frac{\mathrm{J}}{\mathrm{L}} = 2\mathrm{bar}$$

To determine the exact final pressure, P_{new}, we can do a shortcut. The temperature went up by a factor 310/300, while the volume changed (was lowered) by a factor of 23/25, so the final pressure, being proportional to $\frac{T}{V}$ for an ideal gas, becomes

$$P_{\mathrm{new}} = \frac{\frac{310}{300}}{\frac{23}{25}}P = 1.123 \cdot 2\mathrm{bar} = 2.246\ \mathrm{bar}$$

I.e., $\Delta P = P_{\mathrm{new}} - P = \mathbf{0.246\ bar.}$

We see that the differential result (0.237 bar) agrees reasonably well (to within 4%) with the exact result (0.246 bar).

1.9) Conclusions – Chapter I

- P, T: intensive, V, n: extensive
- Units: $P^{\mathrm{o}} \equiv 1\mathrm{Atm} \simeq 1\mathrm{bar} = 10^5\frac{\mathrm{N}}{\mathrm{m}^2} = 10^5\frac{\mathrm{J}}{\mathrm{m}^3} = 100\frac{\mathrm{J}}{\mathrm{L}}$
- Molar volume and density

Examples of equations of states:

- Ideal gas law $PV = nRT$ (appropriate below ~ 100 bar, depending on the substance).

- vdW equation: $PV = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$. Small correction to ideal-gas-law until pressures of hundreds of bars. Has an unphysical region (at temperatures below the critical temperature, there will be a portion in an isotherm where, as V lowered, P is lowered too – and that's unphysical), but at least, once we "correct" this unphysical "wiggle", the vdW equation displays qualitatively the gas-liquid transition and critical temperature.

Mathematical prelude-Conclusions

- Integration of a few simple functions, differentiations.
- Differentials: , $\Delta f = \frac{df}{dx}\Delta x$.
- Partial differentiation: $z = z(x,y)$, $\left.\frac{\partial z}{\partial x}\right|_y, \left.\frac{\partial z}{\partial y}\right|_x$
- Relations: $\left.\frac{\partial y}{\partial x}\right|_z = \frac{1}{\left.\frac{\partial x}{\partial y}\right|_z}$, and chain rule $\left.\frac{\partial y}{\partial x}\right|_z \left.\frac{\partial x}{\partial z}\right|_y \left.\frac{\partial z}{\partial y}\right|_x = -1$. (Note the -1).
- General definitions: thermal expansion coeff. $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$,
- Compression coeff. $\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$
- Differentials of a 2D function: $\Delta z \simeq \left.\frac{\partial z}{\partial x}\right|_y \Delta x + \left.\frac{\partial z}{\partial y}\right|_x \Delta y$

II. The First Law

2.1) Overview

Motto: energy is conserved, but can be transferred in different ways.

Concepts: preview

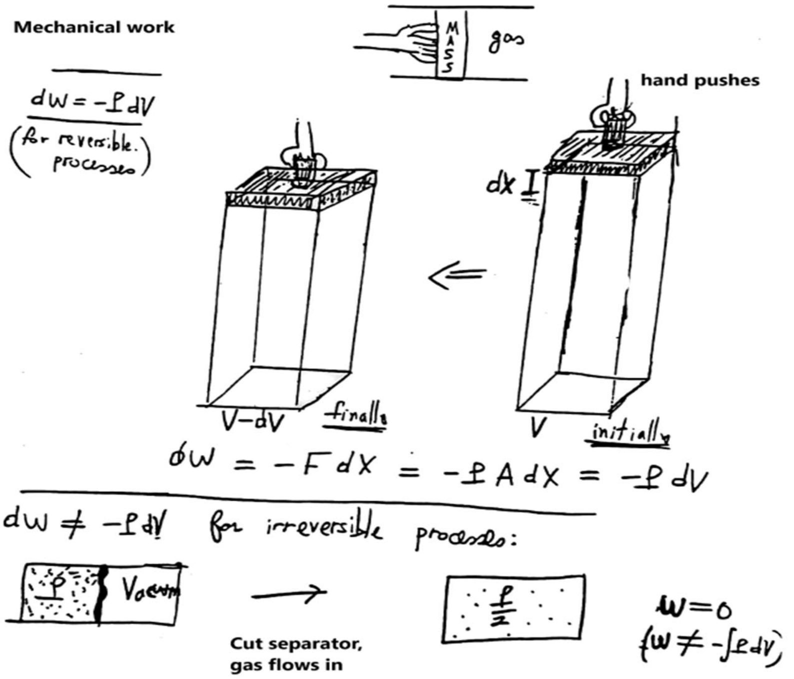
- Work: ordered energy transfer, $dw_{\text{mech}} = -PdV$. Heat: disordered energy transfer (dq)
- First law: energy change= $dU = dq + dw$; q, w: both path dependent; U isn't.
- Reversible and irreversible processes.
- Examples: gases in piston (isobaric, isochoric, isothermal expansions)
- Heat capacity: $dq = C_V dT$ or $dq = C_P dT$.
- Properties of C_P, C_V.
- Enthalpy ("trick") $H = U + PV,\ dH = dq + VdP + dw_{\text{non-mech}}$
- Examples of using enthalpy
- Adiabatic expansion (**difficult!**)

2.2) Work and Heat

Energy can be transferred by **work or heat.**

Work refers to: **ordered motion** (see figure). Work can be mechanical (**i.e., pushing)**, or also **electrical**.

The amount of mechanical work can be derived by considering a piston, of area A, moving in the x direction.



We know that the amount of energy given to the system is **force*distance.** So when the piston moves, the work done on it (more formally, the energy given to it in the form of work) is:

$$dw = -F dx$$

The reason for the **minus**: we measure energy for the **system**, which is here the gas in the piston. So **if dx is negative**, i.e., the piston is compressed, then it is being "pushed" by the environment, i.e., energy is **given to the system** in the form of work so dw should be positive.

But since the force **is pressure*area**, $F = PA$, then

$$dw = -PA\, dx = -P\, dV$$

where we used $dV = A\, dx$ as the change of the volume of the gas in the piston.

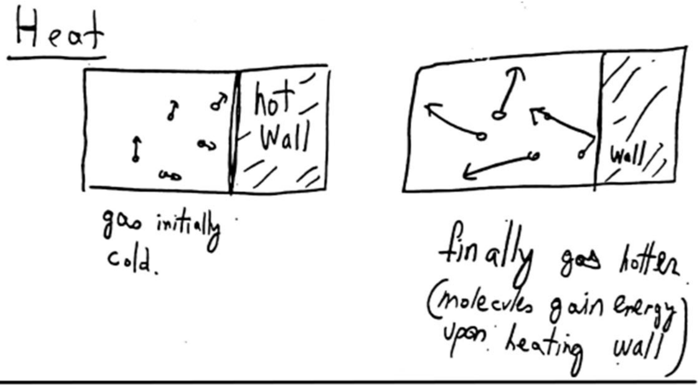
> Note that this work is mechanical, so we should have labeled it as w_{mech}. We will abbreviate w_{mech} as w in this chapter, but remember that we could have also electrical work (e.g., electrons coming from an outlet) – we won't discuss electrical work in this chapter but will incorporate it in Chapter 4.

The $dw = -PdV$ relation was derived for a tiny change. For a big change we need to **sum** the small changes, i.e., **integrate**

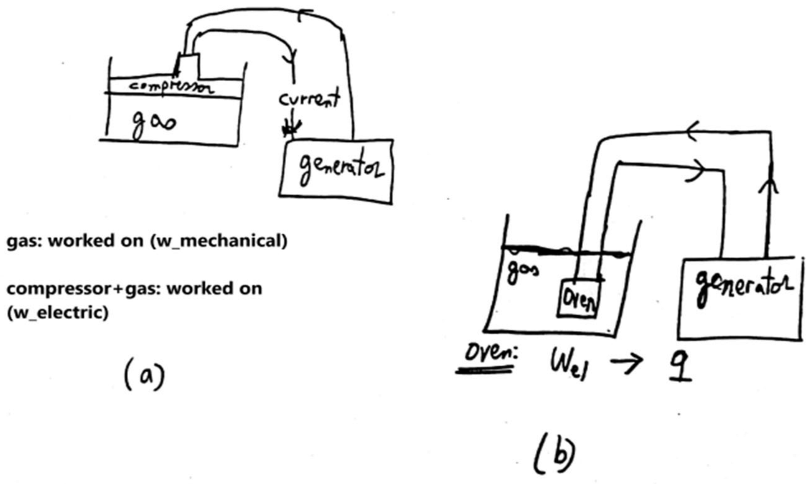
$$w = -\int P\, dV$$

Reversible and Irreversible processes

A note on reversible work. Strictly, $dw = -PdV$ is only valid for **reversible processes**, i.e., processes that **with a little change can be reversed at any stage**. In our case this means that the pressure inside and outside almost match, so that a tiny raise or decrease of the outside pressure will cause compression or expansion.



Energy transfer depends on system's definition.



An example of an **irreversible work** is puncturing a hole (small or large, doesn't matter) in a separation in a container, in which one side is full of gas and the other is in vacuum. Then the gas expands from one chamber to the other, without doing work, **since there was no counter force.** See figure in the previous page.

Note that if the hole is small we can **stop** the process by a tiny change, but we still can't **reverse it** by a tiny change.

Next: heat.

Heat.

Transfer by heat means obtaining energy by disordered motion. Colloquially we'll say we give heat to the system, but remember that the formal definition (**transfer by heat**) is the true one.

See figure above.

2.3) The first law:

The change in energy = amount transferred by ordered motion+ amount transferred by disordered motion.

If the amounts transferred are tiny, we write

$$dU = dq + dw.$$

If we sum up many changes, then:

$$\Delta U = q + w$$

where ΔU is the total change in energy.

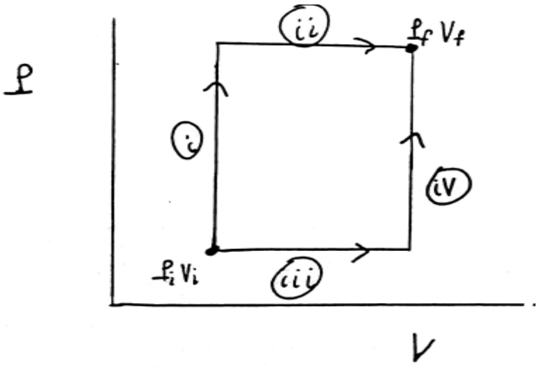
Note that when heat only (no work) is given to the system, the energy rises, and T rises.

> Careful – this isn't necessarily true when work is involved.
>
> Example: If $dq = 10\text{J}$ but $dw = -30\text{J}$, i.e., we extract work while giving heat, then $dU = -20\text{J} < 0$ and the system's temperature will decrease while the heat input is positive!

<u>Important: we can get from one initial condition to another using different amounts of q, w (but the same $q + w$, i.e., ΔU).</u>

Example: paths in P, V diagram

We will **exemplify** using a piston with <u>one mole of monoatomic gas</u> (He, Ne, etc.)



Before starting, <u>we need now to know the</u> **<u>energy</u>** of the gas. We learned that for all **ideal gases, the energy depends <u>only on the temperature</u> $U = U(T)$**. (In an ideal gas it does not matter to the energy if the volume is doubled or otherwise changed, since the molecules are so far away they don't interact).

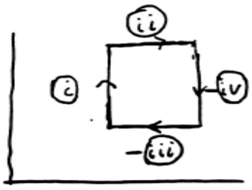
This is true for all ideal gases, i.e., gases where the molecules are far enough from each other. In fact, that's the **definition** of an ideal gas (gas where $U = U(T)$ only).

But for monoatomic gases we can know more than that. We'll assume, without proof, that for monoatomic gases the energy is

$$U = \frac{3}{2}nRT \qquad \text{monoatomic gases}$$

You may have seen a proof of it in 1st -year chemistry.

<u>Cyclic:</u>



$\Delta U = 0$, but

$q \neq 0$

$(q = q_i + q_{ii} - q_{iii} - q_{iv})$

$w \neq 0.$

> BTW, the "3" in the expression above is because a particle can move in 3 dimensions – x,y,z. In some electronic devices we can make a layer where electrons behave as if they were in a 2D ideal gas, so that they are constrained to move as if on a map, i.e., they float freely in the x-y plane but are held to a specific z point (not exactly, but close). Then the "3" is replaced by "2".
>
> Separately, back to regular 3D space: non-monoatomic gases (*e.g.*, N_2, CO_2) will have the same overall kinetic energy associated with movement of their center-of-mass, but in addition will have an additional energy associated with intramolecular vibration and rotation, so their energy will be higher.

For the process indicated in the figure below, involving a mole of monoatomic gas, and where we start from $P_i = 1\text{bar}, V_i = 25\text{bar}$ and end up at $P_f = 3\text{bar}, V_f = 50\text{bar}$, we indicated two paths.

- The first path is $i + ii$, i.e., first raise the pressure at fixed volume, and then increase the volume at fixed pressure;
- The 2nd path is $iii + iv$ in the figure.

Question: Calculate: q, w for each of these two paths. Show that q, w are path dependent, while ΔU is not.

Answer: First, the initial and final temperatures. The initial T is:

$$T_i = \frac{P_i V_i}{nR} = \frac{1\text{bar } 25\text{ L}}{1\text{ mol } 8.3\frac{\text{J}}{\text{K mol}}} = \frac{100\frac{\text{J}}{\text{L}}\ 25\text{ L}}{8.3\frac{\text{J}}{\text{K}}} \simeq 300\text{K}$$

i.e., room temperature.

We don't have to do the calculation above for T_f; just notice that when going from the initial to the final point, the pressure increases threefold, and the volume twofold, and since $T \propto PV$, T rises sixfold, i.e., $T_f = 1800K$.

Now let's calculate the energies.

Since the energy depends linearly on the temperature,

$$U_i = \frac{3}{2} \cdot 1\text{mol} \cdot R \cdot 300\text{K}$$

We noticed earlier that $1\text{mol} \cdot R \cdot 300\text{K} = 2500\text{J}$, so

$$U_i = \frac{3}{2} \cdot 2500\text{J} = 3750\text{J}$$

Since U is a constant times T (**true only for a monoatomic ideal gas**) and the final temperature is 6 times higher than the initial one, then

$$U_f = 6U_i = 22500\text{J}$$

so the energy difference is

$$\boldsymbol{\Delta U} \equiv U_f - U_i = 22500\text{ J} - 3750\text{ J} = \mathbf{18750\text{ J}}.$$

Now consider path $\boldsymbol{i + ii}$. In segment i, the volume is fixed, so the work is 0:

$$w_i = -\int_i P\, dV = 0 \quad (V \text{ fixed }).$$

In segment ii the pressure is fixed, so it comes out of the work integral

$$\boldsymbol{w_{ii}} = -\int_{ii} P\, dV = -3 \text{ bar} \int_{ii} dV = -3 \text{ bar} \cdot \left(V_f - V_i\right) = -3 \cdot 100 \frac{\text{J}}{\text{L}} \cdot (50\text{L} - 25\text{L}) = \mathbf{-7500J}$$

Therefore, by the first law gives:

$$\boldsymbol{q(path\ i + ii)} = \Delta U - (w_i + w_{ii}) = 18750 \text{ J} - (-7500 \text{ J}) = \mathbf{26250\ J.}$$

Similarly, <u>for path $\boldsymbol{iii + iv}$,</u> $w_{iv} = 0$ (volume fixed throughout segment iv), while

$$w_{iii} = -\int_{iii} PdV = -1\text{bar} \cdot \left(V_f - V_i\right) = -100 \frac{\text{J}}{\text{L}} \cdot (50\text{L} - 25\text{L}) = -2500 \text{ J}$$

Since the work is less negative by 5000J then in the $i + ii$ path, the heat will be 5000J smaller (since the sum of the work and the heat is fixed, i.e., it is ΔU).

Therefore:

$$q_{iii+iv} = 21250 \text{ J}$$

So, the **amount of heat and amount of work are path dependent**.

Circular paths

To understand what we do better, consider **a circular clock-wise path (bottom part of figure two pages ago)** i.e., starting from P_i, V_i, then going in steps i, ii (i.e., first raising pressure; then raising volume); then going <u>backwards along step iv</u> (lowering pressure), finally backwards along step iii (lowering volume).

We'll label this circular path $i, ii, -iv, -iii$ ("minus" denotes backward).

Since at the end of the path we're back where we started, $\Delta U = 0$.

But the net heat and work are not 0!

For the work,

$$w = w_i + w_{ii} - w_{iv} - w_{ii} = 0 + (-7500\text{J}) - 0 - (-2500\text{J}) = -5000\text{J}$$

i.e., a net amount of 5000 J was done <u>by the system on the environment.</u>

> This is clear – within a cycle the system (the gas in the piston) pushed against a high pressure, doing a lot of work (in part ii) and was pushed back at low pressure (part -iii), where much less work was done on it.

Similarly, the net amount of heat is non-zero; the first law states $\Delta U = q + w$, i.e., in our case

$$0 = q + (-5000\text{J}) \quad \rightarrow \quad q = 5000\text{J}$$

This cycle is actually our **first example of** an **engine**. We'll talk later about engines, but essentially, they are **circular devices** so that in <u>each cycle</u> a **net amount of work is done by the** system (the piston), and that net work equals minus the **net amount of heat given to the system**; after each cycle the engine is back to where it was.

Work as area

You learned in calculus that if we plot a function of x ($f(x)$ vs. x), then the integral $\int_{x_a}^{x_b} \boldsymbol{f(x)dx}$ equals the area under the curve limited by $\boldsymbol{x_a \le x \le x_b}$.

Similarly, the **enclosed** area of a **closed** curve is the net **clockwise integral,** $\int_{\text{enclosed}} f(x)dx$.

As an example, the net work in the example above,

$$w_{\text{net}} = -\int_{enclosed} PdV$$

is simply (minus) the **area** of the curve, i.e., in this simple rectangle case

$$w_{\text{net}} = -(50\text{L} - 25\text{L}) \cdot (3\text{bar} - 1\text{bar}) = -50\text{ L bar} = -5000\text{ J}$$

as we got earlier.

> **Caution**: be **very careful** when applying this rule. We need the net area, which is the area within clockwise-turning regions **minus** anticlockwise. So unless you have a very simple curve, I advise to calculate the work by an actual integral

Next, to consider the first law from another angle, we'll now study:

2.4) Isothermal expansion of gases in a piston

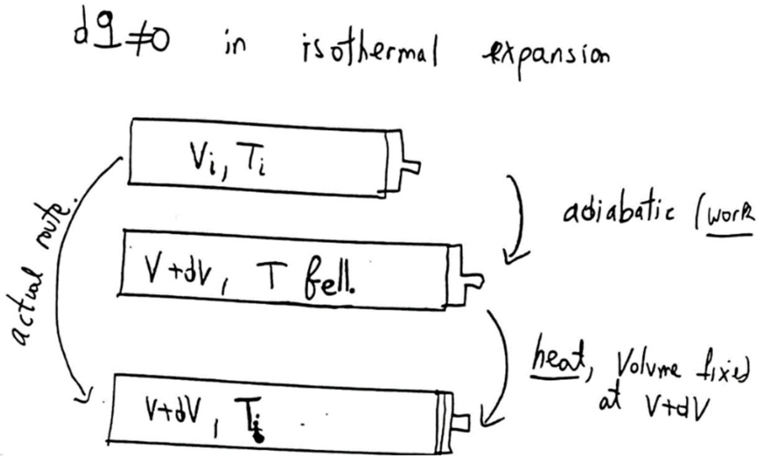
For us all gases are ideal gases (unless stated otherwise), so $P = \frac{nRT}{V}$, So P is proportional to $\frac{1}{V}$ for a fixed T.

Common mistake: thinking that since $\boldsymbol{T = \textbf{fixed}}$, $\boldsymbol{q = 0}$! **Wrong**!!

Physically, when a gas expands it does work on the environment, i.e., it spends energy. So for the energy to be conserved (and therefore for T to be conserved) heat needs to be constantly put in.

Analogy – a runner that tries NOT to lose weight while running – so continuously drinks chocolate shakes during the run, to compensate the loss of energy and fluids due to the run. (Not recommended in real life, you may get a stomachache...)

Another way to see it is to consider an infinitesimal (i.e., small) change in isothermal expansion, and break it in our minds into two small substages (see figure):



- First expanding the volume (i.e., performing work) without heat input (so T falls).
- And then, at the new volume, not expanding but pumping heat to the system so T rises again.

So say we start from P_i, V_i and expand isothermally (T=fixed throughout) to to P_f, V_f. (Since T is fixed, we need to have $P_f V_f = P_i V_i$, as both products equal nRT).

The total work done in going from P_i, V_i to P_f, V_f in an **isothermal** route (i.e., keeping the temperature fixed **throughout** the expansion) is then

$$w = -\int PdV = -\int nRT\frac{dV}{V} = -nRT\int\frac{dV}{V} = -nRT\left(\ln V_f - \ln V_i\right) = \boldsymbol{-nRT\ln\frac{V_f}{V_i}}$$

(we took the T out of the integral since it is fixed). Similarly,

$$\boldsymbol{q} = \Delta U - w = 0 - \left(-nRT\ln\frac{V_f}{V_i}\right) = \boldsymbol{nRT\ln\frac{V_f}{V_i}}$$

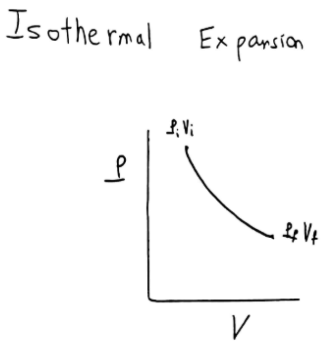
where we used the fact that U depends only on T, so it doesn't change in an isothermal expansion (so $\Delta U = 0$).

Exercise: initially $P_i = 1\text{bar}$, $V_i = 1\text{L}$. We double the volume, halving the pressure, and we do this in an isothermal process. What will be w, q?

Answer:

$$\begin{aligned} w = -nRT\ln\frac{V_f}{V_i} &= -P_iV_i\ln 2 \\ &= -1\text{bar}\cdot 1\text{L}\cdot\ln 2 \\ &= -100\text{ J}\cdot\ln 2 = -69\text{ J} \end{aligned}$$

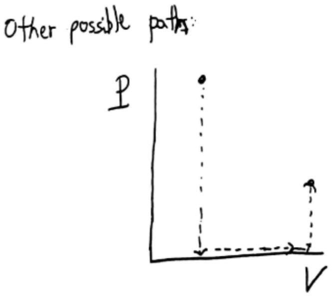
And $q = 69\text{J}$. (Note that instead of calculating nRT, I got its value using the ideal gas law, $nRT = PV$.)



$P_i\cdot V_i = P_f\cdot V_f (= nRT)$
$W < 0.$

Again I caution – this result for w is only true if the WHOLE process is isothermal, i.e., T is kept fixed throughout the expansion.

The figure on the right shows two paths: an isothermal route and another path where there's almost no work **(think on why $\boldsymbol{w \simeq 0}$ for that 2nd path on the right)**.



$\underline{\underline{W \approx 0}}\,!$

2.5) Heat Capacity

So far we understood $dU = dw$, followed what q & w mean, and quantified $dw = -PdV$.

Now we'll **quantify $\boldsymbol{dq}$.** A general quantification is difficult at this stage – wait till next chapter. But already now, for different physical circumstances we can **quantify the relation between $\boldsymbol{dq}$ and $\boldsymbol{dT}$.**

This is important since it is usually easy to measure how much heat is input to a system, i.e., what's $\boldsymbol{dq}$, and also easy to measure $\boldsymbol{dT}$.

In the first two cases we'll quantify, **$\boldsymbol{dq}$ is proportional to $\boldsymbol{dT}$**

i) When we do experiments where V is strictly constant (hard to realize exactly for solids and liquids), we'll label by C_V the proportionality constant between dq and dT:

$$C_V = \frac{dq}{dT} \quad \text{for fixed V}$$

i.e., $dq = C_V\, dT$ at fixed volume. C_V is labeled as the heat capacity at constant volume, and we define also the **molar heat capacity at constant volume** as

$$C_{Vm} = \frac{C_V}{n}$$

ii) Similarly, when P is fixed (much easier to do in the lab), we'll define the heat capacity at const. pressure as $dq = C_P\, dT$, i.e.,

$$C_P = \frac{dq}{dT} \quad \text{for fixed } P$$

iii) However, there's no heat capacity associated with isothermal processes (where dT=0) – where we saw earlier that $dq \neq 0$. So we CAN'T write then $dq = C_T dT$ WRONG!

> Later we'll see that **even though q is not a state-function** (i.e.., it depends on history, not just on the present state), **dq is RELATED to a change of a state function**, labeled the entropy, S; specifically $dq = T\, dS$.

C_V : general relation

First, let's establish a simple relation between C_V and the energy.

The first law says $dq = dU - dw$. But for fixed volume process $dw = 0$, so

$$dq = dU \text{ (for } V \text{ fixed).}$$

Therefore,

$$C_V = \frac{dq}{dT}(V \text{ fixed}) = \frac{dU}{dT}(V \text{ fixed})$$

i.e., mathematically the heat capacity at fixed volume is the **partial derivative of the energy w.r.t. temperature at fixed volume**

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V \quad \text{generally.}$$

This expression above simplifies for ideal gases, where the energy depends only on temperature, ($U = U(T)$ for ideal gases), since for those the partial derivative becomes a regular derivative

$$C_V = \frac{dU}{dT} \quad \text{for ideal gases (only!).}$$

Further, for the simplest ideal gases, i.e., monoatomic ideal gases (He, Ne, Ar, ...), we can easily calculate C_V; recall that $U = \frac{3}{2}nRT$ for monoatomic ideal-gases, and therefore

$$C_V = \frac{d\frac{3}{2}nRT}{dT} = \frac{3}{2}nR \quad \text{for monoatomic ideal gases.}$$

i.e., the molar heat capacity is simply 1.5R for monoatomic ideal gases

$$C_{Vm} \equiv \frac{C_V}{n} = \frac{3}{2}R \quad \text{for monoatomic ideal gases.}$$

We need to wait to Statistical Mechanics to prove this; but we can understand this physically- -- as we raise the temperature each "degree of freedom" (i.e., the kinetic energy associated with moving in the x, y or z direction) gets more energy.

C_V and degrees-of-freedom

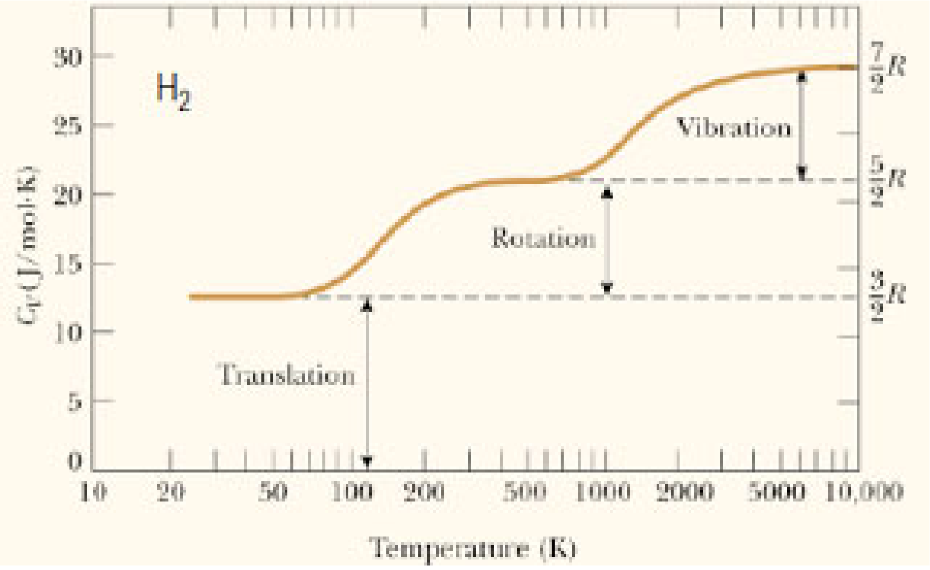
What happens when we go to diatomics, triatomics, and bigger and bigger molecules? Then C_V rises, because, when we raise the temperature by 1K, we NOT ONLY raise the kinetic energy, but also raise the intermolecular rotational and vibrational energy.

C_V will approximately fulfill:

$$C_{Vm} \simeq \frac{R}{2} \cdot (\text{Number of active DOF })$$

(DOF means Degrees of Freedom). Basically, the bigger the molecule the more degrees of freedom it has, so C_V rises. This relation above is qualitatively valid for gases, liquids, and solids. Its meaning is made more precise and it is proved in Stat. Mech.

Example: Diatomic gases: (e.g., $\mathrm{H_2}$, $\mathrm{O_2}$, NO, $\mathrm{N_2}$, $\mathrm{Cl_2}$).
Quite interesting! – see C_{V_m} for H_2 below.[4]



Here, at low temperatures, C_{V_m} is only 3R/2, like a monoatoic gas. That's because at low T, H_2 does not have enough energy even to rotate, so only its center-of-mass kinetic motion is "active".

This will be true up to a temperature-range around a temperature that we label T_R (the subscript "R" refers to "rotation", and is unrelated to the gas constant "R").

As you see from the figure T_R is around 100K for H_2.

> For O_2 or other heavy diatomics T_R is much lower, around 15K or lower. So O_2 can rotate freely already above 15K-20K. This is because it is more classical due to the higher masses. This is covered in 110B

Above T_R (i.e., from way below room temperatures to much beyond it) the diatomic molecule can rotate -- so then 5 degrees of freedom are active (3 center-of-mass, 2 rotations for this linear molecule – see class), so $C_{V_m} = \frac{5}{2} R$.

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[4] https://www.miniphysics.com/uy1-crisis-for-equipartition-theorem.html

At very high temperatures the molecules can start vibrating. This happens around $T_{vib} \simeq$1000-2000K for H_2 (and a similar temperature for O_2, N_2, NO, or other light, fairly rigid diatomics; for floppier diatomics such as I_2, T_{vib} would be only a few hundred Kelvin).

> Note: T_{vib} will approximately fulfill $k_B T_{\text{vib}} \sim \frac{1}{3}\ h\nu_{vib}$ where ν_{vib} is the vibrational frequency of the diatomic bond which is around 20-100 THz; here $k_B = \text{Boltzman's constant} \equiv \frac{R}{N_{\text{Avogadro}}} = 1.38 * 10^{-23} \frac{\text{J}}{\text{K}}$.

If $T \ll T_{\text{vib}}$ then only the ground vibrational state is populated, but starting at $T \sim T_{\text{vib}}$ more states are "active".

One complication is that each "active" vibration gives two DOF (one associated with the kinetic energy and one with the potential energy).

Thus at high temperature $C_{\text{V}} \sim \frac{7}{2} R$ for diatomics (3 kinetic DOF, 2 rotational, and 2 vibrational).

C_P

C_P is almost always larger than C_V. Physically that's because when we raise the temperature at a fixed pressure, a substance will almost always also increase its volume.

> A famous exception is water shrinking between 0 and 4°C due to breaking of H bonds; but the effect is really tiny.

So in the typical case, when we give heat to a substance at a fixed pressure, part of each amount of heat we give needs to also go to "pushing" the environment as it expands, i.e., to work.

Example:

Say that for a certain amount of a certain gas we need to give $dq = 500$ J to raise its temperature by 5K at a fixed volume. So $C_V = \frac{500\text{ J}}{5\text{K}} = 100 \frac{\text{J}}{\text{K}}$ for this gas.

At fixed volume all that $dq = 500$J goes to raise the energy.

But when we the give the same amount dq at a fixed pressure, the gas expands, doing work of, say, 100J on the environment, so $dw = -100$J,
i.e., dU will now be only $dq + dw = 500 - 100 = 400$J, i.e., 80% of what is was earlier.

Therefore, since the energy and temperature change are proportional, the temperature change in the second, fixed-pressure case will be 80% of what it was at fixed volume:

$$dT_{\text{fixed P}} = 80\% * dT_{\text{before}} = 0.8 * 5\text{K} = 4\text{K}$$

and therefore

$$C_P = \frac{dq}{dT} = \frac{500\text{J}}{4\text{K}} = 125 \frac{\text{J}}{\text{K}} > C_V = 100 \frac{\text{J}}{\text{K}}$$

We'll soon see that for gases, $C_{Pm} = C_{Vm} + R$, while for liquids/solids $C_{Pm} \simeq C_{Vm}$; i.e., for **condensed phases – liquids and solids --** C_{Pm} is only a tiny bit slightly larger (or, rarely, slightly smaller) than C_{Vm}.

2.6) Enthalpy

We related earlier C_V to a partial derivative, $C_V = \frac{\partial U}{\partial T}\Big|_V$.

Now let's do the same for C_P!

Recall first that the 1st law, when written with both forms of the work, **mechanical and electronic,** explicitly, is

$$dU = dq + dw = dq + dw_{\text{mech}} + dw_{\text{elec}}$$

i.e.

$$dU = dq - PdV + dw_{\text{elec}}$$

(we usually ignore dw_{elec} but it is time to introduce it again, at least temporarily).

To "get rid" of the $-PdV$ term, define the **enthalpy**:

$$H = U + PV$$

Calculus Insert: we know that for any two functions f, g

$$\frac{d(fg)}{dx} = f\frac{dg}{dx} + g\frac{df}{dx}$$

Multiply by dx, to get

$$d(fg) = fdg + gdf$$

Now apply it on the "PV" tern to get

$$d(PV) = PdV + dP$$

Therefore:

$$dH = dU + d(PV) = dU + PdV + VdP$$

i.e.,

$$dH = (dq - PdV + dw_{\text{elec}}) + PdV + VdP$$

The terms in red cancel each other, so

$$dH = dq + VdP + dw_{\text{elec}}$$

In the remainder of this chapter $dw_{\text{elec}} = 0$, as before. Then

$$dH = dq + VdP$$

So, for processes where the pressure is fixed:

$$dH = dq \quad (P \text{ fixed}, dw_{\text{elec}} = 0)$$

which we also write (the "P" subscript means: P is fixed)

$$dH = dq_P$$

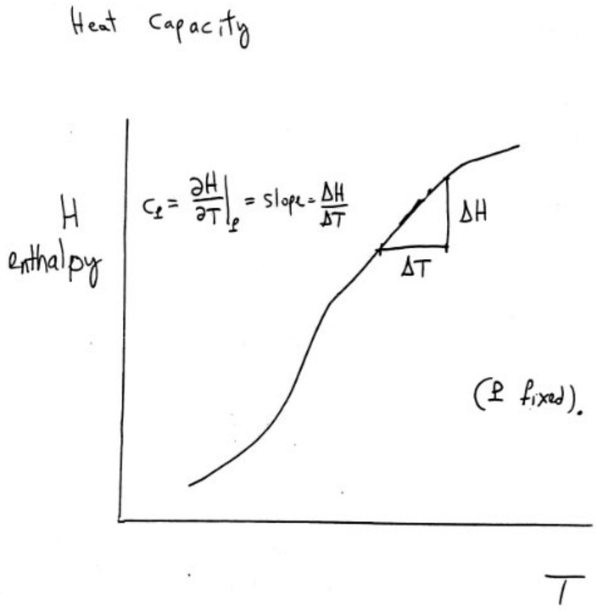
Therefore, for heat transfer at fixed pressure:

$$dH = dq_P = C_P dT$$

i.e.

$$C_P = \frac{dq_P}{dT} = \left(\frac{dH}{dT}\right)_{P \text{ fixed}} = \left.\frac{\partial H}{\partial T}\right|_P$$

Therefore: If C_P is constant in a given range of temepratures (for a fixed P) then H rises linearly with T (at that P):



$$H(T_f, P) - H(T_i, P) = \int dH = \int C_P dT \simeq C_P \cdot (T_f - T_i)$$

See figure above.

> Another more general observation is that since it is easy to measure heat-input, and since we usually do chemistry reaction experiments at a fixed pressure, the **relation $dH = dq_P$ implies that it is easy to measure fixed pressure enthalpy differences. Therefore, Tables of Reaction will always show the enthalpies of chemical substances, rather than the energies, since enthalpies are easier to measure.**

Example for getting C_p from H

Say we know

$$H = anTP^2 + \mathrm{n}(bT + \beta P)^3$$

(some crazy function I invented). Then

$$U = anTP^2 + n(bT + \beta P)^3 - PV$$

Question: determine C_P, C_V.

The first is easy:

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P = anP^2 + 3nb(bT + \beta P)^2$$

But $C_V = \left.\frac{\partial H}{\partial T}\right|_V$ cannot yet be determined since we can't differentiate the terms in U at fixed volume! For example, let's try differentiating the first term:

$$\left.\frac{\partial aTP^2}{\partial T}\right|_V = aP^2 + aT\left.\frac{\partial P^2}{\partial T}\right|_V = aP^2 + 2aTP\left.\frac{\partial P}{\partial T}\right|_V = ?$$

and we can't determine it since we don't know yet what's $\left.\frac{\partial P}{\partial T}\right|_V$.

End of example.

2.7) Relation between C_P and C_V for ideal gases

For ideal gases, the partial derivatives simplify.

As we mentioned C_V becomes a regular derivative since U depends only on T, $U = U(T)$; so

$$C_V = \frac{dU}{dT} \quad \text{(ideal gases only)}$$

Similarly, for ideal gases the PV term only depends on temerpatuee, so $H = U + PV = U(T) + nRT$, i.e., for ideal gases $H = H(T)$, so C_P becomes a regular derivative, $C_P = \frac{dH}{dT}$ (ideal gases only).

Therefore:

$$C_P - C_V = \frac{dH}{dT} - \frac{dU}{dT} = \frac{d(nRT)}{dT} \quad \text{(ideal gases only)}$$

i.e.,

$$C_P - C_V = nR \quad \text{(ideal gases only!)}$$

or

$$C_{Pm} - C_{Vm} = R \quad \text{(ideal gases only).}$$

This is true for any ideal gas.

C_P for monoatomic gases:

We know that for monoatomic gases $C_{V_m} = \frac{3}{2}R$, so $C_{P_m} = \frac{5}{2}R$ (He, Ne, etc.)

Example: **How much heat** do we need to give to a 1 kg of Helium to raise it from −20°C to +100°C at **room pressure.** And what's the **energy difference**.

Answer: 1kg=1,000g, so it contains $n = 250$mol of He. So

$$C_P = \frac{5}{2}nR = \frac{5}{2}\cdot 250\text{mol}\cdot 8.31\frac{\text{J}}{\text{K mol}} \simeq 5{,}200\frac{\text{J}}{\text{K}}$$

(Note: that's ignoring the heat capacity of the container, which may or may not be justified – you need to check that depending on the container mass and heat-capacity.)

So

$$q = C_P\Delta T = 5{,}200\frac{\text{J}}{\text{K}}\cdot 120\text{K} = 624{,}000\text{J} = 624\text{kJ}$$

And that's of course also the enthalpy difference, $\Delta H = 624$kJ.

The energy difference is

$$U = \frac{3}{2}nRT \rightarrow \Delta U = \frac{3}{2}nR\,\Delta T = \frac{3}{2}\cdot 250\text{mol}\cdot 8.31\frac{\text{J}}{\text{K mol}}\cdot 120\text{K} \simeq 374\text{ kJ}$$

Note that the same energy difference would have been obtained if we wrote

$$\Delta U = \int_i^f dU = \int_i^f \frac{dU}{dT}dT = \int_i^f \boldsymbol{C_V}dT = \boldsymbol{C_V}\,\Delta T = \frac{3}{2}nR\,\Delta T$$

You are most likely **confused on how come we use C_V here for the energy calculation, when the volume is not fixed.** The answer is that for ideal gases, since U depends only on T, the derivative $\boldsymbol{\frac{dU}{dT}}$ is independent of what is fixed – volume, pressure, etc., so we can apply it in any circumstance.

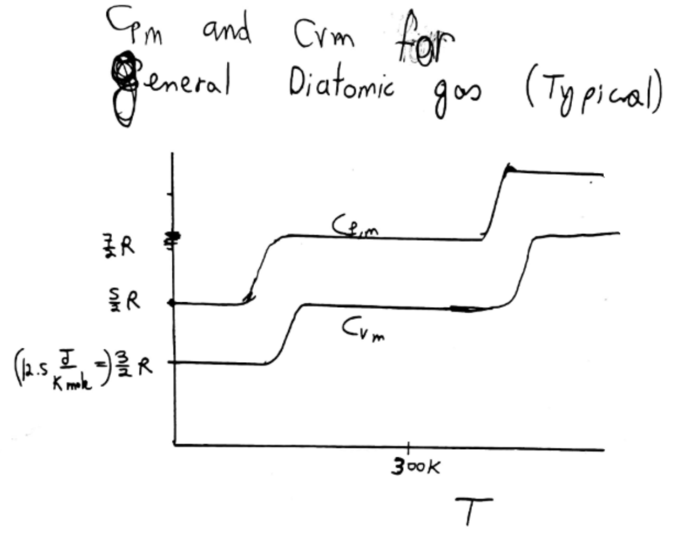
I.e.,

- To MEASURE $\frac{dU}{dT}$ we may do an experiment where V is fixed, measure the heat input per dT, then obtaining it as C_V ,
- But once we measure $C_V = \frac{dU}{dT}$ we can apply $\frac{dU}{dT}$ **no matter what C_V is**!

This will be crucial later when we talk about adiabatic expansions.

C_P for diatomic gases:

We know that or diatomics C_{Vm} varies with temperatre;
and since at any temperature $C_{P_m} = C_{V_m} + R$, then C_{P_m}varies similarly to C_{Vm}, as shown in the graph on the next page.



C_P , C_V for solids and liquids

For condensed phases (solids, liquids), U and H are very close, since their difference (PV) is tiny relative to either of them (as the volume of condensed phases is really small).

Further, the properties of condensed phases depend mostly on the temperature unless the pressure is very high.

Therefore, $C_V = \left.\frac{\partial U}{\partial T}\right|_V$ and $C_P = \left.\frac{\partial H}{\partial T}\right|_P$ are very similar for condensed phases, and will be, like we mentioned, $C_V \sim (\text{\# of active DOF}) \cdot \frac{R}{2}$, and $C_P \sim C_V$ for conndeed phases.

Example: $\boldsymbol{C_P}(\mathbf{H_2O})$ in different phases.

- $C_{Pm}(\text{ice}) \simeq C_{Vm}(\text{ice}) \simeq 37 \frac{\text{J}}{\text{K mol}} \approx 9 \cdot \frac{R}{2}$ i.e., each ice molecule has a net amount of around 9 degrees of freedom; we can **qualitatively guess that** these could be three vibrations of the center of mass for this triatomic molecule, contributing $3 * 2 = 6$ DOFs, as well as another three associated with shared hydrogen bonds.
- $C_{Pm}(\text{water}) \simeq C_{Vm}(\text{water}) \simeq 75 \frac{\text{J}}{\text{K mol}} \simeq 18 \cdot \frac{R}{2}$.

  So water has a huge heat capacity, twice that of ice. Explanation:

  - Each water molecule has many neighbors that it can share its hydrogen bonds with.
  - Also, a water molecule can "librate" (i.e., rotate somewhat back and forth).
  - Further, its O-H bonds somewhat vibrate one relative to each other in a "bending" mode similar to a butterfly motion (see class).

Finally:

- $C_{Pm}(\text{water vapor}) \simeq 36 \frac{\text{J}}{\text{K mol}} \sim 8.5 \cdot \frac{\text{R}}{2}$, i.e.,

$$C_{Vm}(\text{water vapor}) = C_{Pm}(\text{water vapor}) - R \simeq 28 \frac{\text{J}}{\text{K mol}} \sim 7.5 \cdot \frac{\text{R}}{2}$$

i.e., each water vapor molecule has "7.5" active DOF – 3 from the kinetic motion of the center-of-mass, 3 from rotation, and another "1.5" from the bending mode vibration (recall that each vibration is associated with two DOF, one kinetic and one potential). The precise value of heat-capacity changes of course with temperature, rising as the temperature rises, since more vibrations are "active" at higher temperatures.

Some examples for using $\boldsymbol{H}$:

Say we have a substance with:

Initially, $P_i = 1\text{bar}, V_i = 3\text{Liter}, \ U_i = 200\text{J}$.

Finally: $P_f = 3\text{bar}, V_f = 2\text{L}, \ U_f = 300\text{J}$.

Question: what's $\Delta H =$?

Answer: $\Delta H = \Delta U + \Delta(PV)$. But

$$\boldsymbol{\Delta(PV)} = P_f V_f - P_i V_i = 3\text{bar} \cdot 2\text{L} - 1\text{bar} \cdot 3\text{L} = 600\text{ J} - 300\text{ J} = \mathbf{300J}$$

So

$$\boldsymbol{\Delta H} = \Delta U + \Delta(PV) = 100\text{J} + 300\text{J} = \mathbf{400\ J}$$

> Note that $\Delta(PV) \neq P\Delta V + V\Delta P$. $P\Delta V$ as well as $V\Delta P$ are not even defined here, since P in front of ΔV could mean the initial or the final value, and those are very different.

2.8) Enthalpy associated with phase-change

When a phase change occurs at constant pressure, e.g., ice melting, or water boiling to make vapor, heat is needed (as input). Since we assume that P is fixed, there is an enthalpy change equaling to the heat input. We label it ΔH, and since usually the enthalpy change is at room pressure we should label it ΔH^o (but we often omit the "o" subscript).

Different phase-changes have specific names:

Solid→ Liquid: Heat of fusion. Example: $\Delta H_{\text{fus}}(\text{H}_2\text{O}, 0°\text{C}) = 6.00 \frac{\text{kJ}}{\text{mol}}$

Liquid→ Vapor: Heat of vaporization. $\Delta H_{\text{vap}}(\text{H}_2\text{O}, 100°\text{C}) = 40.65 \frac{\text{kJ}}{\text{mol}}$

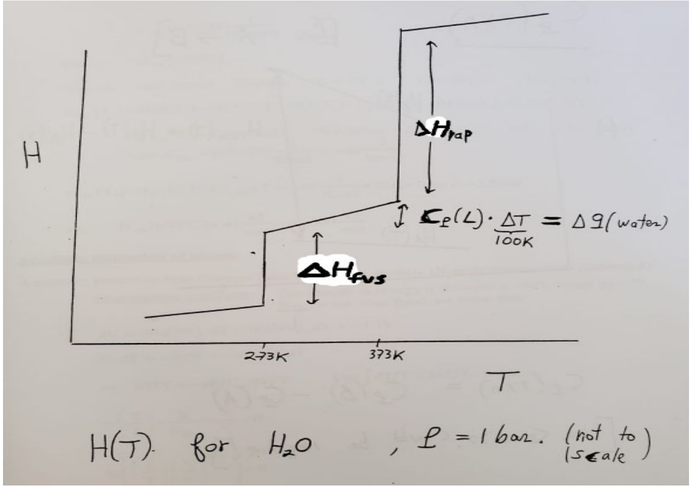
Example: (from Levine)

Part i: Calculate q and ΔU for converting, at $P = P^o$, 1kg of H_2O ice from -50°C all the way to vapor at 130°C.

Answer:

First, note that 1kg is $\frac{1000\text{g}}{18.01\frac{\text{g}}{\text{mol}}} = 55.5$ mol of water.

Next, refer to a schematic (not-to-scale) figure below, showing H vs. T at a fixed pressure (1 bar). Note that H rises linearly with T since the derivative of H w.r.t. T, i.e., $\left.\frac{\partial H}{\partial T}\right|_P$ (i.e., C_P), is approximately constant for each phase.



However, at the phase transition points (0°C and 100°C for out 1bar pressure) you need to put in heat to melt (or vaporize) the H_2O, so the enthalpy curve jumps.

For example, ΔH_{vap} is the amount of heat needed to vaporize a mole of water at 100°C, and is very large, larger than all the other contribution to the change of enthalpy in our figure.

Thus, per mol:

$$\frac{q}{n} = \frac{\Delta H}{n} = \int_{-50°\text{C}}^{0°\text{C}} C_{\text{Pm}}(\text{ice})dT + \Delta H_{\text{fus}}(0°\text{C})) + \int_{0°\text{C}}^{100°\text{C}} C_{\text{Pm}}(\text{water})dT + \Delta H_{\text{vap}}(100°\text{C}) + \int_{100°\text{C}}^{130°\text{C}} C_{\text{Pm}}(\text{vapor})dT$$

And since the heat capacities are essentially constant as a function of temperature, we take them out of the integral, e.g.,

$$\int_{-50°\text{C}}^{0°\text{C}} C_{\text{Pm}}(\text{ice})dT \simeq C_{\text{Pm}}(\text{ice}) \int_{-50°\text{C}}^{0°\text{C}} dT = C_{\text{Pm}}(\text{ice}) \cdot 50\text{K}$$

Thus:

$$\frac{q}{n} = C_{\text{Pm}}(\text{ice}) \cdot 50\text{K} + \Delta H_{\text{fus}}(0°\text{C}) + C_{\text{Pm}}(\text{water}) \cdot 100\text{K} + \Delta H_{\text{vap}}(100°\text{C}) + C_{\text{Pm}}(\text{vapor}) \cdot 30\text{K}$$

i.e.,

$$\frac{q}{55.5\text{ mol}} = 38\frac{\text{J}}{\text{K mol}} \cdot 50\text{K} + 6000\frac{\text{J}}{\text{mol}} + 75\frac{\text{J}}{\text{K mol}} \cdot 100\text{K} + 40650\frac{\text{J}}{\text{mol}} + 36\frac{\text{J}}{\text{K mol}} \cdot 30K$$

i.e.,

$$\frac{q}{55.5\text{mol}} \approx 57{,}000\frac{\text{J}}{\text{mol}} = 57\frac{\text{kJ}}{\text{mol}}$$

i.e.,

$$q = 3{,}170\text{kJ} = 3.17\text{ MJ}.$$

Note the two green-emphasized parts above. You see that out of the 57kJ/mol heat, over 70% (i.e., 40.65 kJ/mol) was needed to vaporize the water. The rest was needed to melt the ice and to raise the temperature in each phase.

Also, for ΔU:

$$\Delta U = \Delta H - \Delta(PV) = q - \left(1\text{bar} \cdot V_{\text{gas}} - 1\text{bar} \cdot V_{\text{ice}}\right)$$

The volume of ice is miniscule relative to the gas. So (since the volume of the gas is calculated at 130°C=403K),

$$PV_{gas} = n \cdot R \cdot 403K = 55.5\text{ mol} \cdot 8.31\frac{\text{J}}{\text{K mol}} \cdot 403\text{K} = 186\text{kJ}$$

$$\Delta U \simeq \Delta H - P \cdot V_{\text{gas}} = (3170 - 186)\text{kJ} = 2984\text{kJ} = 2.98\text{ MJ}.$$

Next question: Similar to Part i, but now we add an additional step, Segment ii, whereby, after Part i, the vapor at 130°C is isothermally expanded to 0.5bar.

Question: what's ΔH for the whole process (Part i + Segment ii), and what's q.

Answer: The last segment is isothermal. The enthalpy of the gas depends only on its temperature (since $H = U(T) + PV = U(T) + nRT$ for ideal gases). So the overall $\Delta H = H_f - H_i$ did not change.

But q changed – we learned earlier than in an isothermal expansion the heat input is $q_{\text{segment ii}} = nRT \ln \frac{V_2}{V_1} = nRT \ln 2$ (i.e., the volume doubled). I.e.,

$$q_{\text{segment ii}} = 55.5 \text{ mol} \cdot 8.31 \frac{\text{J}}{\text{K mol}} \cdot 403\text{K} \cdot \ln 2 = 129 \text{ kJ}$$

So for the overall Part i + Segment ii:

$$\boldsymbol{\Delta H = 3170 \text{ kJ}}$$

$$\boldsymbol{q}(\textbf{ Part i + Segment ii}) = q(\text{Part i}) + q(\text{Segment ii}) = 3170\text{kJ} + 129\text{kJ} \simeq \mathbf{3350 \text{ kJ}}$$

So note again: $q = \Delta H$ automatically ONLY if the whole process was done at fixed pressure!

And note again that if we were to take a different path from the initial point (T_i =-50°C , P_i=1bar) to the final point (T_f =130°C , P_f=0.5bar), then:
ΔH would **not change,** but q **would change.**

2.9) Enthalpy and reaction heat-capacity.

Let's consider a "reaction"

$$A \rightarrow B$$

We'll assume also that the pressure is fixed, $P = P^{\text{o}}$.

The **heat of reaction** is simply the heat needed for a mole of this reaction.

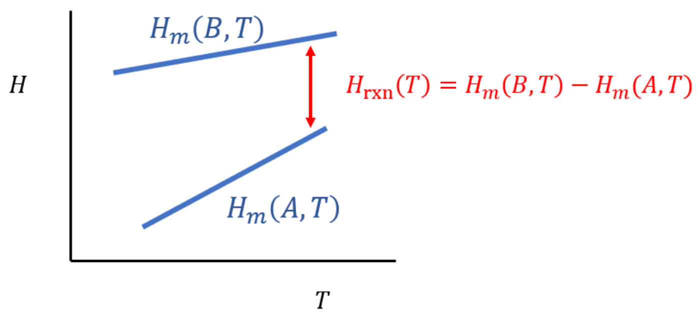
$$H_{\text{rxn}}(T) = H(B,T) - H(A,T)$$

This reaction could be just a phase change, e.g., in this example we'll assume that A is water (liquid) and B water vapor. In this case $\Delta H_{\text{rxn}} \equiv \Delta H_{\text{vap}}$.

We wrote earlier the heat of reaction for the "reaction" (i.e., phase change), water→ water-vapor at 100°C is $\Delta H_{\text{rxn}}(100°\text{C})$ =40.65 kJ.

We could calculate it also **at other temperatures.** This is important, for example when you consider **sweating at room temperature** -- i.e., vaporization of water at 25°C.

To calculate note that the enthalpy rises with temperature linearly.



Slope of H w.r.t. T: C_P.
Slope of ΔH w.r.t. T: ΔC_P (in this case negative!)

I.e., for the same phase

$$H_m(B,T) = H_m(B,T_0) + \int_{T_0}^{T} C_{P,m}(B)dT = H_m(B,T_0) + C_{P,m}(B)(T - T_0)$$

Similarly,

$$H_m(A,T) = H_m(A,T_0) + C_{P,m}(A)(T - T_0)$$

And therefore, when you subtract the two Eqs.

$$H_m(B,T) - H_m(A,T) = H_m(B,T_0) - H_m(A,T_0) + \left(C_{P,m}(B) - C_{P,m}(A)\right)(T - T_0)$$

i.e. (see figure):

$$\Delta H_{\text{rxn}}(T) = \Delta H_{\text{rxn}}(T_0) + \Delta C_{P,\text{rxn}} \cdot (T - T_0)$$

where

$$\Delta C_{P,\text{rxn}} \equiv C_{P,m}(B) - C_{P,m}(A)$$

is the **reaction heat-capacity** (that's a historical name, it would have been better named as heat-capacity-difference).

Later on in Chapter 5 we'll see the extension of this to multicomponent reactions.

Example: (alluded to earlier) what's the vaporization enthalpy of water at room temperature?

Answer: (recall that for us room temperature is 27°C, not 25°C):

$$\Delta H_{\text{vap}}(T = 27°\text{C}) = \Delta H_{\text{vap}}(100°\text{C}) + \Delta C_{P,\text{rxn}}(27 - 100) \cdot \text{K}$$

i.e.,

$$\Delta H_{\text{vap}}(27°\text{C}) = \mathbf{40650}\frac{\text{J}}{\text{mol}} + (36 - 75)\frac{\text{J}}{\text{Kmol}}(-73\text{K}) \simeq \mathbf{43500}\frac{\text{J}}{\text{mol}}$$

i.e., the heat needed for vaporizing one mol of water at room temperature is higher by about 7% than at 100°C.

Now to the final (and difficult) part of this chapter.

2.10) Adiabatic expansion of gases

Adiabatic: means no heat is input/outputted during the reaction. Note the difference from isothermal, where expansion is accompanied by heat input.

Plan for deriving the results: We'll consider a tiny expansion. Then, we'll end up with a mathematical expression that we'll integrate.

When a gas expands adiabatically, it does work on the surrounding. Because of that (and since there's no heat input) its energy decreases.

Mathematically:

$$dU = -PdV$$

On the other hand, since we consider ideal gases, we can relate dU to the change in temperature:

$$dU = \frac{dU}{dT} \cdot dT$$

But we know that for an ideal gas $\frac{dU}{dT} = C_V$. Therefore:

$$dU = C_V \, dT$$

And therefore

$$\boldsymbol{C_V dT = -PdV} \; (= dU)$$

Side note: You are probably very confused. How come we use $\boldsymbol{C_V}$ here? The volume changes, and $\boldsymbol{C_V}$ is defined as the heat capacity at constant volume!

The answer is that we need $\frac{dU}{dT}$. For ideal gases, since U depends only on T, the derivative $\boldsymbol{\frac{dU}{dT}}$ will be the same regardless of whether we measure it in a process where V is fixed or not.

So the trick is:

- **If** $\boldsymbol{\frac{dU}{dT}}$ was measured in a process where V was fixed, then (and only then) $dw = 0$ so for this fixed-V process $dU = dq$; and since then $dq = C_V dT$, we can say that **for that fixed-volume process** $\boldsymbol{\frac{dU}{dT} = C_V}$**.**
- **But since** $\boldsymbol{\frac{dU}{dT}}$ **is independent of process** (and depends only on T) it is ok to apply $\boldsymbol{\frac{dU}{dT} = C_V}$ **to other processes too, where** $\boldsymbol{V}$ **changes**

Example:

Say that we take away a certain amount of energy of a certain gas in a piston.

And say that we had two alternative small steps

- One in which V was fixed, so $dw = 0$, and we pulled out 5J from the system $dq = -5\text{J}$. Say in this process $dT = -0.1\text{K}$.

  So: $C_V = \frac{dq}{dT}(V \text{ fixed}) = -\frac{5\text{J}}{-0.1\text{K}} = 50\frac{\text{J}}{\text{K}}$, and therefore $\frac{dU}{dT} = 50\frac{\text{J}}{\text{K}}$
- Alternatively, say $dq = 0$, but that $dw = -5\text{J}$. What will be dT?

Answer:

Well, in this process $dU = -5\text{J}$ again, just like the first process, ie., dT **has to be the same as before, since the energy change correlates only to the temperature change.**

$$\boldsymbol{dT = \frac{1}{\frac{dU}{dT}} dU = \frac{1}{C_V} dU}$$

So It has to be $dT = -0.1K$ again.

Thus you see that it is OK to apply $\boldsymbol{dU = -C_V dT}$ regarless of whether V is fixed or not. (But $dq = C_V dT$ is true ONLY if V if fixed!)

<u>Back to the math</u>: since we have an ideal gas, the adiabatic expansion eq. from above becomes:

$$C_V dT = -PdV = -\frac{nRT}{V} dV$$

and the trick to solve this equation is by isolating the temperature terms on one side, and the volume terms on the other:

$$\frac{dT}{T} = -\frac{nR}{C_V}\frac{dV}{V}$$

This is a differential relation, between dT and dV.

Now let's **integrate (i.e., sum over many such changes),** over the path between an initial state (P_0, V_0, T_0) and up to a given point (P, V, T), presuming of course that the expansion is adiabatic **throughout** the path. **Then:**

$$\int \frac{dT}{T} = -\int \frac{nR}{C_V}\frac{dV}{V} = -\frac{nR}{C_V}\int \frac{dV}{V}$$

where in the last equality we assumed that C_V does not change much during the expansion so we can pull it out of the integral

Now remember your calculus refresher, which had:

$$\int_{x_0}^{x} \frac{dx}{x} = \ln\left(\frac{x}{x_0}\right)$$

So the eq. from above becomes

$$\ln\left(\frac{T}{T_0}\right) = -\frac{nR}{C_V}\ln\left(\frac{V}{V_0}\right)$$

Where T_0 and V_0 refer to the initial temperature and volume.

Now recall the logarithm property: $a\ln(x) = \ln(x^a)$, which gives, when applied to the RHS of the yellow equation:

$$\ln\left(\frac{T}{T_0}\right) = -\ln\left(\left(\frac{V}{V_0}\right)^{\frac{nR}{C_V}}\right)$$

Move the RHS term to the left

$$\ln\left(\frac{T}{T_0}\right) + \ln\left(\left(\frac{V}{V_0}\right)^{\frac{nR}{C_V}}\right) = 0$$

Using another logarithm gives rule: $\ln x + \ln y = \ln(xy)$ givs

$$\ln\left(\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\frac{nR}{C_V}}\right) = 0$$

So, since $\ln(1) = 0$,

$$\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{\frac{nR}{C_V}} = 1.$$

Almost there, but we typically want to see a relation between the pressure and volume, not just the temperature and volume. So use the ideal gas law $\frac{T}{T_0} = \frac{PV}{P_0V_0}$ to get

$$\frac{PV}{P_0V_0}\left(\frac{V}{V_0}\right)^{\frac{nR}{C_V}} = 1$$

i.e., if we define

$$\gamma \equiv 1 + \frac{nR}{C_V}$$

we get

$$\frac{P}{P_0} \cdot \left(\frac{V}{V_0}\right)^{\gamma} = 1$$

Multiply by $P_0V_0^{\gamma}$ to get

$$PV^{\gamma} = P_0V_0^{\gamma}$$

This is the **key result of adiabatic expansion – during the expansion, PV^{γ} is unchanged.**

To conclude, several more points:

- The light-blue eq. we have above, relating the temperature and volume, can be rewritten as $TV^{\frac{nR}{C_V}} = T_0V_0^{\frac{nR}{C_V}}$, i.e.,

  $$TV^{\gamma-1} = T_0V_0^{\gamma-1}$$

- Recall that we learned that $C_P = C_V + nR$. Therefore, γ can be rewritten $\gamma = 1 + \frac{nR}{C_V} = \frac{C_V+nR}{C_V}$, i.e.,

  $$\gamma = \frac{C_P}{C_V}$$

- Values of γ: Since $\gamma = 1 + \frac{nR}{C_V}$, its maximum value will be when C_V is minimal. Monoatomic gases have the lowest heat capacity and as we learned, for them $C_V = \frac{3}{2}nR$, so **the largest value of γ will be** $1 + \frac{nR}{\frac{3}{2}nR} = 1 + \frac{2}{3}$, i.e.,

  $$\gamma_{\max} = \gamma(\mathrm{He, Ne, etc.}) = 1.666$$

- For light diatoms from 100-2000K we learned that there are 5 active degrees of freedom (3 center-of-mass, 2 rotations perpendicular to the diatomic axis), so for them $C_V = \frac{5}{2}nR$, i.e., $\gamma = 1 + \frac{nR}{\frac{5}{2}nR}$, i.e.,

$$\gamma(\mathrm{H_2}, \mathrm{O_2}, \mathrm{NO}, \ldots \text{at room temperture}) = 1.4$$

- For bigger and bigger molecules γ will decrease, but will always be bigger than 1.

Example: 20 moles of ideal gas expands adiabatically from $V_0 = 100\mathrm{L}$, $T_0 = 300\mathrm{K}$

Questions: what will be:

- The initial pressure
- The pressure and temperature after the volume doubles in an adiabatic expansion, presuming the gas is monoatomic
- The same, for a typical diatom.

Answers:

- We calculated earlier that for one mole of an ideal gas at room temperature and 25 L, the pressure is 1bar. Comparing to our case, and noting that $P = \frac{nRT}{V}$, where again $T = T_{\mathrm{room}}$ but n is 20mol rather than 1, and V is 100L rather than 25L, then the initial pressure is

$$P_0 = \frac{20}{4} \cdot 1\mathrm{bar} = 5\ \mathrm{bar}$$

 (don't confuse the symbol for the initial pressure, P_0, with the symbol for one atmosphere -- or bar-- P^{o})

- Next, for <u>monatomic</u> gases, $\gamma = 1.666$. So during the adiabatic expansion $PV^{1.666}$ is fixed.

 Thus when V rises by a factor of 2, P changes by a factor of $\frac{1}{2^{1.666}}$, i.e.,

$$P = P_0 \cdot \frac{1}{2^{1.666}} = \frac{5}{2^{1.6666}}\mathrm{bar} = 1.57\ \mathrm{bar}.$$

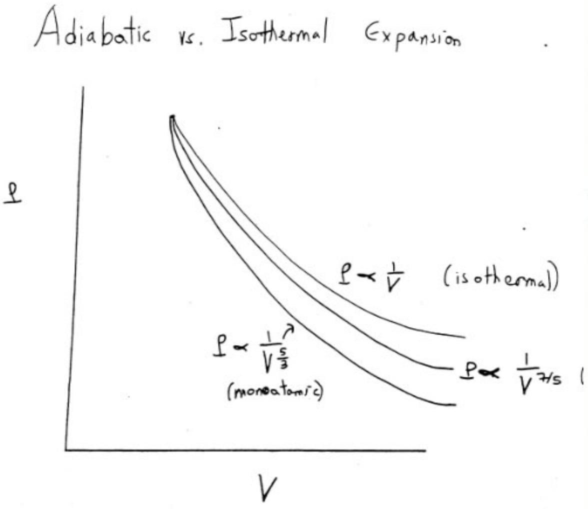
 Further, since $TV^{\gamma-1} = TV^{0.666}$ stayes fixed, then upon volume doubling,

$$T = \frac{T_0}{2^{0.6666}} = \frac{300\mathrm{K}}{2^{0.6666}} = 189\mathrm{K}$$

- I will leave to you to show that if the gas was <u>diatomic</u>, with $\gamma = 1.4$, then upon volume doubling

$$P = 1.90\mathrm{bar}$$

(i.e., higher than for monoatomic gas upon the same expansion) and $T = 228\mathrm{K}$.



The picture above shows P vs. V for isothermal and for adiabatic expansions of monatomic and diatomic gases, starting from the same initial state.

Note how as the molecule gets heavier, its pressure upon expansion gets closer and closer to the isothermal expansion case.

Physically, the reason is that monoatomic gases have very little energy in them, only due to the kinetic energy of the center of mass. So when they expand a little adiabatically and lose an amount of energy through work,
$dU = dw = -PdV$ (without being compensated by heat), this leads (for monoatomic gases) to a percentage-wise big loss of energy.

In contrast, consider an ideal gas of big molecules with many active vibrations and therefore a lot of energy. Then the same loss, i.e., the same $dU = dw = -PdV$, will have little effect percentage wise (since U is so much larger in this case).

> To exemplify again, say two gases with same number of molecules have initially the same pressure and temperature and volume. Both expand adiabatically by the same volume change, so both do the same amount of work of, say, $dw = -10\mathrm{J}$. So $dU = -10\mathrm{J}$ for both.
>
> The first is a monoatomic gas which has U is, say, 200J. So $\frac{dU}{U} =-\frac{10\mathrm{J}}{200J} = 5\%$.
>
> The second is an ideal gas of a large molecule, with $U = 800\mathrm{J}$, so $\frac{dU}{U} = -\frac{10}{800} = -1.25\%$. I.e. the <u>relative</u> energy change is much smaller for the second gas, so its relative temperature change will be much smaller.

2.11) Chapter 2: Conclusions

- In this chapter you learned the concepts of heat and work (disordered and ordered transfer of energy) and the conservation of energy rule, in either microscopic

  $$dU = dq + dw$$

  or macroscopic form

$$\Delta U = q + w$$

Examples showed that while q and w are path dependent, ΔU isn't.

- You learned that for ideal gases U depends only on T,

$$U = U(T)$$

and for a monoatomic ideal gas $U = \frac{3}{2}nRT$.

- You learned about a new state function, enthalpy, $H \equiv U + PV$, such that at "usual" laboratory processes, where P is fixed, $dH = dq$, or, for large changes (with P fixed), $\Delta H = q$.
- For general materials, you learned the concept of heat capacities, e.g., $C_V \equiv \left.\frac{dq}{\partial T}\right|_V$ and we understood why that means that $C_V = \left.\frac{\partial U}{\partial T}\right|_V$.

  Similarly you saw that $C_P \equiv \left.\frac{dq}{\partial T}\right|_P$ equals $C_P = \left.\frac{\partial H}{\partial T}\right|_P$.

  For an ideal gas $U = U(T)$ where the partial derivatives can be replaced by total derivatvies, this implied $C_V = \frac{dU}{dT}$, $C_P = \frac{dH}{dT} = C_V + nR$ (but only for ideal gases!)
- $dH = dq$ implied that for continuous changes at fixed pressure $\Delta H = \int C_P dT$ (with appropriate limits) while for phase change ΔH was labeled appropriately as ΔH_{fusion}, ΔH_{vap}, etc.

These concepts were exemplified through expansion of ideal gases, e.g., at

- Fixed volume $dw = 0 \rightarrow dU = dq$
- Fixed pressure $dH = dq$
- Isothermal expansion, where for ideal gases:

$$dq + dw = 0 \rightarrow q = -w = \int PdV = nRT \int \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right),$$

- While for adiabatic expansions $dq = 0 \rightarrow dU = dw \rightarrow C_V dT = -PdV$, which led to

$$PV^\gamma = const.$$

  during the expansion, with

$$\gamma = 1 + \frac{nR}{C_V} = \frac{C_P}{C_V}$$

  These results will be very important later.
- You further learned that the heat capacity of an ideal MONOATOMIC gas is a constant,

$$C_V = \frac{3}{2}nR \quad \left(\text{so } C_P = \frac{5}{2}nR\right) \qquad \text{He, Ne, ...}$$

  while for gases of DIATOMIC molecules at room temperatures,

$$C_V = \frac{5}{2}nR \qquad \text{H}_2, \text{O}_2, \text{NO}, \text{N}_2, \text{etc.}$$

- And in general (without proof):

$$C_V = n\frac{R}{2} * (\textbf{active} \text{ degree of freedom})$$

III Entropy

3.1) Overview

Here we'll define dq in terms of a **state function**, **entropy,** labeled S. So

$$dS = \frac{dq_{\text{rev}}}{T}$$

we'll explain what dq_{rev} is below.

Reaction theory (chemical thermodynamics) would be developed in the following chapters based on the 2nd law of thermodynamics:

The total entropy of the world never decreases (is constant for reversible processes and rises for irreversible processes).

We'll then learn to:

- Use the 2nd law to derive the efficiency of engines and refrigerators (not really chemistry, but important culturally).
- Evaluate $\Delta S = \int \frac{dq_{\text{rev}}}{T}$ in different constext. E.g.,
  - For fixed P: $\Delta S = \int C_P \frac{dT}{T}$
  - ΔS for an ideal gas expansion, isothermal and adiabatic.
  - ΔS for a mixture of two different gases – very important, non- intuitive result.
- And conclude by the 3rd law, $\boldsymbol{S \to 0 \quad \text{as}\ T \to 0}$.

3.2) Definition of Entropy

q is not a state function, as we saw. This implies that we can get from an initial state V_1, T_1, P_1 to another state V_2, T_2, P_2 using different routes with different q.

We'll state without proof: There is a state function, RELATED to q, called entropy. This function, labeled S, measures disorder!

I remind you **what is a state function**: a function, like V, T, P or U and H which is **independent of history.** For example, a cold-water tea-cup has a temperature of, say, 10°C regardless of whether it was previously hot or icy.

In the same way, the disorder in a room or the disorder in a molecule can have a value, say $50.38\frac{\text{J}}{\text{K}}$ (these are the units, energy per temperature) – regardless of its history.

This entropy function is **extremely important,** and is related to q in the following way:

$$dS = \frac{dq_{\text{rev}}}{T}$$

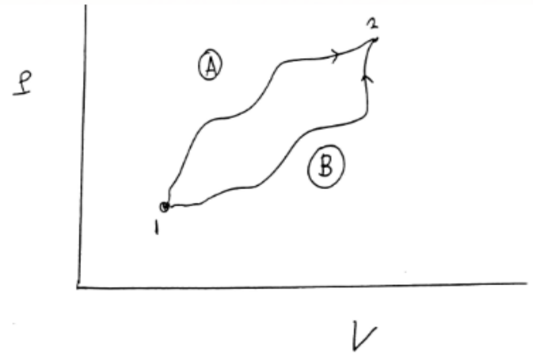
so in a macroscopic change between an initial state ("1") and a final state ("2")),

$$S(T_2, P_2, V_2) - S(T_1, P_1, V_1) = \Delta S = \int dS = \int \frac{dq_{\text{rev}}}{T}$$

Here dq_{rev} is the amount of heat spent in **any real or fictitious reversible path** that connects the initial and final states.

> Important: if the actual path is irreversible, you cannot use it to calculate ΔS. You have to find instead a reversible path that takes you from the initial to the final state, and use it to calculate ΔS. We'll exemplify soon.

To understand the eq. above deeper, refer to the figure. Consider two reversible paths. The claim that S is a state function is equivalent to saying that each of these paths (or any other reversible path) will be sufficient for calculating S!



$q(\text{route A}) \neq q(\text{route B})$

But either route would do for calculating ΔS!

$$\Delta S = \int_{Ⓐ} \frac{dq}{T} = \int_{Ⓑ} \frac{dq}{T}$$

if both are reversible!

Formally this means (presuming the two paths are reversible) that in spite of the fact that the heat is path-dependent

$$q(\text{route A}) \neq q(\text{route B})$$

i.e., in spite of

$$\int_{\text{route A}} dq \neq \int_{\text{route B}} dq,$$

we can still make the integrals agree if we divide dq by T:

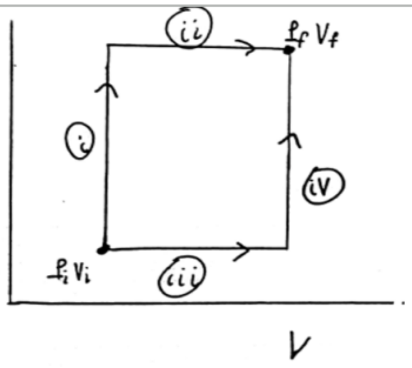
$$\int_{\text{route A}} \frac{dq}{T} = \int_{\text{route B}} \frac{dq}{T}$$

> You may be frustrated to hear that we don't define the entropy directly, only the entropy difference. Later on I will show you the equivalent statistical mechanics definition for entropy, which does not rely on differences, and we'll see that it matches the thermodynamic entropy.

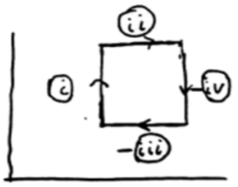
Example:

Let's show that the entropy difference is path-independent for our previous very simple example of 1 mole of a monoatomic gas, starting from $T = 300\text{K}, V = 25\text{L}$, and ending at 1800K and 25L (see figure.)

$$S_{final} - S_{inital} = \Delta S_i + \Delta S_{ii} = \Delta S_{iii} + \Delta S_{iv}$$



Cyclic:



$$q(\text{cycle}) = q_i + q_{ii} - q_{iii} - q_{iv} \neq 0$$

But

$$\Delta S(\text{cycle}) = \Delta S_i + \Delta S_{ii} - \Delta S_{iii} - \Delta S_{iv} = 0$$

- Take first the clockwise route $i + ii$.

  The change in entropy <u>throughout</u> leg i (with fixed volume, and P rises 3-fold from 1bar to 3bar, so T also rises from 300K to 900K) is $dq = C_V dT$, so

$$\Delta S_i = \int_{\text{leg } i} \frac{dq}{T} = \int_{\text{leg } i} \frac{C_V dT}{T}$$

  But since C_V is constant $\left(C_V = \frac{3}{2} nR\right)$ we take it outside the integral so

$$\Delta S_i = C_V \int_{\text{leg i}} \frac{dT}{T} = C_V \ln \frac{T(\text{end leg})}{T(\text{begin leg})} = C_V \ln\left(\frac{900\text{K}}{300\text{K}}\right) = C_V \ln(3)$$

  In the second leg the pressure is fixed, and the temperature doubles (900→1800K)

$$\Delta S_{ii} = \int_{\text{leg ii}} \frac{C_P dT}{T} = C_P \ln\left(\frac{1800}{900}\right) = C_P \ln 2$$

  So adding gives

$$\Delta S = C_V \ln 3 + C_P \ln 2$$

- What about the other (counterclockwise) path, $iii + iv$? It is trivial to prove that **leg iii has the same entropy change as leg ii,**

$$\Delta S_{iii} = C_P \int_{\text{leg iii}} \frac{dT}{T} = C_P \ln\left(\frac{600}{300}\right) = C_P \ln 2$$

and leg iv has the same entropy change as leg i, so this finishes the demonstration that ΔS is **independent of path.**

End of Example.

We'll now go and try to understand the basic ingredients in the entropy definition:

3.3) Meaning of Reversible

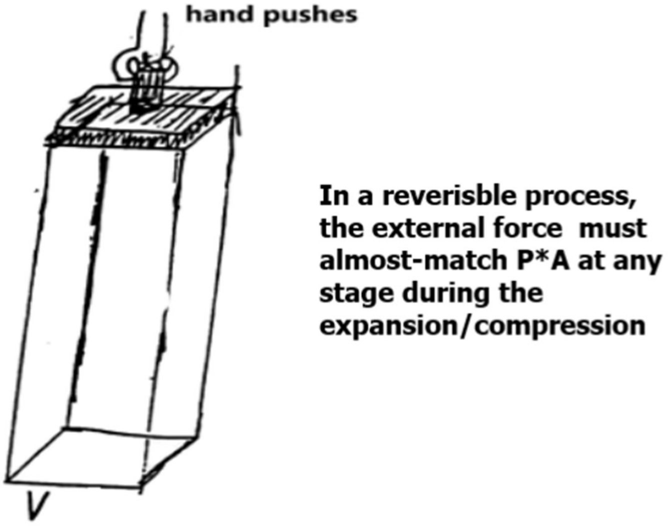
We finessed so far the meaning of reversible. It just means that a very small change can **reverse** the path (not just stop it, but actually reverse).

For example, the flow of heat between your body (at 37°C) and the room (at 25°C) is **irreversible** (we can stop it for a while by wearing an isolating cloth, but **no small change can reverse** it so the heat would I from the room to the body).

A slow isothermal or adiabatic expansion of an ideal gas in a piston is **reversible.** That's because a slow piston expansion (see figure) will be slow only if **at any given moment the "hand" holding the piston from the outside exerts almost the same external force as the internal force of the gas,** $P \cdot A$rea.

Therefore, by a slight raise/lowering of the external pressure we can reverse the direction of the process (form expansion to compression or vice versa).

If the forces were not almost equal than, for example if the external force is much weaker than the internal, the piston will rapidly expand, not slowly.

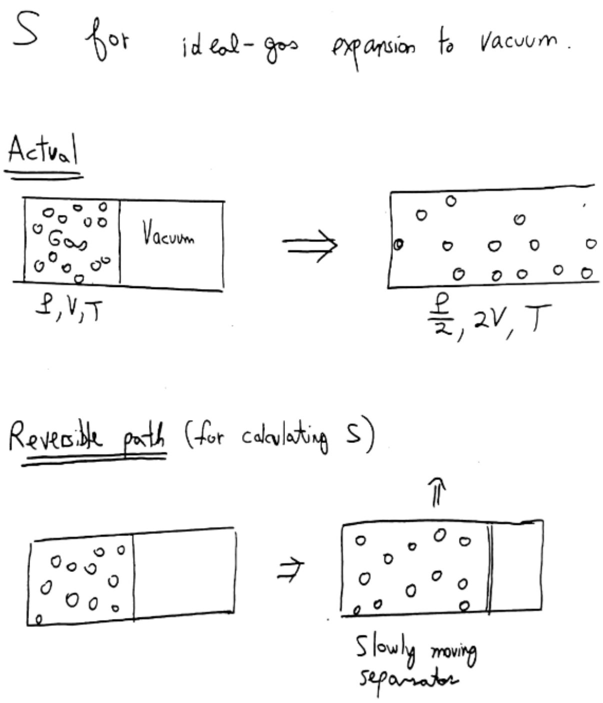


Important to reemphasize: If an expansion is irreversible, you should evaluate ΔS not by the actual (irreversible) path but by (any) different, reversible path.

Example of entropy calculation for an irreversible process: ideal gas expansion to vacuum (see figure below).

- First put a separation in a container, and fill up one half with a gas. The initial state of the gas is denoted as P_1, V_1, T.

- Then pock a hole in the separation. No heat is input ($dq = 0$), and the gas will transfer irreversibly filling up the entire volume. There's no work (no opposing force) so the energy is conserved, and since for an ideal gas $U = U(T)$, this implies that T is conserved (so by the ideal gas law P will halve). Thus the final state will be ($P_2 = \frac{P_1}{2}, V_2 = 2V_1, T$)



- Because the transfer is irreversible, $dS \neq \frac{dq}{T}$ (since $dq \neq dq_{\text{rev}}$), so we can't use the actual path for calculating the entropy difference upon expansion.

> Note that even if the hole is small the transfer through the hole will be irreversible; we could seal the hole and stop the transfer, but we cannot **reverse** it by a small change.

- To calculate ΔS, consider a completely different path which would lead however from the same starting point to the same final point. That simplest path we can choose would be in our case an isothermal reversible (slow!) expansion. For such as path, as we learned,

$$dq_{\text{rev}} = dU - dw = dU + PdV = 0 + PdV = PdV$$

so

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{PdV}{T} = \int_1^2 \frac{1}{T} \cdot \frac{nRT}{V} dV = nR \int_1^2 \frac{dV}{V} = nR \ln\left(\frac{V_2}{V_1}\right)$$

i.e., in our case of volume doubling:

$$\boldsymbol{\Delta S = nR \ln 2}$$

Note that the ENTROPY INCREASES when the VOLUME INCREASES (at fixed T). This makes sense since a bigger volume means more disorder, the atoms have more space to roam through.

The importance of $\frac{1}{T}$ in $dS = \frac{dq_{\text{rev}}}{T}$.

Physically, the reason for $\frac{1}{T}$ is: entropy measures how disordered a system is.

Think of dq_{rev} as a measure of how much "mess" (or "dirt") is put into a system.

But we know that for a "clean" system (low $\boldsymbol{T}$), even a little dirt $\boldsymbol{dq_{\text{rev}}}$ will make it look disordered, i.e., raise its entropy a lot. And indeed mathematically, dividing dq_{rev} by T when$T$ is small will magnity the effect of dq_{rev}, leading to a large dS

In contrast, for a "disordered" system (i.e., at a high temperature), adding more mess will not make it look much messier. Then indeed, dividing dq by the large T will reduce its effect, leading to a smaller dS.

Note: in statistical mechanics the energy and entropy are the fundamental quantities; there, the temperature is **defined** by the relation between the entropy and energy, i.e., $\boldsymbol{T = \frac{dU}{dS}}$. We'll also see this relation in a latter chapter in thermodynamics – where it is more of a curiosity than an important relation.

The importance of entropy comes from:

3.4) The 2nd law: the entropy of an isolated system never decreases (and remains constant for reversible processes)

The 2nd law expresses the fact that **disorder cannot decrease in nature.** All chemical reaction theory is based on this fact, as explained later.

This is an extremely important law.

For example, we all "know" that a falling glass will shatter to pieces. But the process-run-in-reverse is impossible -- pieces of the shattered glass can't recombine spontaneously to form a glass cup.

The first law (energy conservation) alone allows such an absurdity – only the 2nd law lets us know that the pieces cannot recombine. The shattering increases the entropy of the universe; spontaneous recombination would have decreased the entropy of the world and is therefore not possible.

The 2nd law is so important that we would spend some time discussing its consequences for ENGINES. This is part of physical thermodynamic rather than chemical thermodynamics, but it is an important culture.

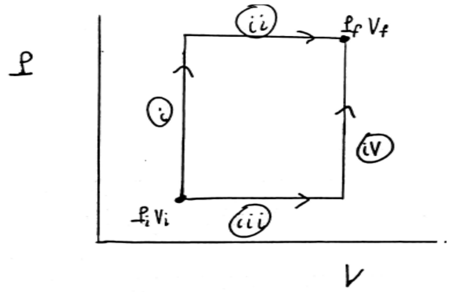
3.5) Engines

An ideal engine is in thermodynamics a device which works in cycles; **after each cycle, the engine is back to where it was (it is unchanged)**, but in the cycle the engine does a net amount of work on its environment,

> Note: it is easy to get confused on whether a quantity should be negative or positive, since this depends on the definition of what is a system
>
> (Example -- when the system does a work of 10 J on the environment, the environment does work of -10J on the system).
>
> We will therefore **label quantities by their absolute value,** and **attach a minus or plus to the absolute value explicitly when we need to.** You'll get used to it quickly

Heat engines (the only ones we consider) are very simple: in each cycle they

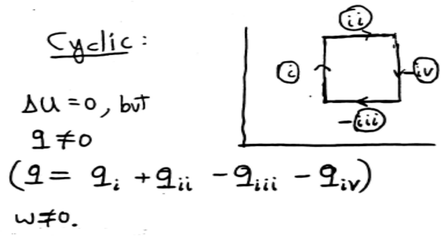
- Take heat $|q_{\mathrm{h}}|$ from a hot object,
- Produce a neat amount of work $|w|$,
- And, as we'll see soon, they also need to **throw heat somewhere colder,** labeled $|q_{\mathrm{c}}|$.



At the end of each cycle they (the engines) come back to where they started from (so they are reusable).

This does not sound like the engines we know from cars, but it is almost the same thing.

> We have already seen something very similar to this type of engines when we considered a **closed square cycle** in a P vs. V diagram (see figure, reposted here).
>
> That device (the bottom part of figure, labeled "cyclic") produced a net amount of work, and obtained a net amount of heat from the outside work. At the end of the cycle the piston was back to where it started from.



But the prime example of heat engines, the **Carnot engine**, is slightly different.

Carnot Engines

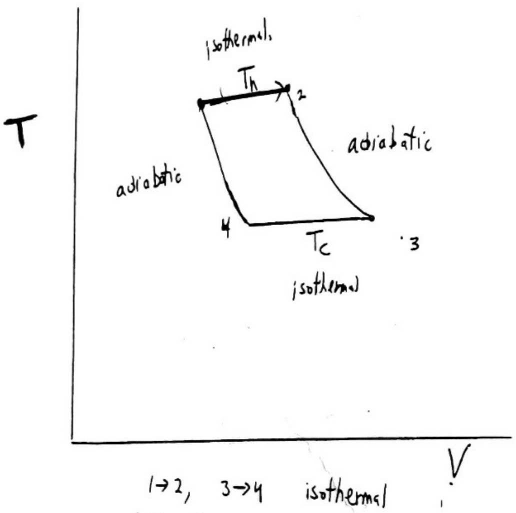
Again the system is **gas in a piston,** but this time it would do the following (see the T vs. V diagram in the next page):

- Stage 1→2. The gas **isothermally** expands at a high temperature, labeled T_h (i.e., the piston is attached to a large hot object while it slowly expands).
- Stage 2→3. The gas **adiabatically expands**. T is reduced from T_h to a colder temperature, labeled T_c. The piston does work but no heat is input into it.

- Stage 3→4. Now the piston is attached to a cold object (at T_c), and is isothermally compressed at T_c. An amount $|q_c|$ is given from the piston to the cold object.

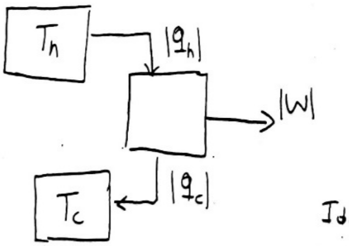
We can determine the **efficiency of such an engine**. But first we need to define the efficiency!

Engines



1→2, 3→4 isothermal

2→3, 4→1 adiabatic



Ideal reversible engine

$|W| = |q_h| - |q_c|$ (1st law)

$\frac{|q_h|}{T_h} = \frac{|q_c|}{T_c}$ (2nd law).

Coefficient of performance

We'll define generally a coefficient of performance of a device, as

$$\text{c. o. p.} = \frac{\textbf{amount of desired output}}{\textbf{amount of resource needed}}$$

The numerator and denominator **depend on what device we consider (either** engines, or an AC, or a heat pump, or a refrigerator)

For an **engine, and only for an engine,** the desired output is $|w|$, and the resource needed is the heat produced by the hot object $|q_{\mathrm{h}}|$ (e.g., heat produced by burning oil).

Note that for engines $|q_C|$ is not a resource – we produce it and damp it, so it does not enter the definition of the coefficient of performance c. o. p.

Also, for engines (and only for engines) we relabel the coefficient of performance as "efficiency", and replace its abbreviation by ε rather than c.o.p.:

$$\varepsilon = \textbf{efficiency(engine only!)} = \frac{|w|}{|q_h|}$$

The amazing thing is that we can calculate the efficiency <u>without calculating the detailed steps in the Carnot engines,</u> as we'll show now.

And let's go a step further in simplifications, and use numbers instead of variables. It is much more illuminating and then it will be trivial to get the general equations.

So let's say in the Carnot engine, $T_h = 1000\text{K}$ and $T_c = 400\text{K}$.

We input to the engine in its higher-temperature stage an amount of, say, 500J. I.e., in the isothermal expansion stage $q_h = 500\text{J}$

Now physically we cannot convert all this heat to net work after one cycle. I.e., $w < q_h = 500\text{J}$.

That's because **after one cycle, the net entropy change of the world** (which must be nonnegative) **is** the change of the hot environment, the change of the cold environment, and the change of the entropy of the engine:

$$\Delta S_{\text{world}} = \Delta S_{\text{engine}} + \Delta S_{\text{h}} + \Delta S_{\text{c}} \geq 0$$

Among the terms:

- The entropy of the hot object decreased

$$\boldsymbol{\Delta} S_h = -\frac{|500\text{J}|}{1000\text{K}} = -0.5\frac{\text{J}}{\text{K}}$$

Note the minus sign --- the entropy of the hot object decreases since it gives heat (or, as we should say, energy in the form of heat) to the system

- **The entropy of the engine is unchanged (**the engine is where it was after one cycle) so $\Delta S_{\text{system}} = 0$
- **So we need to have $\boldsymbol{\Delta S_{\text{c}} \geq +0.5\frac{J}{K}}$** since otherwise the entropy change of the world would have been negative. And therefore:

$$q_c = T_c \Delta S_c \geq 400\text{K} \cdot \left(+0.5\frac{\text{J}}{\text{K}}\right) = 200\text{J}$$

i.e., we need to damp at least 40% of q_h to the cold environment, leaving at most 60% available to work (i.e., i.e., w ≤300J). I.e.,

$$\boldsymbol{\varepsilon \leq 0.6}$$

In <u>the general case</u>, the expression is

$$\boldsymbol{\varepsilon \leq 1 - \frac{T_c}{T_h}}$$

Proof: let's repeat the previous derivation, replacing the values for T_c, T_h etc. by variables. The change of entropy of the world after one cycle is

$$0 \leq \Delta S_{\text{world}} = \Delta S_{\text{engine}} + \Delta S_h + \Delta S_c = 0 - \frac{|q_h|}{T_h} + \frac{|q_c|}{T_c}$$

i.e.,

$$|q_c| \geq |q_h| \cdot \frac{T_c}{T_h}$$

So

$$|w| = |q_h| - |q_c| \leq |q_h| - |q_h| \cdot \frac{T_c}{T_h} = \left(1 - \frac{T_c}{T_h}\right)|q_h|$$

i.e.,

$$\varepsilon \equiv \frac{|w|}{|q_h|} \leq 1 - \frac{T_c}{T_h}$$

as we stipulated.

Example for Carnot Engines

Take a reversible Carnot engine, full of ideal gas (air), with

$$V_1 = 1\text{L}, \;\; T_h = 1000\text{K}, \qquad P_1 = 10P^0$$

$$V_2 = 2\text{L}, \quad \text{same } T_h \qquad (\text{so } \; P_2 = 5P^0)$$

$$T_c = 300\text{K}$$

Question: Determine its:

- Efficiency
- Total work obtained
- $P_3, \; V_3,$
- $P_4, \; V_4$

Answer:

- $\boldsymbol{\varepsilon} = 1 - \frac{T_c}{T_h} = \mathbf{0.7}$

- $w = q_h \cdot \varepsilon$ and we learned that in an isothermal expansion:

  $$q_h = nRT \ln \frac{V_2}{V_1} = nRT \ln 2$$

  Since $nRT = P_1V_1 = 10 \cdot 100 \frac{\text{J}}{\text{L}} \cdot 1\text{L} = 1000\text{ J}$, it follows that

  $$q_h = 1000 \cdot 0.693 = 693\text{ J}$$

  So

  $$\boldsymbol{w} = q_h \cdot \varepsilon = 693\text{J} \cdot 0.7 = \mathbf{485\ J}$$

- The 2→3 stage is adiabatic, so

  $$T_3V_3^{\gamma-1} = T_2V_2^{\gamma-1}$$

  Divide by T_3

  $$V_3^{\gamma-1} = \left(\frac{T_2}{T_3}\right)V_2^{\gamma-1}$$

Take to the power $\frac{1}{\gamma-1}$, to get

$$\boldsymbol{V_3} = \left(\frac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}} V_2 = \left(\frac{1000}{300}\right)^{\frac{1}{\left(\frac{7}{5}-1\right)}} \cdot 2\mathrm{L} = \left(\frac{10}{3}\right)^{\frac{5}{2}} \cdot 2\mathrm{L} = \mathbf{40.6\ L}$$

where we used $\gamma = \frac{7}{5}$ for air, i.e., N_2 and O_2.

Note how huge this volume V_3 is – we need to expand the initial volume in this adiabatic expansion, V_2, by a huge factor, 20.3 (from 2L to 40.6L) to lower the temperature by a factor of 300/1000=0.3!

Similarly, we can use the adiabatic expansion relation between P, V to get

$$P_3 V_3^{\gamma} = P_2 V_2^{\gamma}$$

which yields

$$\boldsymbol{P_3} = P_2 \left(\frac{V_2}{V_3}\right)^{\gamma} = 0.5P^0 \cdot \left(\frac{2}{40.6}\right)^{\frac{7}{5}} = \mathbf{0.0074\ bar}$$

i.e., a ratio of $\frac{0.0074}{0.5} = 0.0148$ compared with P_2, i.e., almost 70 times lower!

- $\boldsymbol{P_4, V_4}$: We proved that the V_3 is 20.3 times larger than V_2, and this is after reducing the temperature from 1000 to 300K. The transition from stage 4 to 1 is also adiabatic, and the low/high temperatures are the same as in the transition from stage 2 to 3, so they also obey the same relations, i.e. V_4 will be 20.3 times bigger than in stage 1, and P_4 will be 0.0148 times P_1,
  i.e., in our case (as $V_1 = 1\mathrm{L}, P_1 = P^o$): $\boldsymbol{V_4 = 20.3\ \mathrm{L}, P_4 = 0.0148\ P^o}$

3.6) Heat pumps, Refrigerators, and Air conditions.

Let's run a Carnot engine **backward!**

Formally: take heat from a cold place, add some work, and throw the combined energy as heat into a hotter place.

This is the principle of heat pump, refrigerators, and air conditions: **taking heat from a cold place** (i.e., taking energy in the form of heat from a cold place) **adding some work** (i.e., electrical power from an outlet) **and putting it to a hotter place.**

The mechanism is the same for all these devices, though the purpose is different:

- Refrigerator: remove heat from the inside of the refrigerator, damp it to the room
- AC: removes heat from the room and puts it into the (hotter) outside
- Heat pump (in practice often an AC running "in winter mode") removes heat from the cold ground, and puts it to a room.

Example: **Heat pump.** say the ground is at 280K (about 7°C) and the room is at 300K. We remove $\boldsymbol{q_c = 1000\mathrm{J}}$ from the ground in a cycle

Question: how much electricity we need to damp as much as possible heat from the ground to the room?

Answer: The entropy loss from the ground is (note the minus, since we **remove** heat from the ground):

$$\Delta S_c = -\frac{|q_c|}{T_c} = -\frac{1000\,\mathrm{J}}{280\mathrm{K}} = -3.57\frac{\mathrm{J}}{\mathrm{K}}$$

Since ΔS_{pump}=0 after one cycle, this negative entropy change has to be offset by an entropy gain in the room (the hot environment), i.e., we need to have

$$+3.57\frac{\mathrm{J}}{\mathrm{K}} \le \Delta S_{\mathrm{h}} = \frac{|q_h|}{T_h} = \frac{|q_h|}{300\mathrm{K}}$$

i.e.,

$$|q_h| \ge 3.57\ \mathrm{K} * 300\frac{\mathrm{J}}{\mathrm{K}} = \mathbf{1071\ J}$$

So at least w =**71 J** must come from the outlet, since, $|q_h| = |q_c| + |w|$

Next, the coefficient of performance is defined here, as always, as $\text{c.o.p.} = \frac{\text{valuable output}}{\text{resource used}}$.

Since we want as high a $|q_h|$ as possible (high heat in the room) and the resource is the work from the outlet, we get in this ideal case (where $|q_h| = 1071, |w| = 71\mathrm{J}$)

$$\text{c.o.p.}\,(\text{heat pump}) = \frac{|q_h|}{|w|}$$

So in our case

$$\text{c.o.p.} = \frac{1071\ \mathrm{J}}{71\ \mathrm{J}} = 15$$

i.e., for every 1 Joule we put in from the outlet, we get 15 Joules in the room.

Note: contrast this with an electrical space-heater, where we would need w =1071J from the heater to produce 1071J of heat.

A heat-pump requires in our case 15 times less energy-from-an-outlet (w) to produce the same heat in the room (q_h).

That's because a heat-pump also transports lots of heat from the ground to the room, i.e., $|w|$ is small since $|q_c|$ can be quite large;

while a space heater can only produce as much heat as $|w|$.

We can now derive the coefficient of performance for a general case as following; NOTE THE SIGNS!

We throw heat on the hot environment (so +), and take heat from the cold (so -).

$$0 \le \Delta S_{\text{world}} = \Delta S + \Delta S_{\mathrm{h}} + \Delta S_c = 0 + \frac{|q_h|}{T_h} - \frac{|q_c|}{T_c} = \frac{|q_h|}{T_h} - \frac{|q_h| - |w|}{T_c}$$

i.e.,

$$|q_h| - |w| \le |q_h| \frac{T_c}{T_h}$$

i.e.,

$$|q_h| \left(1 - \frac{T_c}{T_h}\right) \le |w|$$

i.e., the coefficient of performance (in this case only!)

$$\mathbf{c.o.p.} = \frac{|q_h|}{|w|} \le \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c} \quad \textbf{(heat pump)}$$

Note that, as the example before showed, the **closer in temperature are the hot and cold environments, the higher the coefficient of performance will be.** (In contrast to engines, where the efficiency gets better as $\frac{T_c}{T_h}$ get lower)

In the HW you will be asked to derive the coefficients of performance for **AC, and for Refrigerators.**

This finishes our foray to physical thermodynamics.

3.7) Calculation of entropy changes

Let's make a list

- Cyclic processes: $\Delta S = 0$ (e.g., Carnot engines)
- Reversible adiabatic: $dS = \frac{dq_{rev}}{T} = \frac{dq}{T} = 0$ (since $dq_{rev} = dq = 0$)
- Arbitrary change for an ideal gas from a starting stage "i" to a final state "f":
  Recall that for ideal gas $dU = C_V dT$, so:

$$dq = dU - dw = C_V dT + PdV \quad \text{(ideal gas only)}$$

Then (**for ideal gases only!)**

$$\Delta S = \int \frac{dq}{T} = \int \frac{C_V dT + PdV}{T} = \int \frac{C_V dT}{T} + \int \frac{nRT}{VT} dV = C_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

Note that this result is true regardless of the actual trajectory taken.

- Phase changes: usually done at constant T, P so

$$P \text{ fixed: } dq_{rev} = dH \quad \rightarrow \quad dS = \frac{dH}{T}$$

But since T is fixed, we can integrate to get

$$\Delta S = \frac{\Delta H}{T} \quad \text{(phase change)}$$

- Rise in S when P is constant for a fixed phase: similar to the rise in H when P is constant

$$\Delta S = S_2 - S_1 = \int \frac{C_P dT}{T}$$

i.e., if C_P is approximately temperature independent (for the given phase)

$$\Delta S = S_2 - S_1 = C_P \log\left(\frac{T_2}{T_1}\right) \quad \text{(temperature change for a given phase)}$$

Example (per the enthalpy example in the previous chapter): what's the entropy change when ice at -50°C ("i" state) is melted and then the water is vaporized till we have vapor at 130°C (state "f"), and both the initial and final states are at 1bar.

Answer: there will be again 5 stages:

- Raising the temperature of the ice from -50°C (223K) till melting,
- Melting ("fusion") at 0°C (273K),
- Raising the temperature of the water till 100°C (373K),
- Vaporizing at 100°C,
- and Raising the temperature of the vapor to 130°C (403K),

So altogether:

$$S_f - S_i = C_P(\text{ice}) \ln\left(\frac{273}{223}\right) + \frac{\Delta H_{\text{fusion}}}{273\text{K}} + C_P(\text{water}) \ln\left(\frac{373}{273}\right) + \frac{\Delta H_{\text{vap}}}{373\text{K}} + C_P(\text{vapor}) \ln\left(\frac{403}{373}\right)$$

and recalling that in 1Kg of water there are 1000/18=55.5mol, and that (see prev. chapter):

$$C_{Pm}(\text{ice}) = 37\frac{\text{J}}{\text{K mol}}, \qquad C_{Pm}(\text{water liquid}) = 75\frac{\text{J}}{\text{K mol}},$$
$$C_{Pm}(\text{water vapor}) = 36\frac{\text{J}}{\text{K mol}},$$
$$\Delta H_{\text{fus}} = 6000\frac{\text{J}}{\text{mol}}, \quad \Delta H_{\text{vap}} = 40650\frac{\text{J}}{\text{mol}}$$

we get

$$S_f - S_i = 55.5\text{ mol}\left(37\frac{\text{J}}{\text{K mol}}\ln\left(\frac{273}{223}\right) + \frac{6000}{273\text{K}}\frac{\text{J}}{\text{mol}} + C_P(\text{water})\ln\left(\frac{373}{273}\right) + \frac{40650}{373\text{K}}\frac{\text{J}}{\text{mol}} + C_P(\text{vapor})\ln\left(\frac{403}{373}\right)\right)$$
$$= (\mathbf{415} + \mathbf{1220} + \mathbf{1300} + \mathbf{6050} + \mathbf{155})\frac{\mathbf{J}}{\mathbf{K}} = \mathbf{9140}\frac{\mathbf{J}}{\mathbf{K}}$$

Note that out of the five contributions (in bold), **two thirds are from** the 4th one, the **vaporization of the liquid**, which increases the disorder significantly.

Interestingly though, the 3rd and 2nd contributions are the same, i.e., raising liquid-water temperature from freezing to room-pressure-boiling, i.e., 0 to 100°C, has as much effect as melting ice!!

End of example.

The next two entropy change calculations are **interesting and non-intuitive**, so we put them in special sections:

3.8) Entropy changes when superheated water turns to vapor (or supercooled water turns to ice)

Superheating

Water that's heated in a very clean and motion-free environment (e.g., a non-rotating microwave oven in a very clean room) can be heated, at room pressure, past 100°C. It is labeled then "superheated" water. That's not the thermodynamically stable state of water at that temperature and pressure (i.e., above 100°C for a pressure of 1bar), as the stable state then is vapor; but the water does not reach the stable state since it needs to form bubbles to turn from liquid to vapor, which require some energy.

We therefore say there's a **kinetic barrier** to reach from the unstable superheated state to the stable one. If there's a little bit of motion or dust that can give enough energy (or lower the barrier) to overcome the barrier, and then the superheated water quickly turns to vapor.

That's why sometimes you heat water in a microwave, nothing seems to boil, and then you touch the glass and puff…almost all the water in glass vaporizes!

Supercooling

An analogous phenomenon happens when we lower the temperature of liquid water to 0°C and below – if there's no dust for the snowflakes to crystalize on, the water remains in a liquid form (supercooled liquid) that's very unstable and will turn immediately to ice if we shake it or put dust in the air.

Note: except for the instability, supercooled and superheated water are "regular", i.e., they have the same heat capacity, and other properties like "regular" water (i.e., for 1 bar, like water between 0 and 100°C)

Question:

What is the difference in entropy between supercooled water at -10°C (263K) and ice at this temperature.

Answer:

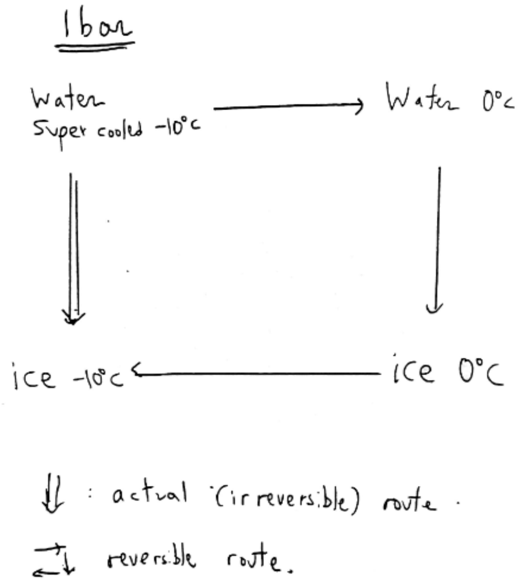
First, note that it is easy to give the wrong answer! i.e.,

$$\Delta S \neq \frac{q_{\text{actual}}}{263\text{K}} = \frac{\Delta H(\text{T} = 263\text{K})}{263\text{K}}$$

where q_{actual} is the heat released when the supercooled water at -10°C turns at water at this temperature.
This "actual" process is **irreversible** – once supercooled water starts turning to ice, it won't stop, and will definitely not reverse via a tiny change!

The reversible process is indicated in the figure (all at 1bar)

- Slowly heat the supercooled water from -10°C to 0°C.
- At 0°C it turns reversibly to ice, by cooling it (with possibly a tiny bit of shaking to ensure it doesn't turn to supercooled water).
- Then, once you cool all the water at 0°C to make ice, cool the ice to -10°C.



The entropy change, calculated along this actual path, is:

$$\boldsymbol{\Delta}S = \Delta S(\text{water}, -10°\text{C} \to 0°\text{C}) + \Delta S(\text{water} \to \text{ice}, 0°\text{C}) + \Delta S(\text{ice}, 0°\text{C} \to -10°\text{C})$$

$$= C_P(\text{ice}) \ln\left(\frac{273\text{K}}{263\text{K}}\right) - \frac{\Delta H_{\text{fus}}(0°\text{Cs})}{273\text{K}} + C_P(\text{water}) \ln\left(\frac{263\text{K}}{273\text{K}}\right)$$

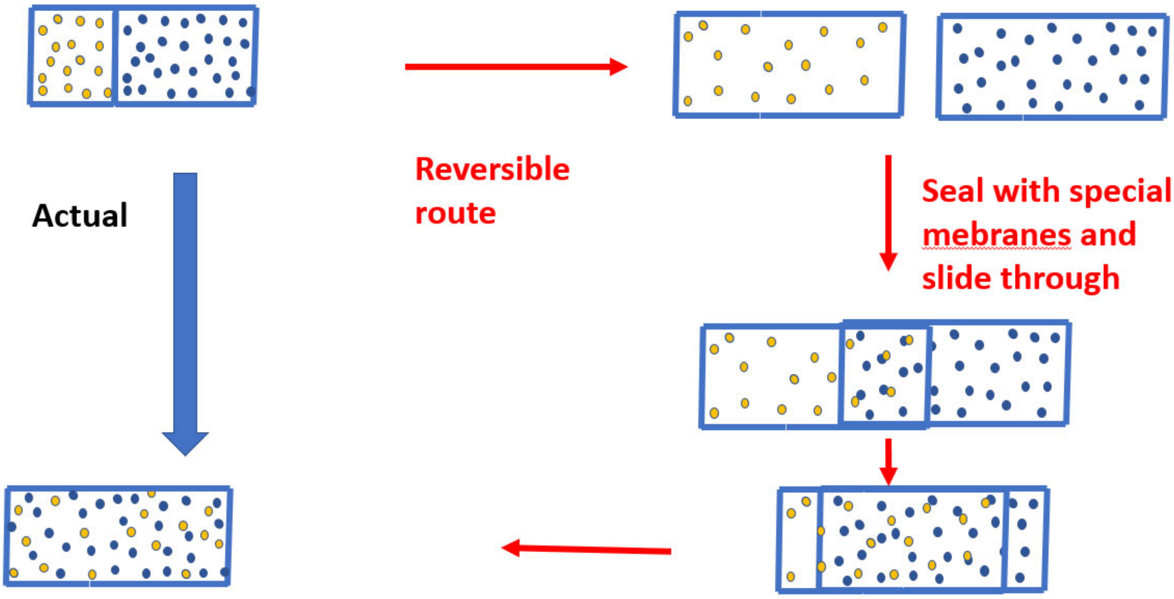
And based on the numbers we gave beforehand we can calculate this entropy change.

To conclude the chapter:

3.9) Entropy changes in mixing two different gases

Start a container with two separate gases, occupying volumes V_1, V_2. For simplicity assume the pressure and temperature are the same, so by the ideal-gas law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \left(= \frac{nRT}{P}\right)$$



Question: remove the separation. What's the entropy change?

Answer: while $q_{\text{actual}} = 0$, for ΔS we need a reversible route! See above

- Expansion Step: First increase **isothermally** the volume of each of the gases. The left, yellow one, from V_1 to $V = V_1 + V_2$, the blue from V_2 to V.

  The entropy change in this stage is, as we learned

  $$\Delta S_{\textbf{expansion}} = n_1 RT \ln\left(\frac{V}{V_1}\right) + n_2 RT \ln\left(\frac{V}{V_2}\right)$$

- Then place special membranes:
  - On the <u>right</u> side of the yellow molecules' container place a membrane that blocks the yellow molecules, but is transparent to blue molecules. **(This is theoretically possible if, and only if, the molecules are different; even different isotopes can be formally treated this way, e.g., mixing of C_{12} and C_{13}.)**
  - And an analogous membrane on the left side of the blue-molecules container, that blocks blue molecules.

- Now take the containers, and **slide** them through each other, <u>as if they were interpenetrating rods in an umbrella</u>.

  To be precise, we need to first ensure that one chamber is slightly smaller than another, say the one with the yellow molecules; and then when the two chambers touch each other, put the blue-molecules-blocker membrane **on the left of the yellow-molecules-blocker membrane.** (plot it and see.)

Think about it and see that the yellow molecules volume will not change (they can't pass their own membrane, but can freely move through the blue-molecules membrane).

Gently slide the two containers into each other it until all molecules occupy an overlapping volume, V (i.e., the original volume).

The **key is that the entropy change in this "merging" ("sliding-in") stage is 0!** The merging is done without energy change and without work (each gas is fixed at its box), so there's no heat. Further, the merging is completely reversible – at any stage we can "unmerge".

Therefore, the total entropy change is **just from the first, expansion step**, i.e.,

$$\Delta S_{mix} = n_1 RT \ln\left(\frac{V}{V_1}\right) + n_2\, RT \ln\left(\frac{V}{V_2}\right)$$

Now define the fraction in the gas at the end to be

$$x_1 = \frac{n_1}{n} = \frac{n_1}{n_1 + n_2} \qquad\qquad (n \equiv n_1 + n_2)$$

and similarly define $x_2 = n_2/(n_1 + n_2)$; of course $x_1 + x_2 = 1$ (if the mole fraction of the first gas is 1/3, the mole fraction of the 2nd gas will be 2/3).

So $n_1 = x_1 n$, $n_2 = x_2 n$.

Further, since $\frac{V_1}{V_2} = \frac{n_1}{n_2}$, i.e., the molar ratios are the same as the volume ratio, the molar fraction will equal the volume fraction:

$$x_1 = \frac{V_1}{V}, \qquad x_2 = \frac{V_2}{V}$$

Therefore:

$$\Delta S_{mix} = nRT\left(x_1 \ln\left(\frac{1}{x_1}\right) + x_2\ \ln\left(\frac{1}{x_2}\right)\right)$$

i.e., the entropy of mixing per the total number of moles is

$$\frac{\Delta S_{mix}}{n} = RT\left(x_1 \ln\left(\frac{1}{x_1}\right) + x_2 \ln\left(\frac{1}{x_2}\right)\right)$$

Note that both terms are positive; that's because, since $x_1 < 1$, its inverse is bigger than 1, so $\ln\left(\frac{1}{x_1}\right) > 0$. Thus, as we know, mixing is spontaneous, i.e., ΔS_{mix} is positive.

Exercise (at home): what's the entropy change when 1 Liter of He is mixed with 2 L of air (essentially N_2) when both gases are initialy at T_{ROOM} and room pressure.

3.10) The third law

The third law is treated in Levine in Chapter 5 (and 21), but I find it easier to treat it here.

The third law is that at zero temperature, the entropy of a HOMOGENOUS substance in equilibrium becomes 0.

(There are some difficulties associated with heterogenous compounds, since there's disorder associated with exchange of particles; let's not worry about these)

The key is that **at zero temperature, there is no disorder.**

> That's easy to understand in Stat. Mech., where **entropy is related to the number of "overall quantum states" (see the stat. mech. set of notes) --** if we also invoke quantum mechanics.
>
> Formally, at zero temperature the number of available states for a system is 1; that's because the system will automatically be at the lowest **(ground)** state.
>
> For example, a bunch of many harmonic oscillators will be **each at its ground state**. There will be NO UNCERTAINTY about where the system is at zero temperature; and no-uncertainty means zero entropy.

You may wonder how the 3rd law is commensurate with what learned, that the entropy increases by $nR\ln 2$ for an ideal gas when we double its volume, independent of temperature! (So it seems that the entropy won't be zero at zero temperature – we just need to increase the volume and it will increase…)

There are 2 (related) answers to this paradox

i) The practical answer is that substances do no remain ideal gases due to attractions, they become liquids and then solids as we reduce the temperature.

ii) But there is a fundamentally more important reason than just attractions. Quantum mechanics tells us that nuclei have an "extent", they are not just point particles. In an ideal gas (i.e., without interaction), as the temperature is lowered, this "extent" (i.e., the **de Broglie wavelength**) of the nuclei **is related to the temperature – as the temperature is lowered the de Broglie wavelength INCREASES further and further --** until eventually it will be comparable to or even larger than the distance between the particles; in that case, we cannot think of the molecules as a classical ideal gas, and the thermodynamics derivation becomes invalid.

3.11) Conclusions: Chapter 3

- We first learned

$$dS = \frac{dq_{\text{rev}}}{T}$$

- We stated that for an isolated system $dS \geq 0$ (2nd law)
- We used the fact that dS is a state function to obtain the efficiency of engines and the coefficient of performance of ACs, heat-pumps, etc.

> The key was using a hot-environment and a cold-one (as in the Carnot engines), where we realized that for reversible (optimal) operation, $\frac{|q_c|}{T_c} = \frac{|q_h|}{T_h}$.

For example, for ACs, refrigerator, etc., while $|q_h|$ needs to be bigger than $|q_c|$, it does not need to be much larger if the temperature difference is small. So for heat pumps, for example, we can move heat from a cold place, and need to bring just a little electricity to damp the total to a hot place.

- We realized that when raising temperature where the initial and final pressure are equal we can calculate ΔS rom a fixed-pressure path:

$$\Delta S = \int \frac{C_P dT}{T} = C_P \ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right)$$

while for a phase change

$$\Delta S = \frac{\Delta H(T = T_{\text{phase change}})}{T_{\text{phase change}}}$$

- We derived the formula for the entropy change for an ideal gas upon an arbitrary change of T, P, V

$$\Delta S(\text{ideal gas}) = \int \frac{dU - dw}{T} = \int \frac{dU + PdV}{T} = \int \frac{C_V dT}{T} + \frac{nRdV}{V}$$

$$\simeq C_V \ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right) + nR \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right)$$

- We derived the entropy of mixing of ideal gas. We saw that the entropy rises in mixing two different gases can be interpreted as the entropy rise when each gas separately expands to fill the full volume; **once the two gases are separately occupying the final volume, the entropy of "merging" them together is actually 0!**

- We learned the 3rd law, **entropy vanishes at 0K** – which we understood as quantum mechanically a system at 0 Kelvin is in a **single** lowest overall state.

Relevance to chemistry

The stuff we learned is interesting and abstract, but in its present form is not trivial to apply for reactions. Take the simplest reaction: phase change. And consider, e.g., supercooled water at say -10°C.

We know that water has a higher entropy than ice. So why does supercooled water turns to ice? That's because when it does, it releases heat. This heat goes to the environment, and raises the entropy of the environment.

So the total world entropy rises

$$\Delta S_{\text{world}} = \Delta S(\text{super cooled water} \rightarrow \text{ice}) + \Delta S(\text{environment}) > 0$$

$$\text{negative} \qquad + \quad \text{positive} \quad = \quad \text{net positive}$$

so the overall process is spontaneous.

In the next chapter we'll learn about a more direct way involving system-only quantities to determine if a reaction will happen.

IV. Gibbs Free Energy

At a specific T, P, consider liquid water. We know that it contains several molecules: mostly H_2O, but also OH^- and H^+.

All 3 species are in equilibrium. We know from 20B that this is enough to determine their concentration. In this chapter we introduce the tool which allows this: the Gibbs Free energy (or just Gibbs Energy). We'll derive the $E = mc^2$ of chemical theormodynamics:

$$\boldsymbol{G} \textbf{ is minimum in equilibrium (for fixed } \boldsymbol{T, P}\textbf{).}$$

with plenty of consequences, discussed here.

4.1) **Overview**

Roughly, this chapter has two parts.

First, the Road to Equilibrium at fixed *T* (and later also fixed *P*):

- We know $dS_{\text{univ}} \geq 0$. We'll get an expression involving the system alone (the Clausius relation):

$$\boldsymbol{T\Delta S \geq q}$$

- We'll then define the Gibbs Free Energy

$$\boldsymbol{G = H - TS = U + PV - TS}$$

and get that, if any electrical work (labeled w_{el}) is applied or obtained from the system, that

$$\boldsymbol{dG \leq dw_{\text{el}}} \qquad \text{when } T \text{ and } P \text{ are fixed.}$$

When no electrical work is obtained or applied, $dG \leq 0$ (at fixed *T, P*), so at equilibrium *G* is minimal.

- We'll introduce a very important quantity, the chemical potential,

$$\mu = \left.\frac{\partial G}{\partial n}\right|_{T,P}$$

We'll see, for example, that equilibrium between, say, A, B in the reaction $A \rightarrow B$ simply implies

$$\mu_A = \mu_B$$

while if the products side is favored, then $\mu_A > \mu_B$ and vice versa. Extensions to more species, different stoichiometric coeff., etc. are trivial.

This equation is the core of chemical thermodynamics!

The next part of the chapter deals with changes of $\boldsymbol{T, P}$

- Moving then to system in equilibrium where T and P are changing, we'll find, e.g.,

$$dU = -PdV + TdS, \qquad dG = VdP - SdT$$

and use this and other similar expressions to derive many **interesting mathematical relations involving P, T, V, S, and U, H or G.**

We'll see that these relations can be used to experimentally obtain S (and therefore G!).

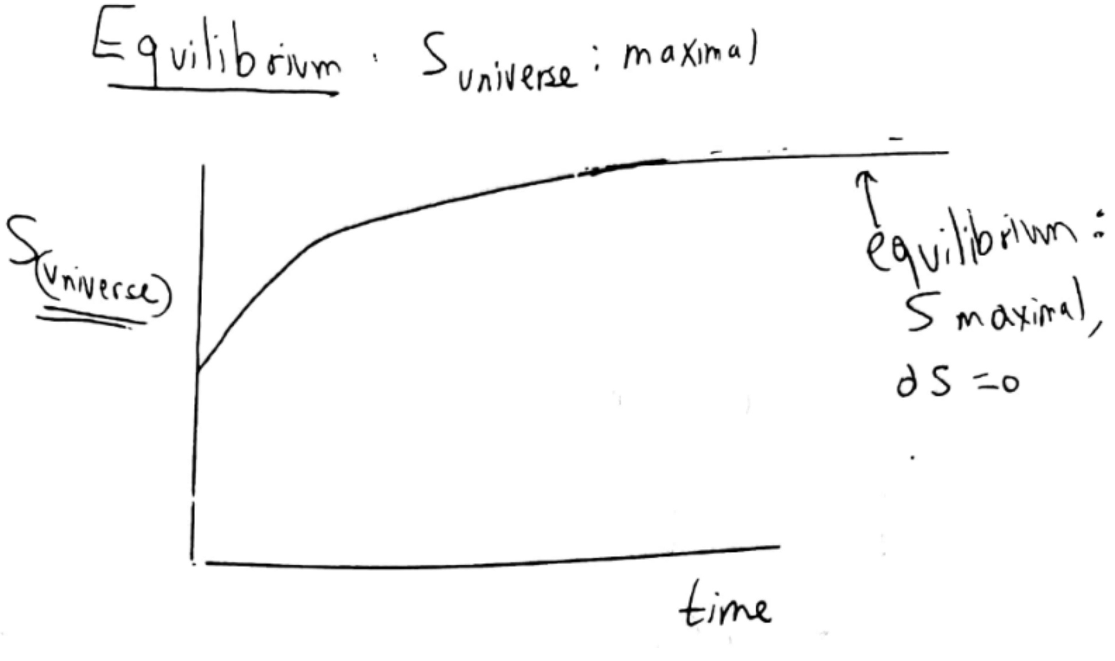
Note: this is a very long and difficult chapter. Do lots of HW, practice makes perfect!

4.2) The Clausius relation.

Take an isolated system (where the environment is not connected to the system, so only the system can change).

Then (Chapter 3) we know that S cannot decrease with time. Therefore, in **equilibrium, S (isolated system) is maximal.**

However, chemical reactions are generally done in non-isolated systems. There, the entropy of the combined *system+environment* (i.e., the entropy of the world) is nondecreasing, and is maximal in equilibrium (see figure below).



This is not convenient, we want to refer only to system quantities. To do this, we'll need some "tricks".

Thus, "world", i.e., the $system + environment$, has non-decreasing entropy

$$0 \leq \Delta S + \Delta S_{\text{environment}}$$

So ΔS can be negative (as in, e.g., freezing water), as long as this is compensated by a rise in $S_{\text{environment}}$.

Now let's assume the surroundings are somehow "**big**", and are at an essentially fixed temperature $\boldsymbol{T}$.

The key realization is that **regardless of whether the process in the system is reversible or irreversible, all the ENVIRONMENT will feel is that a little bit of heat was given or taken from it.**

Thus: any process, reversible or not for the system, will look reversible to the environment.

If the heat input to the system is labeled dq, **the environment heat-"input" will be $-dq$.** The change in entropy is then

$$dS_{\text{environment}} = -\frac{dq}{T}$$

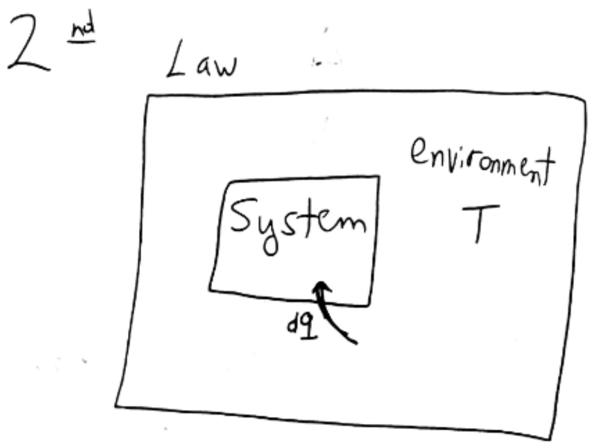
Therefore, since the change of entropy of the "world" is the combination of the system and the environment, and since that total change of entropy must be non-negative, we get:

$$\mathbf{0} \leq dS_{\text{world}} = dS + dS_{\text{environment}} = \boldsymbol{dS - \frac{dq}{T}}$$

(and recall, $0 = dS_{\text{world}}$ for reversible processes only, and $0 < dS_{\text{world}}$ for irreversible) i.e.,

$$dq \leq T\, dS$$

and the equality applies if, and only if, the process is reversible. **This is the Clausius relation.**



$$dS_{tot} = \underbrace{dS_{sys}}_{dS} + \underbrace{dS_{environ}}_{-\frac{dq}{T}} \geq 0$$

Example: Say there's a process where the entropy change of the system is $dS = 20\frac{\text{J}}{\text{K}}$ and during that process the system is attached to a heat bath with temperature $T = 400\text{K}$ (the "environment").

Questions: can there be a process where

- *(i) dq=6000J in heat from the environment?*
- *(ii) What about 8000J?*
- *(iii) and 12000J?*

Answers:

(i) Start with the first case ($dq = 6000\text{J}$). Let's see if it fulfills the Clausis relation.

Since $TdS = 400 * 20\frac{\text{J}}{\text{K}} = 8000\text{J}$, we get

$$6000\mathrm{J} = \mathrm{d}q < T\,dS = 8000\ \mathrm{J}$$

So the process is possible and will be irreversible.

To understand this in more fundamental terms, note that the **environment lost 6000J**. So its change of entropy would be

$$dS_{\text{environment}} = -\frac{dq}{T} = -\frac{6000\mathrm{J}}{400\mathrm{K}} = -15\frac{\mathrm{J}}{\mathrm{K}}$$

and therefore the change of the entropy of the world is

$$dS_{\text{world}} = dS + dS_{\text{environment}} = 20\frac{\mathrm{J}}{\mathrm{K}} - 15\frac{\mathrm{J}}{\mathrm{K}} > 0$$

i.e., the process is possible and irreversible.

(ii) Similarly, when $dq = 8000\ \mathrm{J}$, we can repeat the math above to show that both dq and TdS are equal (i.e., each is 8000J), so the process is reversible (and therefore allowed).

Another way of saying that is that

$$dS_{\text{world}} = dS + dS_{\text{environment}} = 20\frac{\mathrm{J}}{\mathrm{K}} - \frac{dq}{T} = 20\frac{\mathrm{J}}{\mathrm{K}} - \frac{8000\mathrm{J}}{400\mathrm{K}} = 0$$

i.e., the process is **reversible.**

(iii) Finally, the last case does not obey the Clausius relation ($dq = 12{,}000\mathrm{J}$ is larger than $TdS = 8000\mathrm{J}$), so it is impossible.

Indeed, if the heat input to the system would have been so large (and positive), that would have meant that the entropy change of the environment would have been large (and negative), $dS_{\text{evnironment}} = -\frac{12000\mathrm{J}}{400\mathrm{K}} = -30\frac{\mathrm{J}}{\mathrm{K}}$, so the total change of the entropy of the world would have been $dS_{\text{world}} = dS + dS_{\text{environment}} = 20\frac{\mathrm{J}}{\mathrm{K}} - 30\frac{\mathrm{J}}{\mathrm{K}} = -10\frac{\mathrm{J}}{\mathrm{K}}$, i.e., the world's entropy would have decreased – and that's not possible.

4.3) The Gibbs Free Energy

Next, we'll convert the Clausius relation to an equation about **a state function of the system.** Start with:

First case considered: purely mechanical work

So far we only considered mechanical work; then, recall $dU = dq + dw_{\text{mech}}$, i.e., $\boldsymbol{dU = dq - PdV}$. Recall also that we defined $\boldsymbol{H = U + PV}$, which will therefore fulfil, $\boldsymbol{dH = dq + VdP}$

Thus, we recall that **for fixed pressures**

$$dq = dH \quad (P \text{ fixed})$$

Combining with the Clausius relation, $\boldsymbol{dq \le TdS}$ gives

$$dH - TdS \le 0 \ \ (P \text{ fixed, only mechanical work})$$

Note that this equation refers purely to state variables!

Now define a new **state function,** the Gibbs Free energy

$$G = H - TS$$

Then

$$\boldsymbol{dG} = dH - TdS - SdT$$

Let's look at processes happening at **fixed temperature** (in addition to being at **fixed pressure.**) Since $dT = 0$ for fixed temperature

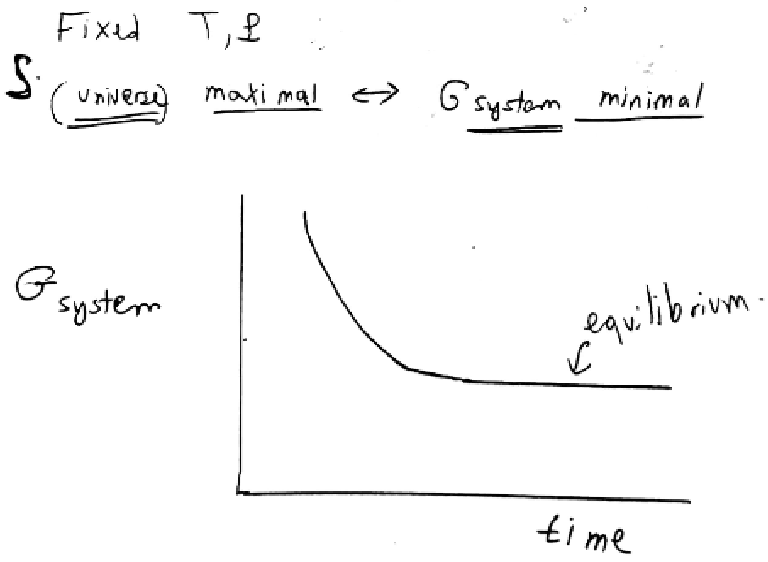
$$dG = dH - TdS \ (T \text{ fixed})$$

Therefore combining the last two turquoise equations, we get

$$dG \le 0 \ (P \text{ and } T \text{ fixed, only mechanical work})$$

Thus, in processes (primarily **reactions)** in which the pressure and temperature are fixed, the Gibbs free energy decreases! Or put differently: at a given pressure and temperature, the **Gibbs free energy will be a minimum in equilibrium!**

See the figure: it shows that we converted the statement that the **world's entropy never decreases** (an earlier figure) to a statement that, for a restricted set of processes (fixed *P* and fixed *T*) **a system quantity decreases**



Example: consider a molecule we'll label "A", and specifically consider its solid and liquid forms. At room pressure, and at a temperature of 77°C (i.e., 350K):

- The energy of the solid is 90 $\frac{\text{kJ}}{\text{mol}}$;
- and that of the liquid is 95 $\frac{\text{kJ}}{\text{mol}}$;
- further, at that temperature the entropy of the solid is 50 $\frac{\text{J}}{\text{K mol}}$, while that of the liquid is 80 $\frac{\text{J}}{\text{K mol}}$.

Question: which form will be more stable at this temperature?

Answer: let's calculate the Gibbs free energy, $G = U - TS + VP$.
Since we consider solids and liquids (both: "condensed phases") which have very low volume, **we can ignore the VP term**.

Note: for water at room pressure:

$$PV_m = 1\text{ bar} * 18\frac{\text{cm}^3}{\text{mol}} \simeq \frac{100\text{J}}{\text{L}} \cdot 0.02\frac{\text{L}}{\text{mol}} = 2\frac{\text{J}}{\text{mol}}$$

Small indeed

Therefore, for the solid:

$$G_{\text{solid}} \simeq U_{\text{solid}} - T\,S_{\text{solid}} = 90{,}000\frac{\text{J}}{\text{mol}} - 350\text{K} \cdot 50\frac{\text{J}}{\text{K mol}} = 72{,}500\frac{\text{J}}{\text{mol}}$$

While for the liquid

$$G_{\text{liquid}} \simeq U_{\text{liquid}} - T\,S_{\text{liquid}} = 95{,}000\frac{\text{J}}{\text{mol}} - 350\text{K} \cdot 80\frac{\text{J}}{\text{K mol}} = 67{,}000\frac{\text{J}}{\text{mol}}$$

Therefore, since $G_{\text{liquid}} < G_{\text{solid}}$, the compound will be a liquid at this temperature.

Next Example:

A reaction $A \rightarrow B$ has, at a $T = 27°\text{C} = 300\text{K}$, a reaction entropy $\Delta S = 40\frac{\text{J}}{\text{K mol}}$, and a reaction energy $\Delta U = 10\frac{\text{kJ}}{\text{mol}}$

(**Note** that we generally don't write the "m" molar subscript in reactions, and usually refer to "one-mole-of-reactions". More details in Chapter 5).

Question: would the reaction take place in an "**elastic balloon**", placed inside a $T = 27°\text{C}$ heat bath inside a room (with room pressure) if:

(i) A, B are liquids; or

(ii) A is a liquid; B is a gas

Answer:

T=const., P=cons., so we need to check ΔG.

$$\Delta G = \Delta(U + PV - TS) = \Delta U + P\Delta V - T\Delta S \quad (\text{since } P, T \text{ both fixed})$$

Consider now the two cases:

(i) Both A, B are liquids: V is **small.** So

$$\Delta G \simeq \Delta U - T\Delta S = 10{,}000\frac{\text{J}}{\text{mol}} - 300\text{K} * 40\frac{\text{J}}{\text{Kmol}} = -2{,}000\frac{\text{J}}{\text{mol}}$$

So the reaction will proceed, B is more thermodynamically stable than A.

(ii) B is a gas:

$$\Delta G = \Delta U - T\Delta S + P\Delta V = -500\frac{\text{J}}{\text{mol}} + PV_m(B)$$

(Note that we write $\Delta V = V_m(B) - V_m(A) \simeq V_m(B)$, since $V_m(A) \ll V_m(B)$ as A is a liquid, B a gas)

But since B is a gas, $PV_m(B) = RT = 8.3\frac{\mathrm{J}}{\mathrm{K{\cdot}mol}} \cdot 300\mathrm{K} \simeq 2{,}500\frac{\mathrm{J}}{\mathrm{mol}}$

So

$$\Delta G = -2000\frac{\mathrm{J}}{\mathrm{mol}} + 2500\frac{\mathrm{J}}{\mathrm{mol}} = 500\frac{\mathrm{J}}{\mathrm{mol}}$$

i.e., the reaction is not favorable.

4.4) The Gibbs Free Energy: allowing for electric work

So far we considered only mechanical work. We'll now consider also non-mechanical work, which we'll label as electric work.

We'll see in this section that with electric work we can compensate a reaction barrier, or, for spontaneous reactions where $\Delta G < 0$, we can use the reaction to produce electric work.

When current runs from your outlet, the electrons run (in average) in the same direction. The electrical energy transfer is therefore ordered, so it is work.

Note: there could be other forms of non-mechanical work, e.g., magnetic, but we label them all as "electrical".

Let's repeat then the derivation from the previous chapter, but allow now for electric work

$$\boldsymbol{dU} = dq + dw = dq + dw_{\mathrm{mech}} + dw_{\mathrm{elec}} = \boldsymbol{dq - PdV + dw_{\mathrm{elec}}}$$

The enthalpy is defined always as $H = U + PV$, so inserting we get

$$dH = dq + VdP + dw_{\mathrm{elec}}$$

And for a fixed pressure case:

$$dH = dq + dw_{\mathrm{elec}} \quad (P \text{ fixed})$$

Or simply $\boldsymbol{dH - dw_{elec} = dq}$ **(for $\boldsymbol{P}$ fixed).**

Inserting the Clausius relation, $dq \le TdS$, gives

$$\boldsymbol{dH - dw_{elec} \le TdS \qquad P\ \textbf{fixed.}}$$

As before, since $G = H - TS$, and since at **fixed $\boldsymbol{T}$** we have $\boldsymbol{dG = dH - TdS}$, we get:

$$dG \le dw_{elec} \quad (P, T \text{ both fixed})$$

which when accumulated gives

$$\Delta G \le w_{\mathrm{elec}} \quad (P, T \text{ fixed})$$

So in general the **amount of electrical work given has to be at least the change in $\boldsymbol{G}$ or higher.** If there's an equality sign, the reaction is reversible, otherwise, it will be irreversible.

Example"

Question: Take the example from a few pages ago.:

- Calculate the amount of electrical work needed, or that can be extracted, for the liquid-liquid case.
- The same, for the liquid --> gas case.
- At which temperature would the liquid-liquid transition be in equilibrium without inputting/extracting electric work (estimate).

Answer:

- In the first case, $\Delta G = -500\frac{\mathrm{J}}{\mathrm{mol}}$, so we can extract up to $\mathbf{500}\frac{\mathbf{J}}{\mathbf{mol}}$ of electrical work (i.e., w_{elec} can be as negative as $-\mathbf{500}\frac{\mathbf{J}}{\mathbf{mol}}$ in which case it will be reversible.)

  And If $\boldsymbol{w}_{\mathbf{elec}}$ is less negative, e.g.,, we extract 300 J/mol or 0, then the reaction is irreversible

- In the 2nd case, $\Delta G = 2000\frac{\mathrm{J}}{\mathrm{mol}}$ so we need to input at least $2000\frac{\mathbf{J}}{\mathbf{mol}}$ for the reaction to proceed (and if we put 2000 J/mol it will be reversible)

- It would be reversible without inserting or removing electric work at a temperature T^* where $\Delta G(T^*) = 0$, i.e.,

  $$\Delta H(T^*) - T^* * \ \Delta S(T^*) = 0$$

  This implies that

  $$T^* = \frac{\Delta H(T^*)}{\Delta S(T^*)}$$

  At this point let's **approximate** that the enthalpy of reaction does not vary much with temperature, and the same for the entropy of reaction, so that we can replace both their values at their values at room temperature

  $$T^* = \frac{\Delta H(T^*)}{\Delta S(T^*)} \cong \frac{\Delta H(T = 300\mathrm{K})}{\Delta S(T = 300\mathrm{K})}$$

  And since it involves liquids, we can replace ΔH by ΔU, thereby getting

  $$T^* \cong \frac{\Delta U(T = 300\mathrm{K})}{\Delta S(T = 300\mathrm{K})} = \frac{10000\,\frac{\mathrm{J}}{\mathrm{mol}}}{40\,\frac{\mathrm{J}}{\mathrm{K\,mol}}} = 250\ \mathrm{K}.$$

  Note: if we were told the heat capacity difference we could have done a little better, since we know that both the enthalpy of reaction and the entropy of reaction depend on ΔC_P, i.e.,

  $$\Delta H(T^*) = \Delta H(300\mathrm{K}) + \Delta C_P * \ \ (T^* - 300\mathrm{K})$$

  $$\Delta S(T^*) = \Delta S(300\mathrm{K}) + \Delta C_P * \ln\left(\frac{T^*}{300\mathrm{K}}\right)$$

  However, that would have produced a complicated equation, and we were anyway not given ΔC_P, so we ignore it.

END OF EXAMPLE.

We're now ready for the highlight of the course:

4.5) Chemical Potentials

The chemical potential of a species in a specific phase measures the "tendency" of the species to react with other molecules or to "change phase". In short – the tendency to change.

Let's first see this for two phases. Say a species A can exist in two phases.

Our discussion is general, for any two substances and/or phases, but as an example think of "A" being sugar or salt, and the phases being:

Phase 1: $A(\text{pure, solid})$ – e.g., pure sugar blocks

Phase 2: $A(solute\ in\ water)$ – e.g., sugar in water.

This is just an example, anything else will do.

The general statement is then:

If $\boldsymbol{\mu_1 < \mu_2}$ the material would move from phase 2 to phase 1, and vice versa; so in equilibrium $\boldsymbol{\mu_1 = \mu_2}$.

Side note: This is reminiscent of what we know about temperature and pressure

If $T_1 < T_2$ (and no work it involved): heat is transferred from 2 to 1; in equilbirum $T_2 = T_1$

If $P_1 < P_2$: mass moves from 2 to 1 (in equilibrium $P_1 = P_2$)

Proof: say T and P are identical but equilibrium was not yet achieved. Formally,

$$G = G(T, P, n_1, n_2).$$

Say we fix T, P but change the number of moles, to $n_1 + dn_1,\ n_2 + dn_2$. The change in Gibbs free energy will be, using what we learned on partial derivatives:

$$dG = G(T, P, n_1 + dn_1, n_2 + dn_2) - G(T, P, n_1, n_2) \simeq \left.\frac{\partial G}{\partial n_1}\right|_{n_2,P,T} \cdot dn_1 + \left.\frac{\partial G}{\partial n_2}\right|_{n_2,P,T} dn_2$$

Now define

$$\mu_1 \equiv \left.\frac{\partial G}{\partial n_1}\right|_{n_2,P,T}$$

$$\mu_2 \equiv \left.\frac{\partial G}{\partial n_1}\right|_{n_1,P,T}$$

So

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

So far this was general. Now consider what would have happened if we moved a tiny number of moles from phase 1 to 2; in that case $dn_1 = -dn_2$.

For example, say we moved 0.01 mols from phase 1 to 2, then

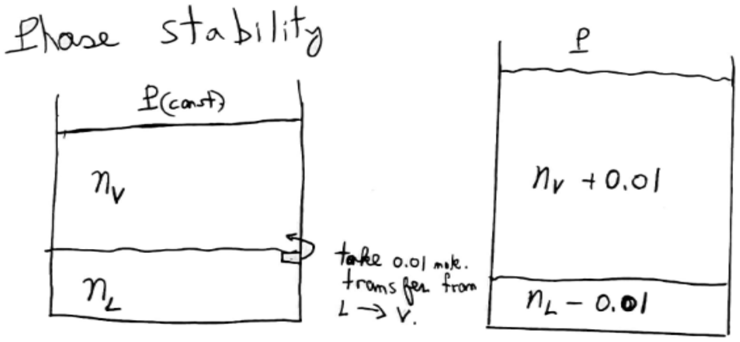
$$dn_1 = -0.01\text{mol}, \qquad dn_2 = +0.01\text{mol}.$$

Then:

$$dG = +0.01\text{mol}\,(\mu_2 - \mu_1)$$

Therefore, **if $\mu_1 > \mu_2$, then $dG > 0$**!

Since we know **that for a fixed T, P a system would like to be in the state with the lowest G**, then in that case some material would spontaneously transfer from phase 1 to phase 2. (For our example, this will mean that some of the liquid vaporized-see figure).



$G(n_v, n_L)$

$$G + \frac{\partial G}{\partial n_v}\cdot(0.01) + \frac{\partial G}{\partial n_L}\cdot(-0.01)$$

$$= G + (\mu_v - \mu_L)\cdot 0.01$$

So: if $\mu_L > \mu_v \Rightarrow \Delta G < 0$: process spontaneous.

if $\mu_L < \mu_v$ then $n_L + 0.01, n_v - 0.01$ would be more favorable than n_L, n_v.

but for: $\mu_L = \mu_v$: $\underline{\underline{\text{equilibrium}}}$

The process will go on until one of two things happen:

- Either the $\mu's$ change as the material transfers till eventally $\mu_1 = \mu_2$.
- Or all of phase 1 has been converted to phase 2.

Before going on to examples, we need one more fact:

<u>For a pure phase:</u> $\mu = G_m$

A substance in a pure phase could be for example:

- Pure liquid (pure water)
- Vapor made from one compound (He in a balloon)
- Pure solid (pure ice)

Examples for what is NOT a material in a pure phase:

- Water with sugar
- Air (essentially 80% nitrogen, 20% oxygen)
- Water mixed with ethanol

When a substance is in a pure phase, **its chemical properties are independent of the number of moles** (1gm of sugar has the same properties at 100gm!) so its Gibbs free energy is proportional to the number of moles

$$G = G_1 = n_1 G_{m1}(P,T)$$

Therefore

$$\mu_1 = \frac{\partial\big(n_1 G_{m1}(P,T)\big)}{\partial n_1} = G_{m1}(P,T)$$

So the chemical potential is simply the molar Gibbs free energy!

> **Note that this is not true for compounds in solution; example – sugar in water.** For a fixed amount of water, for example, the taste (and other chemical properties) of the solution will depend of course on the **amount** of sugar. A water cup with three sugar cubes is different than with one!

Now we can proceed to our example:

(VERY LONG) Example: "solid" ←→ "solute" reaction.

Notation:

- n_1 is the number of moles of solid "A",
- n_2 is the number of moles of the solute "A" in the solution, and n_{H_2O} the number of moles of the water solvent.

The Gibbs free energy will be the sum of the solid + liquid parts

$$G = G_{solid} + G_{liquid}$$

- So let's say that: the molar Gibbs free energy of solid "A" is $G_{m1}(P,T) = -80\,\frac{\mathrm{kJ}}{\mathrm{mol}}$. Since the solid is pure, the Gibbs free energy is proportional to the amount of n_1, so $G_{solid} = n_1 G_{m1}(P,T) = -n_1 \cdot\ 80\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

- And say that $G_{liquid} = n_{\mathrm{H_2O}} \cdot 10\,\frac{\mathrm{kJ}}{\mathrm{mol}} + n_2 \cdot 20\,\frac{\mathrm{kJ}}{\mathrm{mol}} \ln\left(\frac{n_2}{n_{H_2O}}\right)$
(this is some function I made up which is <u>vaguely</u> reminiscent of the correct behavior – as we'll see later).

Questions:

(i) Determine the chemical potential

(ii) If we pour into a container with 200 moles of water, 4 moles of solid "A" (think of pouring 4 moles of sugar), what will be the equilibrium amounts of solid "A" and solute "A". Determine it both graphically (by drawing G) and from the equation for the chemical potentials

(iii) Same for pouring 1 mole of solid "A" into the same 200 moles water container.

(iv) What is the chemical potential of water and is it relevant to the preceding parts.

(v) How much electrical work can we get in part (ii) – determine your answer graphically.

Answers

(i) The total G is

$$G = -n_1 \cdot \ 80\frac{\text{kJ}}{\text{mol}} + n_{\text{H}_2\text{O}} \cdot 10\frac{\text{kJ}}{\text{mol}} + n_2 \cdot 20\frac{\text{kJ}}{\text{mol}}\log\left(\frac{n_2}{n_{H_2O}}\right)$$

The chemical potentials are then

$$\mu(A, solid) \equiv \mu_1 = \frac{\partial G}{\partial n_1} = \frac{\partial\left(n_1 \cdot \left(-80\frac{\text{kJ}}{\text{mol}}\right) + (n_1 - \text{independent part})\right)}{\partial n_1}$$
$$= -80\frac{\text{kJ}}{\text{mol}}$$

while the chemical potential of the solute-A is

$$\mu(A, solution) \equiv \mu_2 = \frac{\partial G}{\partial n_2} = \frac{\partial\left(n_2 \cdot 20\frac{\text{kJ}}{\text{mol}}\ln\left(\frac{n_2}{n_{H_2O}}\right) + (n_2 - \text{independent part})\right)}{\partial n_2}$$
$$= 20\frac{\text{kJ}}{\text{mol}} \cdot \frac{\partial\left(n_2 \cdot \ln\left(\frac{n_2}{n_{H_2O}}\right)\right)}{\partial n_2}$$

Differentiate each term

$$\frac{\partial\left(n_2 \cdot \log\left(\frac{n_2}{n_{H_2O}}\right)\right)}{\partial n_2} = \frac{dn_2}{dn_2}\ln\left(\frac{n_2}{n_{\text{H}_2\text{O}}}\right) + n_2\frac{d\ln\left(\frac{n_2}{n_{\text{H}_2\text{O}}}\right)}{dn_{\text{H}_2\text{O}}}$$
$$= \ln\left(\frac{n_2}{n_{\text{H}_2\text{O}}}\right) + n_2 \cdot \frac{1}{\frac{n_2}{n_{\text{H}_2\text{O}}}} \cdot \frac{1}{n_{\text{H}_2\text{O}}} = \ln\left(\frac{n_2}{n_{\text{H}_2\text{O}}}\right) + 1$$

Therefore,

$$\mu_2 = 20\frac{\text{kJ}}{\text{mol}}\left(\ln\left(\frac{n_2}{n_{H_2O}}\right) + 1\right)$$

(ii) For an equilibrium where both phases are present, the chemical potential of "A" in both phases needs to be equal, i.e., $\mu_1 = \mu_2$; plugging in from above we get

$$-80\frac{\text{kJ}}{\text{mol}} = 20\frac{\text{kJ}}{\text{mol}}\left(\ln\left(\frac{n_2}{n_{H_2O}}\right) + 1\right) \quad i.e., \qquad -4 = \ln\left(\frac{n_2}{n_{H_2O}}\right) + 1$$

i.e.,

$$\ln\left(\frac{n_2}{n_{H_2O}}\right) = -5$$

i.e.,

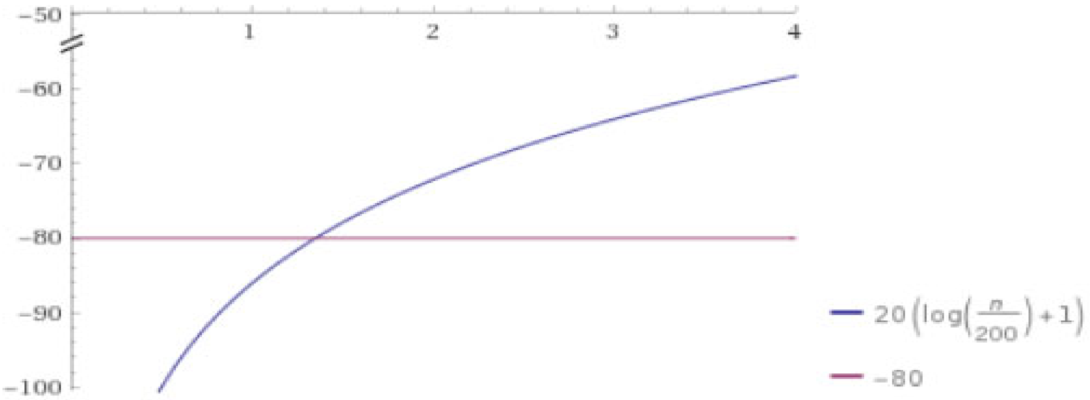
$$\frac{n_2}{n_{\mathrm{H_2O}}} = e^{-5} = 0.0067 \rightarrow \qquad \boldsymbol{n_2 = 0.0067 \cdot 200\mathrm{mol} = 1.35\ \mathrm{mol}}$$

where we recalled that $n_{\mathrm{H_2O}} = 200\mathrm{mol}$.

Since the total number of moles of "A" is 4mols,

$$n_1 = 4\mathrm{mol} - n_2 = (4 - 1.35) = 2.65\mathrm{mol}$$

Thus, most of the "A" will stay in solid form. This is equivalent to what happens when we put too much sugar in water – the water becomes "saturated" in sugar, and any extra amount beyond the "maximal capacity" is precipitated, *i.e.*, falls to the bottom of the cup and is in a solid form.



Chemical potentials in kJ/mol vs $\boldsymbol{n_2}$ for the preticipate-solute case in the figures below: solute (phase "2") in blue, solid (phase "1") in purple-red. Note that

(i) In the first case in the figure, $n_{tot} = 4$, equilibrium is achieved when the two lines cross at $n_2^{equilibrium} = 1.35$ mol.

(ii) In the 2nd case, $n_{tot} = 1$, the chemical potentials don't cross, so all of "A" is in the lower-μ phase, phase "2".

(iii) If we put only 1 mol of solid A in the same amount of water as before, $n(\mathrm{H_2O}) = 200\mathrm{mol}$, we cannot reach equilibrium – all the solid A will be dissolved, so 1 mol of A will be in the solution, and 0 moles will remain solid.

(iv) I leave it up to you to calculate μ_{H_2O} for this case, but note that since the reaction does not involve water directly (the "reaction" involves A in solid an aqueous form, but A does not react with water), then μ_{H_2O} is irrelevant to the previous parts.

(v) We need to determine

$$w_{elec} = G_{equilbibrium} - G_{initial} =$$
$$G(P,T,n_1 = 2.65\text{mol}, n_2 = 1.35\text{mol}) - G(P,T,n_1 = 4\text{mol}, n_2 = 0)$$

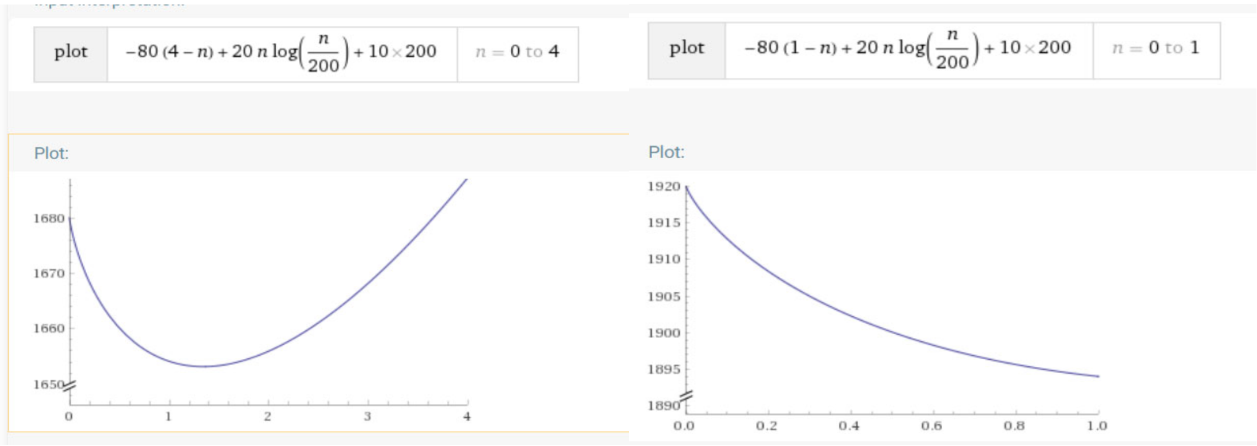
We can calculate this numerically from the explicit expression for G earlier. It is more instructive instead to do it graphically. Look at the figure of G vs. n_2 below: (the left figure above, associated with $n_{total} = 4\text{mol}$). From the figure:

$$G_{initial} \sim 1680\text{kJ}$$
$$G_{final} \sim 1653\text{kJ}$$

So therefore

$$w_{\text{elec}} = -27\text{kJ}$$

i.e., up to 27kJ of electric work could be extracted from this "reaction" (i.e., phase change).



plot $-80\,(4-n) + 20\,n\log\left(\frac{n}{200}\right) + 10\times 200$ $n = 0$ to 4

plot $-80\,(1-n) + 20\,n\log\left(\frac{n}{200}\right) + 10\times 200$ $n = 0$ to 1

The total Gibbs Free energy (in kJ/mol) vs. n_2, the number of moles of the solute "A" in the aqueous solution:

$$G = -n_1 \cdot 80\frac{\text{kJ}}{\text{mol}} + n_{H_2O} \cdot 10\frac{\text{kJ}}{\text{mol}} + n_2 \cdot 20\frac{\text{kJ}}{\text{mol}} \ln\left(\frac{n_2}{n_{H_2O}}\right)$$

for $n_{\text{H}_2\text{O}} = 200$ mol.

Left: presuming the total number of A is $\boldsymbol{n_1 + n_2 = 4}$ **mol**, (where $\boldsymbol{n_1}$ ≡moles of solid "A"). Note the minimum at the equilibrium point, $\boldsymbol{n_2 = 1.35\text{mol}}$. The rest of A (n_1 =2.65 mol) is precipitating

Right: presuming $\boldsymbol{n_1 + n_2 = 1\text{mol}}$. Note that there's no local minimum; the lowest G is for $\boldsymbol{n_2 = 1\text{mol}, n_1 = 0}$, all of A is in the solute, not precipitated

4.6) Chemical potential for reactions:

We proved that for an $A \to B$ reaction, $\mu_A = \mu_B$ is equilibrium, and if $\mu_A > \mu_B$ the product side (B) is favored

For a general reaction a very similar property follows!

Example:

$$a\,A + b\,B \to c\,C + d\,D$$

- If $a\mu_A + b\mu_B = c\mu_C + d\mu_D$: reaction is in equilibrium
- If $a\mu_A + b\mu_B > c\mu_C + d\mu_D$: products favored, reaction will proceed to the right (or stop if either of the reactants, A, B, is replenished)
- If $a\mu_A + b\mu_B < c\mu_C + d\mu_D$: products favored, reaction will proceed to the left (unless either one of the products, C, D, is replenished)

This is easier to write when we use **stoichiometric coefficients.**

Example:

$$\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \to \mathrm{CO_2}(g) + 2\mathrm{H_2O}(l)$$

Rewrite (drop the phases for brevity)

$$-\mathrm{CH_4} - 2\mathrm{O_2} + \mathrm{CO_2} + 2\mathrm{H_2O} = 0$$

or

$$\nu_{\mathrm{CH_4}}\mathrm{CH_4} + \nu_{\mathrm{O_2}}\mathrm{O_2} + \nu_{\mathrm{CO_2}}\mathrm{CO_2} + \nu_{\mathrm{H_2O}}\mathrm{H_2O} = 0$$

Where we use the **stoichiometric coefficients**

$$\nu_{\mathrm{CH_4}} = -1, \qquad \nu_{\mathrm{O_2}} = -2 \qquad \text{(negative for reactants)}$$
$$\nu_{\mathrm{CO_2}} = 2, \qquad \nu_{\mathrm{H_2O}} = 2 \qquad \text{(positive for products)}$$

In terms of the stoichiometric coefficients, we define

$$\Delta\mu = \sum_i \nu_i \mu_i$$

BTW, most books call this quantity ΔG, but I prefer to call it $\Delta\mu$.

Then, in equilibrium $\Delta\mu = 0$, while if $\Delta\mu < 0$ then the products are favored, and vice-versa.

Another example: say we know that for a reaction,

$$\mathrm{A(s)} + \frac{1}{2}\mathrm{O_2(g)} \to \mathrm{AO(l)},$$

where "A" is some compound, and

$$\mu(\mathrm{A}) = -220\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$
$$\mu(\mathrm{AO}) = -225\,\frac{\mathrm{kJ}}{\mathrm{mol}}.$$

Question: What does $\mu(\mathrm{O_2})$ need to be in order to have equilibrium?

Answer: We need $-\mu(\mathrm{A}) - \frac{1}{2}\mu(\mathrm{O_2}) + \mu(\mathrm{AO}) = 0$, i.e.,

$$\mu(\mathrm{O_2}(g)) = 2\big(\mu(\mathrm{AO}) - \mu(\mathrm{O})\big) = 2 * (-5\mathrm{kJ}) = -10\ \mathrm{kJ}$$

We'll see in chapter 6 that μ_{gas} varies (**increases**) with pressure. Once we know what μ needs to be we can **determine what pressure to have in order to have equilibrium.**

4.7) Reversible processes in equilibrium

Up to now we considered processes that approach equilibrium at a fixed T and P, e.g., reactions.

We learned that we need to find out what G is, as a function of T and P.

We'll now shift to consider processes that are in equilibrium, but where T and P are changed; and further, we'll assume that change is reversible.

Further, we'll assume these processes don't involve electric work

> Note: at any given T and P we can always determine the amount of extractable or necessary electrical work from the difference in G between products and reactants.

For reversible changes, we know $dq = TdS$.

Therefore: $dU = dq + dw_{\text{mech}}$, and thus:

$$dU = TdS - PdV \quad \text{(reversible processes)}$$

Mathematical consequences:

Now we'll deal with the **mathematical consequences** of the yellow-highlighted relation.

Let's consider a change of the conditions (i.e., changing T, P, V , but without changing n). We need to **choose two independent** variables to describe the changes. We have **freedom to choose whichever two variables we want.**

We could have chosen the independent variables to be P and T, and we'll do it later when we talk about G; But for $\boldsymbol{U}$, let's choose the independent variables to be $\boldsymbol{S}$ and $\boldsymbol{V}$.

(That's allowed, since, if S changes and V changes, the change in T, P and U is determined in principle.)

Formally, then, we write

$$U = U(S, V).$$

But we learned in Calculus that the change in a function of two variables is

$$dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV.$$

The two eqs. for dU depend on the same two independent variables: S and V. So the coefficients of $\boldsymbol{dS}$ and $\boldsymbol{dV}$ should be the same! I.e.,

$$\left.\frac{\partial U}{\partial S}\right|_V = T$$

and

$$\left.\frac{\partial U}{\partial V}\right|_S = -P.$$

We know this last equation already: if $\boldsymbol{V}$ is varied in a reversible adiabatic process (with $\boldsymbol{S} = \textbf{fixed}$), then $\boldsymbol{dU = -PdV}$, so

$$-\boldsymbol{P} = \frac{\boldsymbol{dU}}{\boldsymbol{dV}}(\textbf{adiabatic, i.e.,}\ \boldsymbol{S} = \textbf{fixed}).$$

These specific relations above are not usually important for chemistry by themselves; the first, however, $\left.\frac{\partial U}{\partial S}\right|_V = T$, is very important for statistical mechanics, where S iand U are the fundamental quantities, so this relation becomes the **definition** of T.

The main importance of such relations becomes clear when we consider the Gibbs free energy G instead of the energy U.

Consider a system in equilibrium, as before:

$$dG = d(U + PV - TS) = dU + PdV + VdP - TdS - SdT$$

We learned that $dU = -PdV + TdS$, so adding to the last equation gives

$$dG = (-PdV + TdS) + PdV + VdP - TdS - SdT$$

i.e., after cancelation:

$$dG = VdP - SdT \quad \text{(system in equilibrium)}$$

We can then repeat the produce we did with U.

I.e., if we use P, T as the independent variables in describing $G = G(P, T)$, we get

$$dG = \left.\frac{\partial G}{\partial P}\right|_T dP + \left.\frac{\partial G}{\partial T}\right|_P dT$$

So from the last two eqs.:

$$\left.\frac{\partial \boldsymbol{G}}{\partial \boldsymbol{P}}\right|_{\boldsymbol{T}} = \boldsymbol{V}, \qquad \left.\frac{\partial \boldsymbol{G}}{\partial \boldsymbol{T}}\right|_{\boldsymbol{P}} = -\boldsymbol{S}$$

Remember this equation and its derivation!

Example: Given a reaction $C \rightarrow D$ at fixed pressure ($P = P^o$). Define

$$\Delta G = G_D - G_C$$

Then by subtracting $\left.\frac{\partial G_C}{\partial T}\right|_P = -S_C$ from $\left.\frac{\partial G_D}{\partial T}\right|_P = -S_D$ we get

$$\left.\frac{\partial \boldsymbol{\Delta G}}{\partial \boldsymbol{T}}\right|_{\boldsymbol{P}} = -\boldsymbol{\Delta S}.$$

Thus **if we know or measure the Gibbs Free Energy difference at more than one T, we can get the difference in entropy.**

For example, say that this reaction is not spontaneous so that we need to invest, for accomplishing it, an amount of electric work which is:

$$\mathbf{w_{elec}} = \boldsymbol{\Delta G} = \mathbf{10{,}000\ J} \quad \textbf{at}\ \boldsymbol{T} = \mathbf{300K}$$
$$\mathbf{w_{elec}} = \boldsymbol{\Delta G} = \mathbf{9{,}500\ J} \quad \textbf{at}\ \boldsymbol{T} = \mathbf{310K}$$

Then

$$\left.\frac{\partial \boldsymbol{\Delta G}}{\partial \boldsymbol{T}}\right|_{\boldsymbol{P}} = \frac{\textbf{difference of}\ \boldsymbol{\Delta G}\ \textbf{for different temperatures}}{\textbf{difference in T}}$$

$$= \frac{(9500-10000)\mathrm{J}}{(310-300)\mathrm{K}} = -50\,\frac{\mathrm{J}}{\mathrm{K}}$$

Therefore,

$$\Delta S = -\left.\frac{\partial \Delta G}{\partial T}\right|_P = 50\,\frac{\mathrm{J}}{\mathrm{K}}.$$

4.8) Maxwell's relations

There are many thermodynamic relations which can be obtained simply from the fact that $U, H, G,$ or A (which is another state function, defined as $A = U - TS$) **depend only on the current values of P, V, T and not on the previous history.**

Take for example $G(P,T)$, and rewrite its differential:

$$dG = VdP - SdT.$$

We know from calculus that for any function of two variables, $F(x,y)$, the mixed derivative is the same regardless of the order in which we differentiate, i.e.,

$$\frac{\partial^2 F}{\partial x\,\partial y} = \frac{\partial^2 F}{\partial y\,\partial x}.$$

Apply this to $G(P,T,n)$, and get

$$\frac{\partial^2 G}{\partial P\,\partial T} = \frac{\partial^2 G}{\partial T\,\partial P}.$$

But we know $\left.\frac{\partial G}{\partial T}\right|_P = -S$, and $\left.\frac{\partial G}{\partial P}\right|_T = V$, so plugging to the eq. above gives:

$$-\left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P.$$

Note that all the partial derivative w.r.t. one variable (here P or T) are done with the other variable fixed.

This is an example of **a Maxwell's relation – such relations are very useful.** Several other Maxwell's relations are found in the book and the h.w.

The graphical way to remember these relations is delineated in class.

Example: say we have a crazy form of G

$$G(P,T) = n(aT + bP^2)^3 - \frac{nC}{T^2}$$

Determine whatever you can on S, V, and verify Maxwell's relations.

Answer:

$$S = -\left.\frac{\partial G}{\partial T}\right|_P = -3n(aT + bP^2)^2 \cdot a - \frac{2nC}{T^3}$$

$$V = \left.\frac{\partial G}{\partial P}\right|_T = 3n(aT + bP^2)^2 \cdot 2bP$$

And for Maxwell's relations:

$$\left.\frac{\partial V}{\partial T}\right|_P = \frac{\partial}{\partial T}(3n(aT + bP^2)^2 \cdot 2bP) = 12abn(aT + bP^2)P$$

While

$$-\left.\frac{\partial S}{\partial P}\right|_T = \frac{\partial}{\partial P}\left(3\mathrm{n}(aT + bP^2)^2 \cdot a + \frac{2nC}{T^3}\right) = 3n * 2 * a(aT + bP^2)2bP$$
$$= 12nab(aT + bP^2)P \quad Q.E.D.$$

The importance of Maxwell's relations.

One example of the use of Maxwell's relations is for **determining experimentally the entropy of a compound**.

Say we want to start from an initial pressure and temperature, and want to find the change of entropy when we end up at a different pressure and temperature (and assume there's no phase change in between).

We can take any trajectory connecting the two, and integrate

$$\Delta S = \int dS$$

But we know that if we write S as a function of T, P then, from calculus

$$dS = \left.\frac{\partial S}{\partial T}\right|_P dT + \left.\frac{\partial S}{\partial P}\right|_T dP.$$

We already know the first term, $\left.\frac{\partial S}{\partial T}\right|_P$: i.e., if the pressure is fixed then

$$dS(P \text{ fixed}) = \frac{dq_P}{T} = C_P\frac{dT}{T}.$$

Therefore,

$$\left.\frac{\partial S}{\partial T}\right|_P \equiv \frac{dS(P \text{ fixed})}{dT} = \frac{C_P\frac{dT}{T}}{dT} = \frac{C_P}{T}.$$

Adding the Maxwell relation $\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$ leads then to the final relation

$$\Delta S = \int dS = \int \left(\frac{C_P}{T}dT - \left.\frac{\partial V}{\partial T}\right|_P dP\right)$$

which when we combine with the definition (from Chapter I) of the expansion coefficient, $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$, becomes

$$\Delta S = \int \left(\frac{C_P}{T}dT - \alpha V\, dP\right).$$

Of course, if there's a phase change we need to add its contribution too.

This integral is valid no matter which were route we take from the initial to the final part. (See figure in class.)

Note that this expression for the entropy difference is general and is expressed in easily measurable quantities!

The latter part of the highlighted integral **looks very strange**, since we take a derivative at fixed pressure and then multiply by dP, i.e., $\left.\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{T}}\right|_{\boldsymbol{P}} \boldsymbol{dP}$. Are we fixing the pressure or we don't?

The answer is that, at any point along the T, P trajectory, when **calculating (or measuring)** $\left.\frac{\partial V}{\partial T}\right|_P$, the derivative is taken by varying T a little (while fixing P), but then the quantity is multiplied by the actual dP along the trajectory. See the **figure and class.**

Entropy change with pressure for solids and liquids

Maxwell's relations explain something we "guessed" before – that **pressure has a very little effect on liquids and solids** (unless it is enormous, of course, 1000's of bars).

The reason is that as we saw,

$$-\left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P = \alpha V$$

and we know that for liquids/solids both V and α are tiny!

For example, for liquid water $\alpha \cong \frac{2*10^{-4}}{\mathrm{K}}$, and the molar volume is

$$V_m = 18\frac{\mathrm{cm}^3}{\mathrm{mol}} \cong 0.02\frac{\mathrm{L}}{\mathrm{mol}}$$

so

$$-\left.\frac{\partial S}{\partial P}\right|_T = 4 * 10^{-6}\frac{\mathrm{L}}{\mathrm{mol\,K}}$$

To see that this is small, recall that $\mathbf{L} * \mathbf{bar} = \mathbf{L} * \mathbf{P^o} = \mathbf{100}$ **J**, i.e.,

$$-\left.\frac{\partial S}{\partial P}\right|_T = 4 * 10^{-4}\frac{\mathrm{J}}{\mathrm{mol\,K\,bar}}$$

So, for example when we change the pressure of water by 10 bar (i.e., 100-meter-deep – since the pressure in the ocean or in a deep pool rises by 1 bar every 10 meter) the entropy decreases by

$$dS \sim -\left.\frac{\partial S}{\partial P}\right|_T * dP = -4 * 10^{-4}\frac{\mathrm{J}}{\mathrm{mol\,K\,bar}} * 10\mathrm{bar} = \mathbf{-0.004}\frac{\mathbf{J}}{\mathbf{mol\,K}}$$

which is tiny relative to the changes in entropy we considered.

Can Maxwell's relation be experimentally verified? – yes!

Think of an experiment which you may do to verify Maxwell's relation! (Hint – think of how we measured the entropy).

4.9) Conclusions: Chapter 4

We started by proving that $dq \leq TdS$, based on the fact that any change to the environment is reversible as far as the environment is concerned.

That led us to the heart-and-core of this chapter. First:

$$\Delta G \leq w_{el}$$

for fixed T, P. When there's no electric work $\Delta G \leq 0$, so G is minimum at equilibrium.

Later we got to

$$\sum_i \nu_i \mu_i = 0$$

for reactions in equilibrium (and as a special case, $\mu_1 = \mu_2$ for a substance in two coexisting phases).

These results would be essential for deriving phase diagrams and relative concentrations.

In addition, we derived rules which are useful for determining G and therefore U. Experimentally, using $dG = VdP - SdT$, we got:

$$\left.\frac{\partial G}{\partial T}\right]_P = -S$$

$$\left.\frac{\partial G}{\partial P}\right]_T = V$$

and therefore

$$-\left.\frac{\partial S}{\partial P}\right]_T = \left.\frac{\partial V}{\partial T}\right]_P = \frac{\partial^2 G}{\partial T \partial P}$$

so experimentally we can find thermodynamic quantities from

$$\Delta G = \int -SdT + VdP$$

together with $\Delta S = \int \left(\frac{C_P dT}{T} - \left.\frac{\partial V}{\partial T}\right]_P dP\right)$, which, from the definition $\alpha = V^{-1}\left.\frac{\partial V}{\partial T}\right]_P$ gives:

$$\Delta S = \int \left(\frac{C_P dT}{T} - \alpha V dP\right).$$

This is true long as there's no phase changer, otherwise add $\frac{\Delta H(T_{\text{phase chage,}}, P)}{T_{\text{phase-change}}}$ to ΔS.

V. Reactions

A simple chapter; we covered most of it earlier.

5.1) Overview

- Heat of reaction ΔH_{rxn} and heat of formation H_{f} and their T-dependence.
- Similar quantities: $G_{\text{f}}, S_{\text{f}}$, etc.
- Hess law (conservation of energy)

Introduction

Earlier we understood the importance of G. We saw that a reaction would proceed spontaneously at a fixed T, P only if it leads to a decrease in G.

Now is the time to see **how one can determine the Gibbs free energy change.**

5.2) Heat of reaction and heat of formation

Take a general reaction, with stoichiometric coefficients ν_i (recall: these are negative for the reactants, positive for the products).

The **reaction enthalpy** is the enthalpy difference for a "mole of reactions",

$$\boldsymbol{\Delta H}_{\textbf{rxn}} = H_{\text{products}} - H_{\text{reactants}} = \sum_{\boldsymbol{i}} \boldsymbol{\nu_i H_m^o(i)}$$

where we sum over all species in the reactions, and the ^{o} superscript indicates "standard state" at 1 bar (see below). (Of course, for reactions at fixed total pressure, $\Delta H_{\text{rxn}} = q$, the heat of reaction):

> An example will clarify: burning Benzene (at temperature between 0°C and 100°C)
>
> $$2\mathrm{C_6H_6}(l) + 15\mathrm{O_2}(g) \to 12\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l)$$
>
> with stoichiometric coeff.
>
> $$\nu_{C_6H_6} = -2, \qquad \nu_{O_2} = -15, \qquad \nu_{CO_2} = 12 \qquad \nu_{H_2O} = 6$$
>
> So (omitting here the phases of the compounds)
>
> $$\Delta H_{\text{rxn}} = -2H_m^o(\mathrm{C_6H_6}) - 15H_m^o(\mathrm{O_2}) + 12H_m^o(\mathrm{CO_2}) + 6H_m^o(\mathrm{H_2O})$$

We have freedom in describing the individual enthalpies.

> Note: We could have used the absolute enthalpies, including the energies of the electrons, etc. But that would be complicated and the numbers would be big and inconvenient.

We will instead tabulate the **enthalpies of formation** for each compound. These are defined as **the difference in enthalpy between one mole of the compound and ITS ELEMENTS**, when these elements **are EACH at 1bar (and that temperature) and at their "standard state"**.

From Wikipedia: Standard states are as follows:

- For a gas: the hypothetical state it would have assuming it obeyed the ideal gas equation at a pressure of 1 bar

- For a pure substance or a solvent in a condensed state (a liquid or a solid): the standard state is the pure liquid or solid under a pressure of 1 bar

  > Note that for an element this means usually the form in which the element is most stable under 1 bar of pressure. One exception is phosphorus, for which the most stable form at 1 bar is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation for a historical reason.

  Also note: The standard state for a solute is a little complicated. We'll deal with it later

Example: The heat of formation for benzene liquid, at not-too-high a temperature.

We first need to write the reaction associated with making Benzene from its atomic constituents (as their standard states)

$$3\,H_2(g) + 6C(s) \to C_6H_6(l)$$

where "s" for Carbon means graphite. Then

$$H_f^o(\mathrm{C_6H_6}(l)) = \Delta H_{rxn}(3\,\mathrm{H_2}(g) + 6\mathrm{C}(s) \to C_6H_6(l))$$

which is of course

$$H_f^o(\mathrm{C_6H_6}(l)) = H_m^o(\mathrm{C_6H_6}(l)) - 3H_m^o(\mathrm{H_2}(g)) - 6H_m^o(\mathrm{C}(s))$$

> **Note that the heat of formation depends on the phase of the final compound.** I.e., the heat of formation of the benzene depends on whether it is liquid or gas.

This heat of formation is reasonably easily measurable. Further, using Hess law below we could get its values for many compounds without doing these reactions explicitly, which makes life even easier.

Now back to our Benzene-burning example. The water and carbon-dioxide heat of formations, $\Delta H_f(\mathrm{CO_2})$ and $\Delta H_f(\mathrm{H_2O})$ are similarly defined

$$H_f^o(CO_2(g)) = H_{rxn}(C(s) + O_2(g) \to CO_2(g)) = H_m^o(CO_2(g)) - H_{m^o}(C(s)) - H_m^o(O_2(g))$$

And

$$H_f^o\,(H_2O) = H_{rxn}\left(H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l)\right)$$
$$= H_m^o(H_2O(l)) - H_m^o(H_2(g)) - \frac{1}{2}H_m^o(O_2(g))$$

Further, $H_f^o(O_2(g)) = 0$ **by definition** around these temperatures we consider (0 to 100°C)

> Note: $H_f^o(O_2(g))$ is not zero for very low temperature, (e.g., 50K or below) since there the standard state of oxygen is liquid or solid (depending on the temperature), and not gas.

The beauty of heats of formation is that we can get the heat of reaction for our total reaction (burning benzene) using heats-of-formation rather than the molar enthalpies

I.e., rather than using the eq. we had

$$\Delta H_{\mathrm{rxn}} = \sum_J \nu_J H_m^o(J),$$

we can write

$$\Delta H_{\mathrm{rxn}} = \sum_J \nu_J H_f^o(J).$$

I.e., in our case

$$\Delta H_{\mathrm{rxn}}(\mathrm{C_6H_6}) = -2H_f^o(\mathrm{C_6H_6}) - 15H_f^o(\mathrm{O_2}) + 12H_f^o(\mathrm{CO_2}) + 6H_f^o(\mathrm{H_2O})$$

(where the second term vanishes, $H_f^o(\mathrm{O_2}) = 0$).

Temperature dependence

If we want properties at other temperatures we need to construct the heat of reaction, and then we can use the relations we learned.

E.g., we define the reaction heat-capacity from:

$$\frac{d\Delta H_{rxn}^{\mathrm{o}}}{dT} = \sum_J \nu_J \frac{dH_{\mathrm{m}}^{\mathrm{o}}(J)}{dT} = \sum_i \nu_J C_{\mathrm{pm}}^{\mathrm{o}}(J) \equiv \Delta_{\mathrm{rxn}} C_P^{\mathrm{o}}$$

We'll often drop henceforth the "rxn" subscript, so this gives

$$\frac{d\Delta H^{\mathrm{o}}}{dT} = \Delta C_P^{\mathrm{o}}$$

Similarly

$$\Delta S^{\mathrm{o}} \equiv \sum_J \nu_J S_{\mathrm{m}}^{\mathrm{o}}(J), \quad \Delta G^{\mathrm{o}} \equiv \sum_J \nu_J G_{\mathrm{m}}^{\mathrm{o}}(J)$$

and the usual formulae follow (with "Δ" for reaction)

$$\frac{d\Delta G^{\mathrm{o}}}{dT} = -\Delta S^{\mathrm{o}}$$

as well as

$$\frac{d\Delta S^{\mathrm{o}}}{dT} = \frac{\Delta C_P^{\mathrm{o}}}{T}.$$

5.3) Hess Law

Since you should be familiar with Hess law from 1st year chemistry, I just copy here the text from Wikipedia, and would only go over it briefly in class.

Hess's law – Copied from Wikipedia

Hess' law states that the change of enthalpy in a chemical reaction (i.e. the heat of reaction at constant pressure) is independent of the pathway between the initial and final states.

In other words, if a chemical change takes place by several different routes, the overall enthalpy change is the same, regardless of the route by which the chemical change occurs (provided the initial and final condition are the same).

Therefore, Hess' law allows the enthalpy change (ΔH^{o}) for a reaction to be calculated even when it cannot be measured directly.

Hess' law states that enthalpy changes are additive. Thus the ΔH for a single reaction, e.g.,

$$\mathrm{C}(s) + \mathrm{O}_2 \rightarrow \mathrm{CO}_2(\mathrm{g}) \quad \left(\Delta H^o = -393.5\,\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \text{ (direct step)}$$

can be obtained by a sum of two reactions:

$$\mathrm{C}(s) + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{CO}(\mathrm{g})\,; \qquad \left(\Delta H^o = -110.5\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$$

$$\mathrm{CO}(\mathrm{g}) + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{CO}_2(\mathrm{g}); \qquad \left(\Delta H^o = -\,283.0\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$$

Summing the last two reactions gives $\Delta H^o = -393.5\frac{\mathrm{kJ}}{\mathrm{mol}}$ which is equal to ΔH in the reaction above.

Note that you have to be careful about measurement errors and roundoff errors.

VI. Reactions of ideal gases

6.1) Overview

A nice and not too difficult chapter, you've seen much of it in 14B/20B.

> Note: We'll presume in this chapter that we don't have aqueous solutions, only ideal gases and pure liquids and solids. But the language we will use will be very general, allowing us to adopt the techniques of this chapter to also cover solutes and non-ideal gases in latter chapters.

Overview

We promised that $\sum_i \nu_i \mu_i = 0$ will be very useful for determining reaction equilibria. Here we will prove this. The key: a proof that for **ideal gases, $\boldsymbol{\mu}$** has two parts:

- A part calculated at a fixed pressure (1bar), $\mu^{\text{o}}(T)$ --- tabulated;
- And another, analytical part that depends on the actual pressure of the compound, and is universal, i.e., is the same for all ideal gases.
- From the math we will **group** the pressure-dependent parts of the different compounds in a reaction into one "constant" $\boldsymbol{K}$ which only depends on the temperature, so that:
- We will get a relation, relating in equilibrium the partial pressures of all gaseous compounds so that when some of these partial pressures change, the other pressures must change accordingly, in order to keep $\boldsymbol{K}$ constant.

Later, we **will get the temperature variation of $\boldsymbol{K(T)}$, and** its consequences. We'll explain this T-dependence using a simple physical principle, **LeChatelier's principle**.

If we were to deal only with ideal gases, this chapter would be the end of the long and treacherous road leading from the first law to reactions; in the following chapters, we will also see **liquid and solid** solutions.

6.2) The pressure dependence of μ and its consequences.

Pressure dependence of a pure compound (solid, liquid or vapor)

For a pure compound, $\boldsymbol{\mu = G_m(P,T)}$.

So recalling $dG = VdP - SdT$, we get that

$$\boldsymbol{d\mu} = dG_m(P,T) = \textbf{(when } \boldsymbol{T} \textbf{ is fixed)}\ \boldsymbol{V_m dP}.$$

Let's integrate from a convenient common point, **1bar, $\boldsymbol{P^{\text{o}}}$** to any final arbitrary pressure, P

$$\mu(P,T) = \mu(P^{\text{o}},T) + \int_{P^o}^{P} V_m \, dP'.$$

We usually label $\mu^o(T) \equiv \mu(P^o,T)$. Further, let's label the compound we consider as "A", and label μ, V_m with the subscript "A", so

$$\mu_A(P,T) = \mu_A^o(T) + \int_{P^o}^{P} V_{mA}\, dP'$$

Activities

At this point let's **define** the activity of a compound A, labeled a_A, by:

$$RT \ln a_A = \int_{P^o}^{P} V_{mA}\, dP'$$

So that the chemical potential fulfills:

$$\mu_A(P,T) = \mu_A^o(T) + RT \ln a_A$$

The reason for this seemingly strange definition is that for ideal gases we would be able to rewrite it in terms of a quantity you have seen in 14B/20B, i.e., $a_A = \frac{P_A}{P^o}$ for ideal gases. This will be shown shortly.

To be more precise, we really define the activity as

$$\mu_A(P,T) = \mu_A^{\text{reference}}(T) + RT \ln a_A$$

and for pure solids, pure liquids, gases, and solvents, the reference value would be the value of the chemical potential for the pure compound at 1 bar. (But things are different for **solutes**.)

Let's distinguish condensed phases vs. gases:

Pure condensed phases (pure liquids and pure solids)

$\boldsymbol{V_m}$ does not change much with pressure, so we can approximate

$$\mu_A(P,T) = \mu_A^o(T) + V_{mA} \int_{P^o}^{P} dP' = \mu_A^o(T) + V_{mA} \cdot (P - P^o)$$

Further, V_m for condensed phases is usually tiny, so unless the pressure P is quite large (say larger than 100 bar) then the $V_{mA} \cdot (P - P^o)$ term is so small that we can ignore it, as we saw often, so

$$\mu_A(P,T) \simeq \mu_A^o(T) \quad \text{(condesned phases, pressures up to} \sim 100 \text{ bar)}$$

This is equivalent to writing $a_A = 1$ for pure condensed phases, so $RT \ln a_A \sim 0$.

Exercise: calculate the $V_m \cdot (P - P^o)$ term for water, for $P_1 = 0, P_2 = 100\text{bar}$.

Answer: for water

$$V_m = 18 \frac{\text{cm}^3}{\text{mol}} \sim 0.02 \frac{\text{L}}{\text{mol}}$$

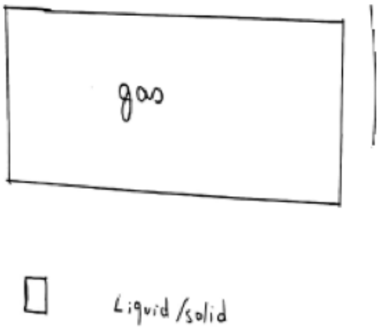
So

$$(P - P^o)V_m = 100 \text{ bar} \cdot 0.02 \frac{\text{L}}{\text{mol}} = 2 \frac{\text{bar} \cdot \text{L}}{\text{mol}} = 200 \frac{\text{J}}{\text{mol}} = 0.2 \frac{\text{kJ}}{\text{mol}}$$

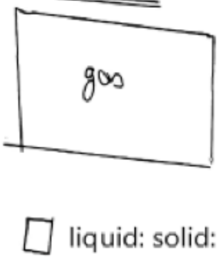
So indeed, given that $\Delta H_{\text{vap}} = 41\frac{\text{kJ}}{\text{mol}}$, $\Delta H_{\text{fus}} = 6\frac{\text{kJ}}{\text{mol}}$, we can safely ignore the 0.2kJ/mol from the PV term, i.e., we can safely set the **activity** of pure solids/liquids as "$a_{\text{condensed}} = 1$".

Understanding P dependence of μ.

Start $P = 1$ atm



Compress $P = 3$ atm



liquid: solid: volume barely changed, remains small

Thus: $\Delta\mu = \int V_m \, dP = \begin{cases} \text{large for gases} \\ \text{small for liquids/solids.} \end{cases}$

Pure ideal gases

For gases, the molar volume changes appreciably with pressure; when the latter is labeled P', $V_{mA} = RT/P'$, so

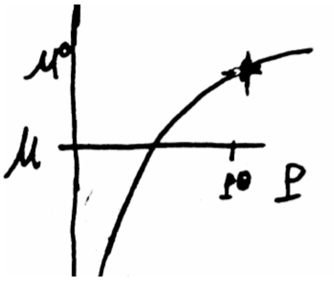
$$\mu_A(P_A, T) - \mu_A^{\text{o}}(T) = \int_{P^{\text{o}}}^{P_A} V_{mA} dP' = \int_{P^{\text{o}}}^{P_A} \frac{RT}{P'} dP' = RT \ln\left(\frac{P_A}{P^{\text{o}}}\right)$$

The argument of the "ln" above is exactly the activity, so we learn that

$$a_A = \frac{P_A}{P^o} \text{ (ideal gases).}$$

Physically, we see **that μ increases when we lower the pressure.** (Higher pressure → less volume → less disorder --> less entropy --> higher G (since $G = H - TS$)

This is true of course for any compound, not just gases, since **the partial derivative of G w.r.t. pressure** (at fixed T) is the volume, i.e., a **positive quantity.**



The chemical potential of an ideal gas: Mixtures of different gases

When we mix several gases in the same container (and all have same T) then they **each will have a partial pressure.**

The chemical potential of each gas in the mixture is simply that of the same gas, pure, with the same partial pressure it has in the mixture.

Example: air in Mexico City.

Recall that air is essentially (ignoring other compounds, and assuming dry air, no water vapor) 80% nitrogen, 20% oxygen.

For example, in Mexico City (about 2.25 km above sea level) the total air pressure is about 0.75bar, so the pressure of nitrogen will be about $80\% \cdot 0.75 = 0.6\text{bar}$, and of oxygen will be about 0.15bar (ignoring other compounds)

The key to the gas properties is that, essentially, the gas molecules don't "sense" the presence of other compounds; i.e., Oxygen in the air in Mexico City will have the same properties as pure oxygen at 0.15bar.

We saw this when we discussed entropy of mixing. There we explained that, in our language, **the entropy of pure oxygen at a partial pressure of 0.15bar would be the same as that of oxygen in air when the oxygen's partial pressure is 0.15bar** (and the nitrogen having whatever partial pressure it has, in this case 0.6bar).

In short: we can think of ideal gases mixture as if it was **several separate pure gases, each at its own partial pressure.** So air in Mexico City has **the same properties, as far as $\boldsymbol{G, H, S}$, etc., as if it we added these properties for two separate containers** – one with oxygen with 0.15bar, the other with nitrogen at 0.6bar**.**

So in an ideal gas "A" with partial pressure $\boldsymbol{P_A}$

$$\mu_A(P_A,T) = \mu_A^o(T) + RT\ln\left(\frac{P_A}{Po}\right) \qquad \text{(gas A with partial pressure } P_A \text{)}$$

Side-note: Consequences for mixing.

Let's use this language to prove again something we know, mixing is favorable.

Mix two gases, with the same T, that initially are each pure, each in its own container, and having each the same pressure P_{tot}.

After mixing -- removing the separation between the containers – the total pressure will still be P_{tot}, and will be made from partial pressures P_A, P_B where now $P_A + P_B = P_{tot}$.

***G* is additive** so (omitting the labeling of the T-dependence)

$$G(\text{pre mixture}) = G_A(P_{tot}) + G_B(P_{tot})$$

(note that $G_A = n_A G_{mA} = n_A \mu_A$).

Similarly:

$$\boldsymbol{G}(\textbf{post mixture}) = G_A(P_A) + G_B(P_B) < \boldsymbol{G}(\textbf{pre mixture})$$

(where we used the fact that $G_A(P_A) < G_A(P_{tot})$ since $P_A < P_{tot}$). Thus, as we proved already, **mixing is favorable**.

6.3) Reactions of ideal gases and solids/liquids

Instead of only using symbols with stoichiometric coefficients, let's derive the expressions using an actual reaction, and then generalize "by inspection" to all reactions.

Consider the methane formation reaction, at a high temperature where the methane is a gas, and where there's equilibrium,

$$2H_2(g) + C(s) \to CH_4(g).$$

Let's write it instead as

$$\nu_A A(g) + \nu_C C(s) + \nu_D D(g) = 0.$$

Here:

$$A \equiv \mathrm{H_2}, \qquad D \equiv \mathrm{CH_4}$$

$$\nu_A = -2\,, \qquad \nu_c = -1, \qquad \nu_D = 1$$

ΔG and Reaction Quotioents

Let's recall that we defined in Chapter 4

$$\Delta\mu \equiv \sum_i \nu_i \mu_i.$$

Henceforth we'll **replace the notation $\boldsymbol{\Delta\mu}$ by $\boldsymbol{\Delta G}$**, to be consistent with how other people use, although I personally don't like the ΔG notation.

Also recall: The condition for equilibrium is $\Delta G = 0$; but we'll consider the general case, i.e., even as there's no equilibrium)

Note:

We note in passing that ΔG is related to the **slope** of G in actual reactions. This is something we have not talked too much about yet, but heuristically, this is related to the voltage difference driving the reaction.

If **$\boldsymbol{\Delta G} = 0$ there's equilibrium,** and if ΔG is highly positive or negative then there's a big tendenecy for the reaction to go one way or another.

We may talk about this again at the end of the course. This is related to electrochemistry, which you have seen in 14B/20B.

For our particular reaction:

$$\Delta G = -2\mu_A - \mu_C(T) + \mu_D = \nu_A\mu_A + \nu_C\mu_c + \nu_D\mu_D$$

so insert from above

$$\Delta G = \nu_A(\boldsymbol{\mu_A^o(T)} + RTa_A) + \nu_C(\boldsymbol{\mu_C^o(T)} + RT\ln a_C) + \nu_D(\boldsymbol{\mu_D^o(T)} + RT\ln a_D)$$

Let’s combine the μ −dependent terms as:

$$\Delta G^o = \sum_i \nu_i\mu_i^o = -2\mu_A^o(T) - \mu_C^o(T) + \mu_D^o(T)$$

Note: ΔG^o can be interpreted is the amount of electric work necessary to convert “2” moles of pure “A” a 1bar and “1” moles of pure C at 1bar, to “1” moles of pure “D” at 1bar. See figure below (for a slightly different reaction)

Then group the μ^o in the “green” equality above (the bold terms) to get

$$\Delta G = \Delta G^o + RT(\nu_A\ln a_A + \nu_C\ln a_C + \nu_D\ln a_D) = 0$$

Now let’s remember basic logarithm properties.

First, $a\ln x = \ln x^a$, and therefore

$$\Delta G^o + RT\ (\ln(a_A)^{\nu_A} + \ln(a_C)^{\nu_C} + \ln(a_D)^{\nu_D}) = 0$$

Further, $\ln x + \ln y = \ln(xy)$, so

$$\Delta G = \Delta G^o + RT\ln((a_A)^{\nu_A}(a_C)^{\nu_C}(a_D)^{\nu_D})$$

Therefore, defining

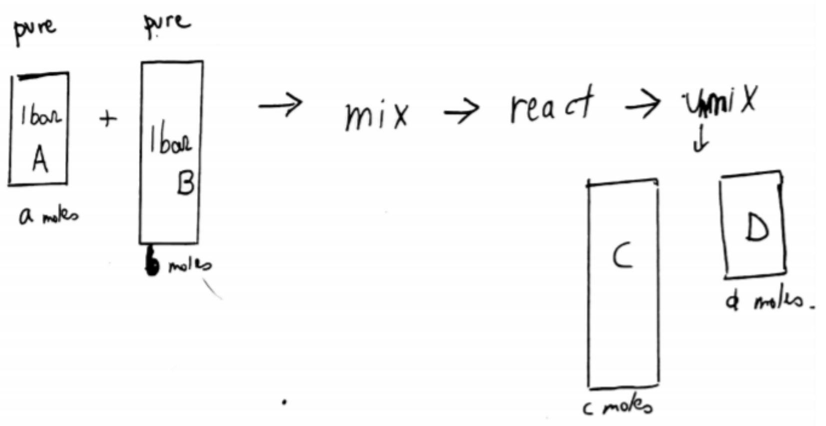
$$Q \equiv (a_A)^{\nu_A}(a_C)^{\nu_C}(a_D)^{\nu_D}$$

Leads to

$$\boldsymbol{\Delta G = \Delta G^o + RT\ln(Q)}$$

Q is usually called: the reaction quotient.

$\underline{\Delta G^{\ominus}(aA + bB \rightarrow cC + dD)}$ (for gases).



$$\Delta G^{\ominus} = c\,G^{\ominus}_{m\,C} + d\,G^{\ominus}_{m\,D} - a\,G^{\ominus}_{m\,A} - b\,G^{\ominus}_{m\,B}$$

Equilibrium

In equilibrium $\Delta G = 0$. We define the quotient **in equilibrium** as

$$K = \boldsymbol{Q(equilibrium)} = (a_A)^{\nu_A}(a_C)^{\nu_C}(a_D)^{\nu_D}\ (\boldsymbol{equlibrium})$$

It is straightforward of course to generalize our derivation to an arbitrary reaction:

$$Q = \prod_i (a_i)^{\nu_i}$$

The condition $\Delta G = 0$ at equilibrium leads to

$$0 = \Delta G^{o} + RT \ln K$$

Don't confuse K with K for Kelvin. Also, at times K is labeled K_P.

The eq. above becomes

$$-\frac{\Delta G^{o}}{RT} = \ln K$$

i.e.,

$$K = e^{-\frac{\Delta G^{o}}{RT}}$$

The Q-K relation and the road to equilibrium

Since we wrote $0 = \Delta G^{\mathrm{o}} + RT \ln K$, it follows that $\Delta G^{\mathrm{o}} = -RT \ln K$, so

$$\Delta G = \Delta G^{\mathrm{o}} + RT \ln Q = -RT \ln K + RT \ln Q$$

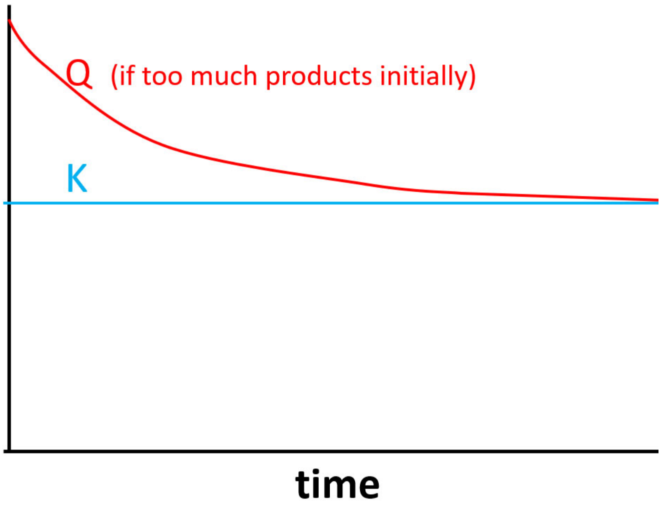
i.e.,

$$\Delta G = RT \ln \frac{Q}{K}$$

Therefore, if initially $Q < K$, i.e., the reaction is too much on the reactants side, then ΔG will be a ln of a number <1, i.e., ΔG will be **negative**, so the reaction would proceed to the products side.

As it does, Q will rise till it reaches asymptotically the equilibrium value, K.

In the opposite case, too much products, $Q > K$ and the reaction would proceed towards the reactants side.



Examples: Ideal gases

The expressions we derived are general. We'll apply them in this chapter using ideal-gases examples, and in latter chapters we'll use these expressions also for solutions.

Example (from the book, slightly extended)

Reaction (all gases, all assumed ideal):

$$2\mathrm{H_2S} + \mathrm{CH_4} \leftrightarrow 4\mathrm{H_2} + \mathrm{CS_2}$$

Initially:

$$n(\mathrm{H_2S}) = 11\ \mathrm{mmol}, \quad n(\mathrm{CH_4}) = 5.5\ \mathrm{mmol}, \quad n(\mathrm{products}) = \mathrm{almost\ zero}$$

At equilibrium:

$$n(\mathrm{CS_2}) = 0.7\ \mathrm{mmol}, \quad P_{tot} = 1\mathrm{bar}$$

Question: Find $\boldsymbol{K}$ and $\boldsymbol{\Delta G^{\mathrm{o}}}$, and explain why are products formed in spite of the fact that $\Delta G^{\mathrm{o}} > 0$.

Answer: (Method: find the n's → P's → K → ΔG^0)

First, n's.

0.7 mmol of CS_2 was formed in equilibrium, starting from 0. Thus:

- 4*0.7=2.8 mmol of H_2 was formed, $n(H_2) = 2.8\text{mmol}$
- 0.7 mmol of methane was destroyed, $n(CH_4) = 5.5 - 0.7 = 4.8\text{mmol}$.
- 2*0.7=1.4 mmol of H_2S was destroyed, $n(H_2S) = 11 - 0.7 * 2 = 9.6\text{mmol}$.

Now for the P's. From the ideal-gas law:

$$\frac{P(\mathrm{H_2S})}{P_{tot}} = \frac{n(\mathrm{H_2S})}{n_{tot}}$$

But $n_{tot} = 0.7 + 2.8 + 9.6 + 4.8 = 17.9$ mmol, and $P_{tot} = 1\text{bar}$, so

$$P(\mathrm{H_2S}) = 1\text{bar} \cdot \frac{9.6}{17.9} \simeq 0.53\text{bar}.$$

Similarly

$$P(\mathrm{CH_4}) = 1\text{bar} \cdot \frac{4.8}{17.9} \sim 0.27\text{bar}$$

$$\mathrm{P(H_2)} = 1\text{bar} \cdot \frac{2.8}{17.9} \sim 0.16\text{bar}$$

$$\mathrm{P(CS_2)} = 1\text{bar} \cdot \frac{0.7}{17.9} \sim 0.04\text{bar}$$

Now the stoichiometry of the reaction implies that

$$K = \frac{(a_{\mathrm{H_2}})^4 (a_{\mathrm{CS_2}})^1}{(a_{\mathrm{H_2S}})^2 (a_{\mathrm{CH_4}})^1}$$

But for ideal gas the activity is determined by the partial pressure: $a_{\mathrm{H_2}} = \frac{P_{H_2}}{P^o}$ **(never apply this for anything except ideal gases).**

We'll use **units where $\boldsymbol{P^0 = 1}$**, so then $a_{\mathrm{H_2}} = P_{H_2}$, i.e.,

$$K = \frac{(P_{\mathrm{H_2}})^4 (P_{\mathrm{CS_2}})^1}{(P_{\mathrm{H_2S}})^2 (P_{\mathrm{CH_4}})^1} = \frac{0.16^4 \cdot 0.04}{0.53^2 \cdot 0.27} = 3.5 \cdot 10^{-4}$$

Thus

$$\Delta G^o = -RT \ln K = -8.3 \frac{\mathrm{J}}{\mathrm{K\,mol}} \cdot 300\mathrm{K} \cdot (-7.95) \cong 20{,}000 \frac{\mathrm{J}}{\mathrm{mol}}$$

Do not make the mistake of assuming that when $\boldsymbol{\Delta G^o}$ is positive (so $K \ll 1$) only products are formed, or vice versa. Here, for example, $\Delta G^0 \gg 0$, so the reactants are "favored" – but there's still a significant amount of products.

As explained, any possible reactant or product gas must be present in a reaction vessel, although perhaps in minute amounts. That's because for very small (partial) pressures the chemical potential μ of a gas is very small so it is favored.

Put differently, in our reaction, initially $n(\text{products})$ is almost zero, so the partial pressure of both H_2 and CS_2 is very small. Thus, μ_{H_2} and μ_{CS_2} are initially very negative numbers, so that there's a tendency to form products. As products are formed, μ_{H_2} and μ_{CS_2} increase until equilibrium is established.

Finally: note that initially Q was almost zero, i.e., much smaller than K.

Another example: $\mathbf{N_2O_4}(g) \leftrightarrow \mathbf{2NO_2}(g)$

Do the reaction in a piston with a total pressure $P_{tot} = 2P^{o}$, and room temperature. Start from $n_{start}(\text{NO}_2) = 0.5 \text{ mol}$, $n_{start}(\text{N}_2\text{O}_4) = 0.3\text{mol}$.

Question: determine the composition in equilibrium.

Answer.

Overall method:

G_f^o(each species) → ΔG^0→K→combine with $P_{tot} = 2P^0$ to get individual P's→ n's.

So let's start.

First, (at room temperature), reading from the table in the book

$$G_f^o(\text{NO}_2) = 51.3\frac{\text{kJ}}{\text{mol}}, \quad G_f^o(\text{N}_2\text{O}_4) = 97.9\frac{\text{kJ}}{\text{mol}} \rightarrow$$

$$\Delta G^o = 2 \cdot 51.3 - 97.9 = 4.7\frac{\text{kJ}}{\text{mol}}$$

and therefore:

$$K = e^{-\frac{\Delta G^o}{RT}} = e^{-\left(\frac{4700 \text{ J mol}^{-1}}{2500\text{J mol}^{-1}}\right)} = 0.15$$

So $\frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = 0.15$.

Combine with $P(\text{NO}_2) + P(\text{N}_2\text{O}_4) = 2$ to get

$$\frac{P(\text{NO}_2)^2}{0.15} + P(\text{NO}_2) = 2$$

The solution of this is $P(\text{NO}_2) = 0.48$, $P(\text{N}_2\text{O}_4) = 2 - 0.48 = 1.52$

(Check: $\frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{0.48}{1.52^2} = 0.15$, as needed.)

Finally, solve for the n's.

$$\frac{n(\text{NO}_2)}{n(\text{N}_2\text{O}_4)} = \frac{P(\text{NO}_2)}{P(\text{N}_2\text{O}_4)} = 0.316$$

Note: Initially, $\frac{n_{start}(\mathrm{NO_2})}{n_{start}(\mathrm{N_2O_4})} = \frac{0.3}{0.5} = \mathbf{0.6}$. So initially there's too much products, the reaction will shift towards reactants.

So say x moles of $\mathrm{N_2O_4}$ were created; then

$$n(\mathrm{NO_2}) = 0.5 - 2x, \quad n(\mathrm{N_2O_4}) = 0.3 + x$$

So

$$0.316 = \frac{n(\mathrm{NO_2})}{n(\mathrm{N_2O_4})} = \frac{0.5 - 2x}{0.3 + x}$$

The result of this linear relation is $x = 0.175$, so the final prediction is

$$n(\mathrm{NO_2}) = 0.5 - 2 * x = 0.5 - 2 * 0.175 = 0.15\mathrm{mol}$$

$$n(\mathrm{N_2O_4}) = 0.3 + 0.175 = 0.475\mathrm{mol}$$

(**Check**: $\frac{n(\mathrm{NO_2})}{n(\mathrm{N_2O_4})} = \frac{0.15}{0.475} = 0.316$ indeed).

6.4) Pressure and Temperature dependence of Equilibrium & LeChatelier's Principle

Total-Pressure dependence

Let's study the P-dependence of reactions by example.

Take the $\mathrm{N_2O_4} \leftrightarrow 2\mathrm{NO_2}$ reaction example we just studied, with the same conditions, except that now compress the volume, i.e., increase the total pressure, to, say, $P_{tot} = 10$ (i.e., 10 bar)

Then, the relation $\frac{\mathrm{P}^2_{\mathrm{NO_2}}}{\mathrm{P}_{\mathrm{N_2O_4}}} = \mathrm{K} = 0.15$ remains, but now $P_{\mathrm{N_2O_4}} + P_{\mathrm{NO_2}} = 10$ so we need to solve

$$\frac{P(\mathrm{NO_2})^2}{0.15} + P(\mathrm{NO_2}) = 10$$

and the solution is $P(\mathrm{NO_2}) = 1.15,\ P(\mathrm{N_2O_4}) = 8.85$

Note the changing composition!

Thus, earlier, the ratio of the pressures was, recall

$$\frac{P(\mathrm{NO_2})}{P(\mathrm{N_2O_4})} = \frac{0.48}{1.52} = 0.316 \quad (\text{For } P_{\mathrm{tot}} = 2)$$

But now that the total pressure increased, the **relative partial pressure of the products (and therefore the percentage of the products) decreased**

$$\frac{P(\mathrm{NO_2})}{P(\mathrm{N_2O_4})} = \frac{1.15}{8.85} = 0.13 \quad (\text{For } P_{\mathrm{tot}} = 10)$$

Clearly, **by raising the total pressure, there was a shift from products to reactants.** This is an example of:

LeChatelier's principle: when subjected to a disturbance, a system usually (**not always!)** shifts its equilibrium in a way that **somewhat (usually not completely) mitigates** the disturbance.

Here the disturbance is: reducing the volume, i.e., increasing the total pressure; the system somewhat reduces the higher total pressure by **reducing the total number of moles**, which in this case is possible by having **some reactant formed, i.e.,** $N_2O_4 \leftarrow 2NO_2$.

> Side note: This $N_2O_4 \leftarrow 2NO_2$ reaction is **quite fast**, but to understand LeChatelier's principle deeper **let's imagine for a second that it would have been slow** (the speed of the reaction does not affect, of course, the final outcome, so assuming it is slow just helps in understanding the principles)
>
> Then we could imagine that what happens when we increase the total pressure is that we: **first reduce the volume, quickly, before any reaction occurs;**
>
> > **This raises the pressure automatically to a high value;**
> >
> > **And then some NO$_2$ is converted back to N$_2$O$_4$ to somewhat reduce the overall number of molecules and therefore the total pressure.**
>
> Once we plug the numbers (I won't do it here, but it is fairly straightforward to show), we find that the stages are:
>
> * First, the **volume is decreased by a factor of 5.35**. This raises the total pressure by a factor of 5.35, **from 2bar to 10.7bar**
>
> * Then 55% of the NO$_2$ is converted to NO$_2$; this reduces the total number of moles by almost 7%, and therefore the total pressure is reduced to 10bar. **I.e., the system "fought" back to somewhat mitigate the increase in the pressure due to the changed external circumstance (the reduced volume).**

Temperature dependence of *K*

Now consider the temperature variation of K.

The absolute simplest way to see it (slightly different from the way the book does it) is to spell out

$$-\frac{\Delta G^{o}}{RT} = -\frac{(\Delta H^{o} - T\Delta S^{o})}{RT} = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R}$$

so

$$K = e^{-\frac{\Delta G^{o}}{RT}} = e^{-\frac{\Delta H^{o}}{RT}} e^{\frac{\Delta S^{o}}{R}}$$

Thus, K is a product of two terms.

The first term in K is a Boltzmann-like term, due to the relative difference in energy between the products and reactants.

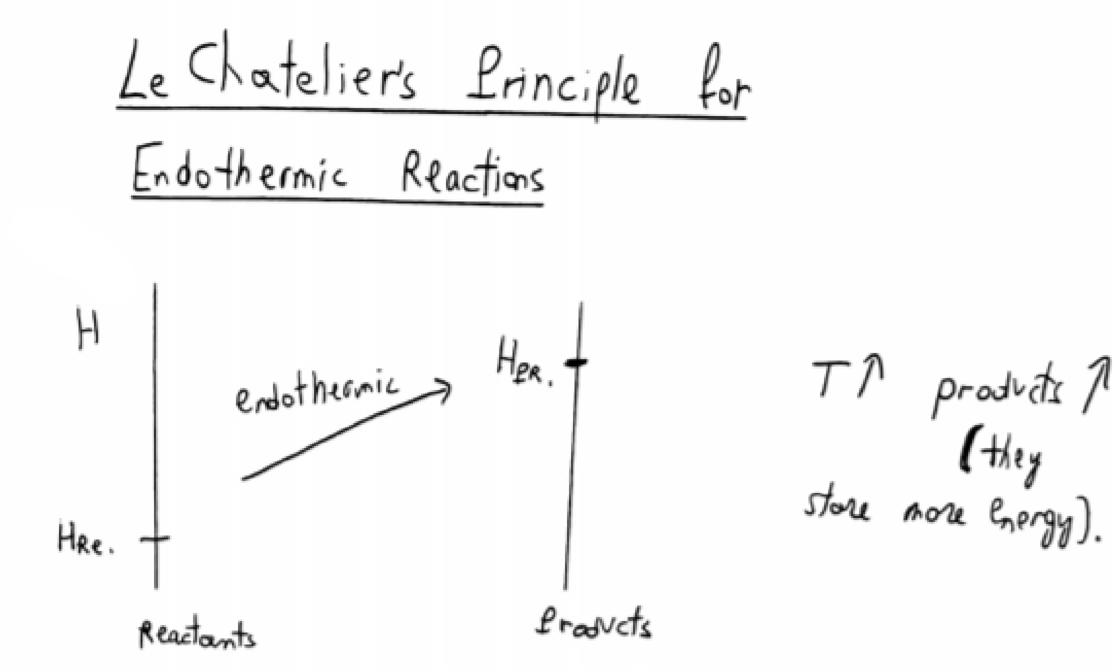
The second is an entropy term; in Statistical Mechanics we'll learn that it measures the ratio of the **number of states** of the products and reactants (we'll see what that means later)

Let's assume that we ignore the variation of ΔH^{o} and ΔS^{o} with temperature (they change, and we know how to calculate that, but they don't change much. We'll talk about that later).

Then: the implications of $K = e^{-\frac{\Delta H^o}{RT}} e^{\frac{\Delta S^o}{R}}$ are again an example of LeChatelier's principle.

- For **exothermic reactions ($\Delta H^o < 0$): $-\Delta H^o$** is then a **positive number, and when we divide it by RT it decreases with temperature**. So K decreases with temperature, i.e.: **for exothermic rxns. an increased T favors the reactants**
- For endothermic reactions ($\Delta H^o > 0$): the **opposite behavior.** An increased T favors the products ($-\frac{\Delta H^o}{RT}$ becomes a smaller-negative number – i.e., a less-negative number – when T is increased, so K increases with T).

Physically, in endothermic reactions, **as T increases, the products are favored because they can store more energy**. Thereby relieving a little the effects of the increased T.



Variation of K with temperature:

Often $\Delta H^o, \Delta S^o$ are approximately T –independent as we mentioned. Thus, when we change the temperature from, say, T_1 to T_2,

$$\ln K(T_2) - \ln K(T_1) = -\left(\frac{\Delta G^o(T_2)}{RT_2} - \frac{\Delta G^o(T_1)}{RT_1}\right) =$$

$$-\left(\frac{\Delta H^o - T_2\Delta S^o}{T_2} - \frac{\Delta H^o - T_1\Delta S^o}{T_1}\right)$$

i.e.,

$$\ln K(T_2) - \ln K(T_1) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Reminder: as we mentioned earlier, you may be confused on how can we assume that ΔS^0 and ΔH^o are fixed, when we previously learned that ΔH rises with temperature, i.e., we learned that
$\Delta H(T_2) - \Delta H(T_1) \simeq \Delta C_P \cdot (T_2 - T_1)$, and similarly for S?

The key is that $\Delta C_p \cdot (T_2 - T_1)$ is relatively **small** compared with typical values of ΔH, especially for reactions involving gases, so we can typically ignore its contribution to ΔH.

Example: $\mathbf{N_2 + 3H_2 \leftrightarrow 2NH_3}(g)$

Given that at room temperature $G_f(\mathrm{NH_3}) = -16.4\frac{\mathrm{kJ}}{\mathrm{mol}}$ at room temperature, and that $H_f(\mathrm{NH_3}) = 46\frac{\mathrm{kJ}}{\mathrm{mol}}$, find out what will be $K(T = 300\mathrm{K}), K(T = 500\mathrm{K})$.

Answer

- First,

$$\Delta G^o = -H_f(\mathrm{N_2}) - 3\,H_f(\mathrm{H_2}) + 2H_f(\mathrm{NH_3})$$
$$= -0 - 3 * 0 + 2 * \left(-16.4\frac{\mathrm{kJ}}{\mathrm{mol}}\right) = -32.8\frac{\mathrm{kJ}}{\mathrm{mol}}$$

So

$$K(T = 300\mathrm{K}) = \frac{\left(P_{NH_3}\right)^2}{P_{N_2}P_{H_2}} = e^{-\frac{\Delta G^o}{RT}} = e^{-\frac{-32.8\frac{\mathrm{kJ}}{\mathrm{mol}}}{2.5\frac{\mathrm{kJ}}{\mathrm{mol}}}} = e^{\frac{32.8}{2.5}} = 5 \cdot 10^5$$

Note that K is very big at $T = 300\mathrm{K}$ so the reaction at this temperature is "products dominated" (that's not an exact statement since the specific product and reactants concentrations depend on the total pressure and starting point, but it is more-or-less correct).

- Second:

$$\Delta H = 2H_f(\mathrm{NH_3}) - H_f(\mathrm{N_2}) - 3H_f(\mathrm{H_2}) = 2 * (-46)\frac{\mathrm{kJ}}{\mathrm{mol}} - 0 - 3 * 0 = -92\frac{\mathrm{kJ}}{\mathrm{mol}}$$

So

$$\ln K(500\mathrm{K}) = \ln K(\,300\mathrm{K}) - \frac{\Delta \mathrm{H}^0}{R}\left(\frac{1}{500\mathrm{K}} - \frac{1}{300\mathrm{K}}\right)$$
$$= 13.2 + \frac{92{,}000\frac{\mathrm{J}}{\mathrm{mol}}}{8.31\frac{\mathrm{J}}{\mathrm{K\,mol}}}\left(\frac{1}{500\mathrm{K}} - \frac{1}{300\mathrm{K}}\right) = -1.64$$

i.e.,

$$K(500\mathrm{K}) = 0.2$$

By LeChatelier's principle, $\boldsymbol{K(500\mathrm{K}) < K(300\mathrm{K})}$ since the reaction is exothermic.

Note how the ammonia gas is so strongly preferable over its constituents (hydrogen and nitrogen) at room temperature, but not at 500K!

6.5) Conclusions – Chapter 6.

We did several different things here:

- Starting with

$$d\mu = dG_m = V_m dP - TdS$$

  we first obtained the pressure dependence of μ (where all the pressures are in units of P^{o}):

$$\mu_A(T,P) = \mu_A^{\mathrm{o}}(T) + \int_{P^{\mathrm{o}}}^{P} V_{mA}dP = \mu_A^{\mathrm{o}}(T) + RT\ln(a_A)$$
$$= \begin{cases} \simeq \mu^{\mathrm{o}}(T) & (\text{for } \textbf{pure} \text{ condensed phases}) \\ \mu^{\mathrm{o}}(T) + RT\ln(P) & (\text{for ideal gases}) \end{cases}$$

- We then defined $\Delta G = \sum_i \nu_i \mu_i$, and dervied

$$\Delta G = \Delta G^{\mathrm{o}} + RT\ln Q\,, \quad Q = \prod_i (a_i)^{\nu_i}$$

For example, for a reaction $aA + bB + \cdots \rightarrow xX + yY + zZ + \cdots$, ΔG^{o} can be thought of as the work needed to take $\boldsymbol{a}$ moles of pure unmixed $\boldsymbol{A}$ at $\boldsymbol{P^{\mathrm{o}}}$ plus $\boldsymbol{b}$ moles of pure unmixed $\boldsymbol{B}$ at $\boldsymbol{P^{\mathrm{o}}}$, ….and convert to $\boldsymbol{x}$ moles of pure $\boldsymbol{X}$ at $\boldsymbol{P^{\mathrm{o}}}$ plus $\boldsymbol{y}$ moles of pure unmixed $\boldsymbol{Y}$ at $\boldsymbol{P^{\mathrm{o}}}$, etc.

- For equilibrium we noticed and defined

$$\Delta G = 0(\text{in equi.}) \qquad K(T) \equiv Q(\text{in equil.}) \rightarrow \quad \Delta G^{\mathrm{o}} = -RT\ln K$$

  K is fixed at a given T, **constraining what pressures the gas reactants can be in.**

- We saw how K determines the **evolution of the reactants with total pressure.** At a higher total pressure the equilibrium shifts to the side with “less gas moles” according to the **LeChatelier’s principle**.

- Finally, we examined the T-dependence of K; we wrote $\boldsymbol{K = e^{-\frac{\Delta H^{\mathrm{o}}}{RT}} e^{\frac{\Delta S^{\mathrm{o}}}{R}}}$ and realized that this implied that for **exothermic reactions $\boldsymbol{K}$ decreases with temperature.**

- We got a practical way to calculate the variation of K between different temperatures as

$$\ln K(T_2) - \ln K(T_1) = -\frac{\Delta H^{\mathrm{o}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  Again this shows LeChatelier’s principle at work. For exothermic reactions, and if $T_2 > T_1$, the RHS is negative, so the equilibrium shifts, at higher temperatures, towards reactants (as these store the extra energy since they have a higher enthalpy).

- We have therefore finished our “Tour de Force” of thermodynamics of pure compounds and gases alone. Now we need to worry about mixtures (and reactions) of gases with solutions and solids. For this we need phase-equilibrium.

VII. Phase equilibrium

7.1) Overview

This chapter has two (almost disconnected) parts.

- We'll first study the **phase rule**, explaining, e.g., why
    - The P, T diagram has a sharp line separating water vapor and liquid;
    - But the same is not true if we talk about a *water+ethanol* mixture where the liquid-vapor separation is not a single line in the P vs. T diagram.

  This rule is very abstract, we'll explain by several examples.

- We'll then study the specific case of liquid/vapor or solid/vapor phase line, and we will be able to get a new angle on results that could have been obtained also by the tools of the previous chapter.

7.2) The Phase Rule

What's a phase

Formally, a **phase** is a homogenous part of a system.

Note that:

- Gases: mix and form one phase (there's one exotic exception involving He that we'll ignore)

- Liquids:
    - Some mix fully (water + ethanol, 1 phase)
    - Some never mix (oil + water, 2 phases)
    - Some partially mix; for example: water + butanol liquids at room temperature will:
        - Break to two different phases if the butanol molar percentage is between about 3% and 48%;
        - Below 3% or above 48% the mixture will be single phase.

- Solids: there are some which can mix, e.g., Ag+Au (especially if you melt them together and cool down), but many don't.

Examples of phases include:

- Ice+water: 2 phases
- Ice+water+ethanol: 2 phases (ice, and liquid water+ethanol)
- Single crystal Fe: one phase
- Steel: many (microscopic) phases

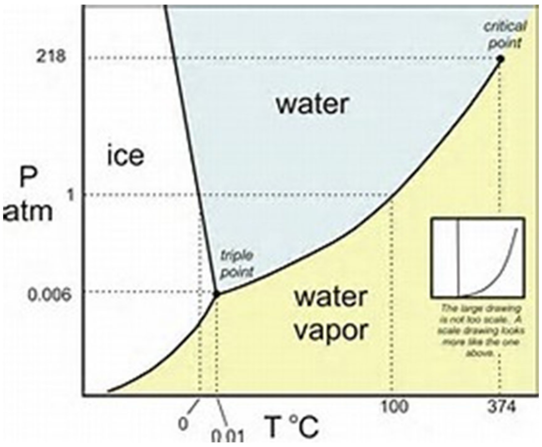
Vapor and gas; subscripts

Henceforth we'll use interchangeably the words vapor and gas (and the subscripts "v" and "g"). For liquids and solids we'll use the subscripts l and s (don't confuse with entropy).

Number of phases

Denoted as p. (Don't confuse with P for pressure!)

Say we have **one component**

> **Component** means a species which can be independently set, e.g. H_2O.
>
> Note: a **water liquid has also** H^+ and OH^-, as well as higher order clusters, but the concentrations of these ions and clusters are fixed for neutral water, so **they are not independent, only the original H_2O is.**
>
> 
>
>
> (figure taken from https://socratic.org/questions/how-do-you-read-the-phase-diagram-of-water)

Then, the compound will **be in the phase which has the lowest μ.** For example, in the region of P, T labeled "water" (i.e., "liquid") in the figure, the chemical potential of the liquid will be lower than that of the solid and vapor, $\mu_l < \mu_s, \mu_v$, so H_2O will be in the form of liquid water.

In other ranges the vapor or solid will be the stable ones. In those single-phase regions $p = 1$.

In the border regions separating two single-phase regions, two phases will coexist. So there $p = 2$. Along those lines the chemical potential of two phase will equal (and will be lower than the chemical potential of any other phases). For example, along the line separating water from vapor, $\mu_l = \mu_v < \mu_s$

Finally, when all chemical potentials are equal, we can have three coexisting phases (so $p = 3$). This is the "triple-point", which for water is at 0.006 bars and 0.01Celsius.

Degrees of freedom

Define: f=the number of "independent conditions" that we can vary while still keeping the same number of phases (i.e., keep p fixed).

The phase rule – example for water.

Let's start with our $c = 1$ example on water.

If P, T are in a single-phase region then we can change **both** the pressure **and** the temperature by a little bit while still keeping the number of phases. So: **if $\boldsymbol{p = 1}$ then $\boldsymbol{f = 2}$**

Similarly (see **figure**) if $\boldsymbol{p = 2}$, i.e., two phases coexist (liquid-vapor, vapor-ice, liquid-ice) then we can move only **along the line.**

For example, say P, T are along the liquid-vapor line, so $\mu_l(P,T) = \mu_v(P,T)$. I.e., if we move the temperature by a little, dT, **then we need to change the pressure $\boldsymbol{dP}$ by a specific amount**, to keep:

$$\mu_l(P + dP, T + dT) = \mu_v(P + dP, T + dT)$$

so $\boldsymbol{f = 1}$ when $\boldsymbol{p = 2}$.

Finally, if $\boldsymbol{p = 3}$**,** three phases coexist (liquid-ice-vapor), then **we can't move,**

$$\mu_l(P,T) = \mu_v(P,T) = \mu_s(P,T).$$

The pressure and temperature are then fixed. So $\boldsymbol{f = 0}$ **when** $\boldsymbol{p = 3}$

Thus, we see a relation for this single-component phase map

$$\boldsymbol{f = 3 - p,} \qquad \textbf{when } \boldsymbol{c = 1}$$

While these results are "obvious", they exemplify the general relation which we'll prove:

7.3) The phase rule – general

The general phase rule is:

$$\boldsymbol{f = 2 + c - p} \quad \textbf{Phase Rule}$$

Let's prove it. We'll refer to a "mock example", of $c = 4$ species: water, ethanol, butanol, propanol. **And we'll make up some numbers in our example**! – so don't take the specific numbers I give too seriously.

Also, our proof is only **for compounds that cannot react with one another**.

- We'll assume that we are at a pressure of 1 bar, room temperature,
- We pour into a container $c = 4$ species, numbered respectively 1,2,3,4: butanol, ethanol, propanol and water.
- And say that we have $p = 3$ phases (see figure below)

Phase I will be a liquid with concentrations

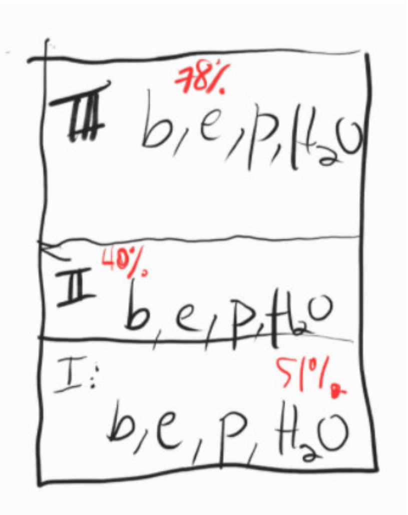
$x_{1,I}$ =10% butanol, $x_{2,I}$ =25% ethanol, $x_{3,I}$ =14% propanol and $x_{4,I}$ =51% water (**all percentages are by mol, not weight).**

Another liquid phase (Phase II) with
40% butanol, 20% ethanol, 34% propanol and 5% water

($x_{1,II} = 40\%,\quad x_{2,II} = 20\%,\quad x_{3,II} = 34\%,\quad x_{4,II} = 5\%$)

And a coexisting vapor (Phase III) with
10% butanol, 10% propanol, 78% ethanol, 2% water vapor
($x_{1,II} = 10\%,\quad x_{2,II} = 10\%,\quad x_{3,II} = 78\%,\quad x_{4,II} = 2\%$

Remember—I made up all these numbers, actual numbers will be different, the numbers here are just to illustrate the proof.



So now's the question: what's f? How many independent variables can we independently change a little, while keeping 3 phases?

Answer:

- First, the total number of degrees of freedom (DOF) is
$$2 + p \cdot c = 2 + 3 * 4 = 14$$
Proof:
  - In each of the p phases there are $c = 4$ concentrations, i.e., $x_{1,I} \ldots., x_{4,I}$ for Phase I, and similarly for Phase II and Phase III. So there are $c * p$=12 degrees of freedom (DOF).
  - Add 2 for pressure and temperature;

- However, we can't vary all of the 14 DOF independently! There are two types of constraints.
  - First, the sum of concentrations in each phase must sum up to 100%. For example, if we vary the concertation of the ethanol, butanol and propanol, then the concentration of the water must vary too, so they all add to 100%.
This gives one constraint for each phase, i.e., ***p* constraints.**

- Next, since the phases coexist, then for each species, its chemical potential must match in each of its phases. For example, for butanol
$$\mu(\text{butanol, phase I}) = \mu(\text{butanol phase II})$$
and
$$\mu(\text{butanol, phase II}) = \mu(\text{butanol phase III})$$

  Thus, for each of the "c" species, there are 2, $i.e.,\ p-1$ constraints (saying that three numbers are equal means that there are two equalities).

Thus, for each species, we'll have $p-1$ constraints; so for "c" independent species, the chemical potential equalities give $\boldsymbol{c*(p-1)}$ **constraints**.

Summing: there are $p + c*(p-1) = 3 + 4*2 = 11$ constraints.
So we have

$2 + c*p = 14$ degrees of freedom, and
$p + c*(p-1) = 11$ constrains.

Thus a total of $f = 14 - 11 = 3$ variables that can be independently varied, and in the general case
$$f = 2 + c \cdot p - c*(p-1) = 2 + c - p$$

What are the independent variables? Here, for example, the three independent variables could be P and T, **and another one** – for example the concentration of ethanol in the vapor.
I.e., we can vary the pressure a little, the temperature a little, and concentration of the ethanol in the vapor by, say, 1%, and all the other concentrations will then vary by a set amount, **and the number of phases will still be 3.**

- Note that this is different than for pure H_2O – there, if we three phases coexisting P and T would be set.

Exercise: in our 4-species example, if there are only two coexisting phases, can we vary P and T and vary the concentration of more than one species by a desired amount (while keeping two phases?)

Answer – yes. Then $f = 2 + c - p = 2 + 4 - 2 = 4$, so we can vary the pressure, the temperature, and two desired concentrations in one of the phases, while keeping the same number of phases.

Counting independent degrees of freedom

Remember: we are only counting **independent** variables, i.e. variables that their concentrations can't be determined from using K for any relevant reaction. If a variable's concentration is constrained it won't be counted.

Example:

Three species A, B, C, in a container. There's a reaction A <--> 2C. How many independent compounds?

Answer: 2. A, and B. The concentration of C is constrained due to the existence of K for the reaction A <--> 2C.

Epilogue to phase-rule part

The phase rule is general – that's its strength and weakness. It can be applied in general circumstances, but is hard to visualize. After we practice phases diagrams (chapters 9 and 12) it would get easier.

We'll now switch to the much-less-abstract 2nd half of this chapter:

7.4) Phase equilibrium in one component systems.

Look at the figure below of two phases. Pick nearby points along the line of equilibrium.

- At point 1:
$$\mu_A(P,T) = \mu_B(P,T)$$
- At point 2: the temperature and pressure changed, but the chemical potential is the same
$$\mu_A(P+dP,T+dT) = \mu_B(P+dP,T+dT)$$
Subtract the last two eq, get.:
$$d\mu_A = d\mu_B$$
where
$$d\mu_A \equiv \mu_A(P+dP,T+dT) - \mu_A(P,T)$$

But μ_A is the chemical potential of **pure** A, and etc. for B, so we can use the eqs. for dG_{mA}, dG_{mB}:

$$d\mu_A = dG_{mA}(P,T) = V_{mA}dP - S_{mA}dT$$

$$d\mu_B = dG_{mB}(P,T) = V_{mB}dP - S_{mB}dT$$

Equate it to get:

$$V_{mA}dP - S_{mA}dT = V_{mB}dP - S_{mB}dT$$

So

$$(V_{mB} - V_{mA})dP = (S_{mB} - S_{mA})dT$$

i.e., since the quantities in parentheses as $\Delta V,\ \Delta S$, so

$$\Delta V\ dP = \Delta S\ dT$$

Where $\Delta V \equiv V_{mB} - V_{mA},\ \Delta S \equiv S_{mB} - S_{mA}$

Thus, once we found $\Delta V_m, \Delta S_m$ we can find the **slope of the *P* vs. *T* phase-separation line**

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad \text{in equilibrium}$$

We can make this equation even more useful by noting that in equilibrium, $\Delta G = 0$, i.e., the difference in Gibbs free energies between phase A and B vanishes (when we are on the phase separation line), so

$$0 = \Delta G = \Delta H - \mathrm{T}\Delta S \rightarrow \quad \Delta S = \frac{\Delta H}{T}$$

so

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

This is the **Clausius-Clapeyron** equation.

Discussion:

Solid-liquid transition (or solid-solid or liquid-liquid)**:** V is small, ΔV is even smaller, so $\frac{dP}{dT}$ is **very steep** (large positive or large negative)

Specifically,

- For all solid-liquid (melting) transitions, $\Delta H > 0$. You need heat to melt a solid.
- Usually, but not always, $\Delta V > 0$, i.e., the liquid is less dense (i.e., has more volume per mol) then the solid. (Exceptions are water and a few other compounds; in water the liquid is denser than ice).
- But regardless of the sign of ΔV, the absolute magnitude $|\Delta V|$ is small for condensed-to-condensed reactions

So: $\boldsymbol{\frac{dP}{dT}}$ for solid-liquid transition is usually **positive**, rarely (including water) **negative**, and always has a large magnitude.

Let's see how steep the curve is.

$$\Delta V(\mathrm{H_2O}, s \rightarrow l) \simeq \frac{(18-20)\mathrm{cm}^3}{\mathrm{mol}} = -2\frac{\mathrm{cm}^3}{\mathrm{mol}}$$

$$\Delta H(\mathrm{H_2O}, s \rightarrow \ell) \simeq 6000\frac{\mathrm{J}}{\mathrm{mol}}$$

So at 0°C:

$$\boldsymbol{\frac{dP}{dT}}\left(\frac{water}{ice}\right) = \frac{\Delta H}{T\Delta V} = \frac{6000\frac{\mathrm{J}}{\mathrm{mol}}}{273\mathrm{K}\cdot\left(-\frac{2\mathrm{cm}^3}{\mathrm{mol}}\right)} = -11\frac{\mathrm{J}}{\mathrm{K\,cm}^3} = -11{,}000\frac{\mathrm{J}}{\mathrm{K\,L}} = \boldsymbol{-110\frac{\mathrm{bar}}{\mathrm{K}}}$$

Thus, for a lake 100m deep, where the rise in pressure is ΔP =10bars (since the pressure rises in water by 1bar per 10 meter), **ice will melt to water at a temperature that's lower than in room conditions by only**

$$\boldsymbol{\Delta T \simeq \frac{\Delta P}{\frac{dP}{dT}} = \frac{10\mathrm{bar}}{-\frac{110\mathrm{bar}}{\mathrm{K}}} \sim -0.1\mathrm{K}}$$

(so ice melts there at 0-0.1=-0.1°C.)

You need to apply extremely large pressures in order to change the melting temperature of ice.

> Actually, at really large pressures (above 1000 bar) different phases of ice appear.

Liquid-vapor transition (or solid-vapor):

For a transition from condensed-phase to vapor, we actually get an equation we already derived in the previous chapter!

Specifically, as usual, the vapor is assumed to be an ideal gas, and we ignore (relative to it) the molar volume of the liquid (or solid), i.e.,

$$\frac{dP}{dT} = \frac{\Delta H_m}{T\Delta V_m} = \frac{\Delta H_m}{T(V_m(v) - V_m(l))} \simeq \frac{\Delta H_m}{T(V_m(v))} = \frac{\Delta H_m}{T\frac{RT}{P}}$$

(where here $\Delta H_m = \Delta H_{\text{vap}}$, or for a solid→vapor transition, $\Delta H_m = \Delta H_{\text{sub}}$):

$$\frac{dP}{dT} = \frac{P\,\Delta H_m}{RT^2}$$

i.e.,

$$\frac{dP}{P} = \frac{\Delta H_m}{R}\frac{dT}{T^2}$$

If we approximate that ΔH_m is fixed then we can **integrate this equation**

$$\int \frac{dP}{P} = \frac{\Delta H_m}{R}\int \frac{dT}{T^2}$$

$$\ln P_2 - \ln P_1 = -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note that this is just a special case of an equation we already know:

$$\ln K_2 - \ln K_1 = -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

In our case, the reaction is $A(\ell) \to A(v)$, so $K = \frac{P(A)}{P^0}$.

Example: at sea level the pressure is about 1.01bar and the boiling temperature of water is about 100°C.

Questions:

(i) What would be the boiling temperature on Mulholland Drive, at a height of 400m (about 1300 ft) where the pressure is about 0.96bar

(ii) The same on the Everest, where the pressure is 0.3bar

(iii) What's the vapor pressure of water at 50°C.

Answers:

(i) From the tables,

$$\Delta \mathrm{H}_{\mathrm{vap}}(\mathrm{H_2O}, \mathrm{T} = 100°\mathrm{C}) \sim 40\frac{\mathrm{kJ}}{\mathrm{mol}}$$

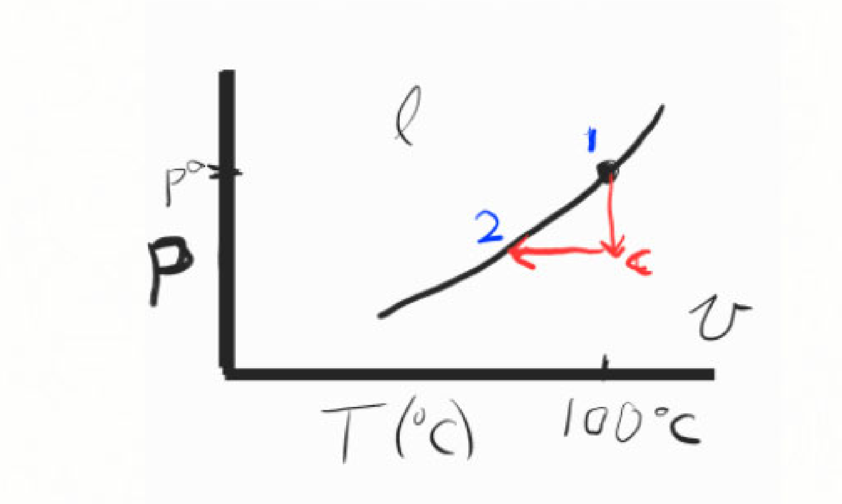
In the first example, measuring relative to sea-level, $dP = -0.05$ bar, which is a small variation. So we can find dT directly from the simple form of the Clausius-Clapeyron formula

$$\frac{dP}{dT}(T = 100°\mathrm{C}) = \frac{P\Delta H}{RT^2} = \frac{1\mathrm{bar} \cdot 40{,}000\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.3\,\frac{\mathrm{J}}{\mathrm{K\,mol}} \cdot (373\mathrm{K})^2} = 0.035\,\frac{\mathrm{bar}}{\mathrm{K}}$$

so

$$dT = \frac{dP}{0.035\,\frac{\mathrm{bar}}{\mathrm{K}}} = \frac{(-0.05\ \mathrm{bar})}{0.035\,\frac{\mathrm{bar}}{\mathrm{K}}} = -1.5\mathrm{K}$$

and therefore $T_{\mathrm{boiling}}(P = 0.96\mathrm{P}^{\mathrm{o}}) = 98.5°\mathrm{C}$.



Physical explanation for the decrease in T: see figure.

Let's start at sea level (see graph above). At that point the vapor and liquid coexist, $\mu(v, \mathrm{point\ 1}) = \mu(\ell, \mathrm{point\ 1})$.

First stage: climb the hill. If we consider H_2O at 100°C, then we'll be in point "c" at the graph. At that point $G_m(v)$ was reduced by a large amount

$$\Delta\mu(v) = V_m(\mathrm{gas})\Delta P = \frac{RT}{P}\Delta P = RT\frac{\Delta P}{P} = \left(8.3\,\frac{\mathrm{J}}{\mathrm{K\,mol}} \cdot 373\mathrm{K}\right) \cdot \left(-\frac{0.05\mathrm{bar}}{1\mathrm{bar}}\right)$$
$$\cong -150\,\frac{\mathrm{J}}{\mathrm{mol}}$$

while $G_m(\ell)$ is virtually unchanged,

$$\Delta\mu(\ell) = V_m(\ell)\Delta P = 18\,\frac{\mathrm{cm}^3}{\mathrm{mol}}\Delta P = \left(0.018\,\frac{\mathrm{L}}{\mathrm{mol}} \cdot (-0.05\ \mathrm{bar})\right) = 0.0009\ \frac{\mathrm{L} \cdot \mathrm{bar}}{\mathrm{mol}}$$
$$= -0.09\,\frac{\mathrm{J}}{\mathrm{mol}}$$

So at point c, $\mu(v) < \mu(\ell)$, i.e., the gas will be more stable. (qualitatively: less pressure → the gas will be less confined → more disordered → will be more stable.)

Next stage: Then we reduce T, fixing P at the new, lower pressure. (Going from point "c" in the graph to point 2.) The vapor becomes less disordered (so does the liquid but by a smaller amount).

But less disorder (S) → G increases (since $dG = -TdS$ here, as P is fixed). So $G_m(v)$ increases faster than $G_m(l)$, until $G_m(v)$ and $G_m(\ell)$ are equal again, at point 2.

(ii) Next: What's the temperature for which $P_{\text{vapor}} = 0.3\text{bar}$. Here the pressure difference is so big that we have to use the integrated formula

$$-\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln P_2 \ \text{(mountain)} - \ln P_1 \ \text{(sea)}$$

Plugging in we get

$$-\frac{40000\frac{\text{J}}{\text{mol}}}{8.3\frac{\text{J}}{\text{Kmol}}}\left(\frac{1}{T_2}-\frac{1}{373\text{K}}\right) = \ln\left(\frac{0.3}{1}\right) = -1.20$$

The only unknown in T_2 which with a little math we get that

$$T_2 = 341\text{K} = 68°\text{C}$$

(iii) The vapor pressure at a given temperature is defined as the pressure of the vapor when it is in equilibrium with the liquid.

For a one component system, the vapor pressure is thus a fancy notation for what we usually call the boiling pressure at that temperature, i.e., the pressure above which the compound will be liquid and below it is a gas, i.e., it is determined by the phase transition $P(T)$ curve.

So formally:

$$\boldsymbol{\ln P_{\text{vap}}\,(T = 323\text{K} = 50\text{Celsius}) - \ln(1\text{bar})} = -\frac{\Delta H_m}{R}\left(\frac{1}{323\text{K}}-\frac{1}{373\text{K}}\right)$$

$$= -\frac{40000\frac{\text{J}}{\text{mol}}}{8.3\frac{\text{J}}{\text{Kmol}}}\left(\frac{1}{323\text{K}}-\frac{1}{373\text{K}}\right) = -2$$

So

$$\boldsymbol{P_{\text{vap}}(T = 323\text{K}) = \text{e}^{-2}\cdot 1\text{bar} = 0.136\text{bar}}$$

Discussion: vapor pressure

If we leave water in an initially dry container (say with air), and seal the container, vapor would start slowly forming. I.e., water molecules will leave the liquid to the gas.

This will go on until **equilibrium**, i.e., until as many molecules leave the liquid as join it from the gas.

At that point, the vapor and liquid would coexist, and the pressure of the vapor would be the "vapor pressure for that temperature". At that point, the air in the container would be at "100% humidity".

> If the container is actually a room with little ventilation, and we are in the room, the 100% humidity will feel very "stuffy" (imagine a small closed room with wet laundry)
>
> At such a room, even if we perspire, the perspiration would not really vaporize, so we will not cool; that's why it feels so hot in Houston (where the air is usually close to 100% humidity) even when the temperature is the same as in California/Nevada, where the air is much drier.

Of course, if initially we did not put a large enough amount of water, it would vaporize without reaching phase equilibrium – so we will have less than 100% humidity, and the pressure of the vapor would be less than "the vapor pressure".

7.5) Conclusions – Chapter 7

In this chapter we:

- **Proved the phase rule**. The presence of $p-1$ equality conditions on the $\mu's$ of each compound:
  $\mu(\text{compound } i, \text{phase } 1) = \mu(\text{compound } i, \text{phase } 2) = \cdots = \mu(\text{compound } i, \text{phase } p)$
  led to the phase rule, $\boldsymbol{f = 2 + c - p}$ **(remember the proof, don't memorize the result!)**

- We derived, for one component, the shape of the line separating two phases:

$$d\mu_A = d\mu_B \rightarrow \Delta V\, dP = \Delta S\, dT$$

  (where Δ designates the difference between the two phases!). Thus:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

  So $\left|\frac{dP}{dT}\right|$ is very large (steep curve) for transitions between <u>two condensed phases</u> where ΔV is small;

  While for phase equilibrium between condensed phases and an ideal gas, we get (assuming ΔH is approximately constant)

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \rightarrow \quad \ln P_2 - \ln P_1 = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \big((\text{liq. or solid}) \rightarrow \text{gas}\,\big)$$

- We understood this equation in terms of general reaction equilibria and defined the **vapor-pressure** (pressure of gas when it is in equilibrium with a condensed phase).

IX. Mixtures

9.1) Overview

Chemical reactions, especially biochemical, are usually carried out in solutions. Before we start understanding how **reactions** occur in solutions, we need to examine the properties of **mixed solutions,** boiling points, vapor pressure, etc. – all are topics that are covered in this chapter.

One basic point we'll see is that **mixing of two liquids increases the disorder** and is therefore **favorable in many** (but **not all**) cases relative to two pure unmixed liquids.

In addition, if the liquids are miscible the **mixing changes the stability of the liquid**. The mixed liquid has different melting and vaporization melting and vaporization points (that would be covered mostly in Chapter 12).

The chapter is organized as follows:

- First, we will encounter strange phenomena ("non-ideal" liquids).
- **Then,** we will mathematically characterize any liquid mixture using the concept of **partial molar volumes – a subtle concept.**
- Finally, we will see how **non-ideal solutions behave in the solute-solvent limit (**one compound much less abundant that the other).

9.2) Mixtures: Partial molar volumes.

Take 2 solutions (A and B in general). Amounts: n_A, n_B.

Mix them: the mixture would have a different total volume, free energy, entropy, etc.

- An extreme example is some salts in aqueous solution, where, under certain conditions (sufficient concentration, not too low and not too high), if we add more salt the TOTAL VOLUME SHRINKS!

  Physically, the salt "breaks" the hydrogen bonding and the collapse of the bonding network shrinks the total volume.

- Another, much more common and less extreme case is what happens for ethanol and water; for these compounds **the total volume** when mixing them is **smaller than the sum of the individual volumes of the separate water and ethanol.**

Mathematically, we define

$$V_A \text{ (labeled: partial molar volume of A)} \equiv \frac{\partial V}{\partial n_A}$$

Note that V_A depends on n_A and n_B. It will be generally different if we use a different B, i.e., it depends on the nature of the other compound too.

We also define henceforth properties for **molar pure compounds with a * (and omit the "m" subscript).** So the molar volume of pure A is denoted as V_A^*

Very important: V_A is not necessarily equal to V_A^* (unless $n_B = 0$). V_A^* , the molar volume of pure A, is evaluated for $n_B = 0$; while V_A depends on n_A and n_B, and in extreme cases can be **negative!**

Physical interpretation of partial molar volume – Example

Add to a solution of 10,000 moles of A and 20,000 moles of B, a mole of "B", i.e., $dn_B = 1\text{mol}$.

The volume of that 1 extra mole of B before you add it to the mixture is

$$V_B^* \cdot 1\text{mol}$$

After adding that 1 mol, the total volume of the mixture changes by

$$\boldsymbol{dV} = V(n_A = 10{,}000, n_B = 20{,}001) - V(n_A = 10{,}00, n_B = 20{,}000) = \frac{\partial V}{\partial n_B} \cdot dn_B$$
$$= \frac{\boldsymbol{\partial V}}{\boldsymbol{\partial n_B}} \cdot \mathbf{1mol}$$

Thus, $\frac{\partial V}{\partial n_B}$, which we labeled as $V_B \equiv \frac{\partial V}{\partial n_B}$, and which **depends of course on $\boldsymbol{n_A, n_B}$** (it changes when you change $n_A,\ etc.$) is the change in volume of the mixture brought about by adding one mole of B to a solution with a fixed amount of n_A, n_B (as long as the total amount is much larger than 1 mol).

All this sounds familiar, and indeed, we previously defined $\mu_A = \frac{\partial G}{\partial n_A}$. The same interpretation here, just **replace $\boldsymbol{G}$ and $\boldsymbol{V}$**. (so μ is the "partial molar Gibbs energy").

Note that this graph below is not for room temperature, so dont use its exact numbers

Relation of total volume and partial volume (subtle!)

In spite of the fact that that the total volume is not a sum of the pure volumes of A, B

$$V \neq n_A V_A^* + n_B V_B^*$$

we can, amazingly, still write a similar looking and physically different equation

$$V = n_A V_A + n_B V_B$$

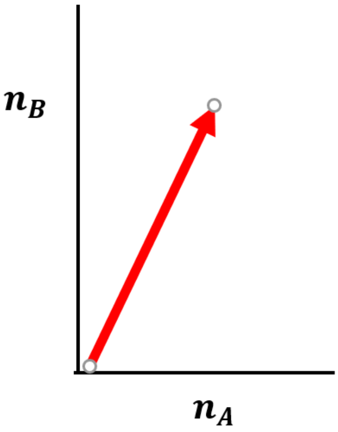
where again I remind you that $V_A \equiv \frac{\partial V}{\partial n_A}$ depends on n_A, n_B!

Proof:

Let's say again that we consider a mixture with, say, 10,00 moles A and 20,000 moles of B (and nothing else). The **key is that the mixture's properties depend only on the molar fraction.** Specifically,

- Take a mixture with one thousandth times less liquid, i.e., 10 mol A and 20 moles of B. The mixture will have the same properties as when it is 10,000 and 20,000 moles of A and B, respectively. In short, the properties depend only on the mole fractions, here
$$x_A = \frac{1}{3}, \qquad x_B = \frac{2}{3}$$
- Now pour in **A and B a tiny bit each time, keeping the proportion fixed,** i.e., add repeatedly, say, drops – each of which has 0.01moles of A and 0.02 moles of B. Keep on doing it and each time you add such a drop then
$$dV = \frac{\partial V}{\partial n_A} dn_A + \frac{\partial V}{\partial n_B} dn_B \equiv$$

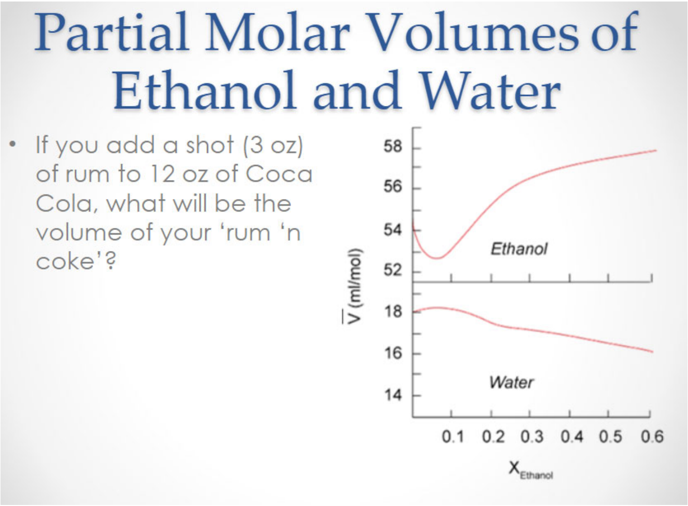
$$V_A\left(x_A=\frac{1}{3},x_B=\frac{2}{3}\right)dn_A+V_B\left(x_A=\frac{1}{3},x_B=\frac{2}{3}\right)dn_B$$



- Integrating (see the figure) over this very specific "trajectory" where we keep the proportion fixed so $\boldsymbol{V_A}$ and $\boldsymbol{V_B}$ don't change, and omitting the explicit mention of $x_A=\frac{1}{3}$, etc. we find that

$$\boldsymbol{V}=\int dV=V_A\int dn_A+V_B\int dn_B=\boldsymbol{V_A n_A+V_B n_B}$$

as promised.



Partial Molar Volumes of Ethanol and Water

- If you add a shot (3 oz) of rum to 12 oz of Coca Cola, what will be the volume of your 'rum 'n coke'?

Taken from https://slideplayer.com/slide/8415870/

Note how the exact same reasoning would have worked for the Gibbs free energy, so we get "as a byproduct" a very important relation,

$$G=n_A\mu_A+n_B\mu_B$$

where μ_A depends generally on n_A, n_B

Numerical example:

Say that the pure liquids are ethanol ("A") and water ("B"), that have as "pure" molar volumes:[5]

$$V_A^* = 58.6\frac{\text{cm}^3}{\text{mol}}, \qquad V_B^* = 18.1\frac{\text{cm}^3}{\text{mol}}.$$

Also say that, again, we consider an $x_A = \frac{1}{3}, x_B = \frac{2}{3}$ combination, and that at combination the numbers are (see the ref. in the footnote):

$$V_A = V_A\left(x_A = \frac{1}{3}, x_B = \frac{2}{3}\right) = 57.1\frac{\text{cm}^3}{\text{mol}}, \ \ V_B = 17.3\frac{\text{cm}^3}{\text{mol}}$$

<u>Questions</u>

Q: What's the total volume of the ethanol and water when they are separate, not mixed

Answer:

$$V_{\text{separate}} = n_A \cdot V_A^* + n_B \cdot V_B^* =$$
$$10\text{ mol} \cdot \left(58.6\frac{\text{cm}^3}{\text{mol}}\right) + 20\text{ mol} \cdot \left(18.1\frac{\text{cm}^3}{\text{mol}}\right) = \mathbf{948}\text{ cm}^3$$

Q: What's the total volume for a **mixture** with $n_A = 10\text{ mol}, \ n_B = 20\text{ mol}$

Answer:

$$V = n_A \cdot V_A\left(x_A = \frac{1}{3}, x_B = \frac{2}{3}\right) + n_B \cdot V_B\left(x_A = \frac{1}{3}, x_B = \frac{2}{3}\right)$$
$$= 10\text{ mol} \cdot \left(57.1\frac{\text{cm}^3}{\text{mol}}\right) + 20\text{ mol} \cdot \left(17.3\frac{\text{cm}^3}{\text{mol}}\right) = \mathbf{917}\text{ cm}^3$$

Note: the volume shrinks upon mixing– we'll quantify it later.

Q: What's the total volume for a solution with $n_A = 20\text{ mol}, \ n_B = 20\text{ mol}$

Answer: we can't know since we are not given $V_A(x_A = x_B = 0.5)$

Q: What's the total volume for $n_A = 10.2\text{ mol}, \ n_B = 20.4\text{ mol}$. Use two methods to answer.

Answer 1: The simplest way to answer is to note that the proportions are the same as they were earlier, $x_A = \frac{1}{3}$ and $x_B = \frac{2}{3}$. All that's different compared with

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[5] Taken from Tables 7 and 8 in D. Ricardo Delgado, M. Angeles Peña and F. Martinez, Revista Colombiana de Ciencias Químico Farmacéuticas 42(2):298, 2013. Available from: https://www.researchgate.net/publication/262561499_Preferential_solvation_of_acetaminophen_in_ethanol_water_solvent_mixtures_according_to_the_inverse_Kirkwood-Buff_integrals_method

the case above is that we have 2% more liquid. Therefore the volume will be 2% higher, i.e.,

$$V = 917 * 1.02 = 935.3 \frac{\mathrm{cm}^3}{\mathrm{mol}}$$

Answer 2: Alternately, we could use the formulae we learned earlier on the variation of a function of two variables when both variables are slightly changed. We'll omit the "mol" and "cm^3".

$$V(n_A = 10.2, n_B = 20.4\,) =$$

$$V(n_A = 10, n_B = 20) + \left.\frac{\partial V}{\partial n_A}\right|_{x_A=\frac{1}{3}, x_B=\frac{2}{3}} \cdot dn_A + \left.\frac{\partial V}{\partial n_B}\right|_{x_A=\frac{1}{3}, x_B=\frac{2}{3}} \cdot dn_B$$

$$= 917 + V_A dn_A + V_B dn_B$$

$$= 917 + 57.1 \ \cdot 0.2 + 17.3 \cdot 0.4 = \mathbf{935.3\ cm^3}$$

So the same answer!

Q: What's the volume when $n_A = 20\mathrm{mol},\ \ n_B = 40.3\ \mathrm{mol}.$

Answer: The proportions are not exactly 1:2, but they are not far. So let's first find the volume with 1:2 proportions that's close to what we're asked:

$$V(n_A = 20, n_B = 40) = 2 \cdot V(n_A = 10, n_B = 20) = 1834\ \mathrm{cm}^3$$

So: relative to $(n_A = 20, n_B = 40)$, the mole #'s we're interested in, $n_A = 20, n_B = 40.3$, are different by $dn_A = 0, dn_B = 0.3$

So

$$V(n_A = 20, n_B = 40.3)$$

$$\cong V(n_A = 20, n_B = 40) + V_A dn_A + V_B dn_B$$

$$= 1834 + 57.1 * 0.0 + 17 \cdot 0.3 = \mathbf{1839.1\ cm^3}$$

9.3) Mixing Volume and Mixing Free Energy

Mixing volume

Let's define a new concept, the **mixing volume,** as the **difference in volume between the mixture and its separate ingredients.** We'll refer to the prev. example.

Q: What's the **mixing volume** when $n_A = 10\ \mathrm{mol}, n_B = 20\ \mathrm{mol}.$

Answer:

$$\Delta V_{\mathrm{mix}} = V(n_A, n_B) - V(\mathrm{separate})$$

We have seen $V(n_A, n_B) = 917\ \mathrm{cm}^3$. Also, we saw that (I repeat)

$$V_{\mathrm{separate}} = n_A \cdot (\text{molar volume of pure A}) + \text{same for B}$$

$$= n_A V_A^* + n_B V_B^* = 10\text{ mol} \cdot 58.6\frac{\text{cm}^3}{\text{mol}} + 20\text{ mol} * 18.1\frac{\text{cm}^3}{\text{mol}} = \mathbf{948\ cm^3}$$

So the mixing volume is here negative

$$\boldsymbol{\Delta V_{mix} = 917 - 948 = -31\ \mathrm{cm}^3}$$

Generally, based on what we learned the mixing volume will be

$$\boldsymbol{\Delta V}_{\boldsymbol{mix}} = V(n_A, n_B) - V(separate) = n_A V_A + n_B V_B - (n_A V_A^* + n_B V_B^*)$$

i.e.,

$$\boldsymbol{\Delta V_{mix} = n_A(V_A - V_A^*) + n_B(V_B - V_B^*)}$$

It is often fruitful to define it in terms of the molar fraction, using $n_A = n\, x_A$, etc. (where $n = n_A + n_B$) so

$$\boldsymbol{\Delta V_{\mathrm{mix}} = n\left(x_A(V_A - V_A^*) + x_B(V_B - V_B^*)\right)}$$

Mixing Free energy

Completely analogous, just replace V by G.

Thus, since the equivalent of $V_A \equiv \left.\frac{\partial V}{\partial n_A}\right|$ is $\mu_A \equiv \left.\frac{\partial G}{\partial n_A}\right|$, we get an expression for G

$$G = n_A \mu_A + n_B \mu_B$$

Similarly

$$\boldsymbol{\Delta G_{\mathrm{mix}} = G_{mix} - G_{premix} = n\left(x_A(\mu_A - \mu_A^*) + x_B(\mu_B - \mu_B^*)\right)}$$

Note: **in order for substances to mix, $\boldsymbol{\Delta G_{\mathrm{mix}}}$ need to be negative.**

To understand better, let's write $G = H - TS$, i.e.,

$$\boldsymbol{\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}}$$

Note that generally, for any compounds, mixing increases disorder, so $\boldsymbol{\Delta S_{\mathrm{mix}} > 0}$.
So $\boldsymbol{-T\Delta S_{\mathrm{mix}}}$ would be negative.

But $\boldsymbol{\Delta H_{\mathrm{mix}}}$ could be

- Negative (for compounds that really like each other, e.g., ethanol and water)
- Close to 0 (for compounds where the A-A and A-B and B-B interactions are similar) – these are the **ideal solutions** that we'll deal with
- Positive (compounds that don't really like each other). And then, the question is how positive is $\boldsymbol{\Delta H_{\mathrm{mix}}}$?
  - If it is really high, i.e., higher than $\boldsymbol{T\Delta S_{\mathrm{mix}}}$, then the compounds won't mix at all (e.g., oil and water).
  - But if it is positive yet not too big, the compounds would mix, but would be more volatile (less strongly bound to the liquid) than they were before – we'll see that later for an acetone-with-CS_2 solution.

Exercise: the mixing free energy for **ideal-gases** that are initially both at the same pressure, say 1bar for simplicity. (Of course, for ideal gases, $\Delta H_{\text{mix}} = 0$.)

So before mixing, since each gas is at one bar

$$\boldsymbol{\mu_A^* = \mu_A^{\text{o}}}$$

After mixing, the partial pressure of A would be

$$P_A = x_A P^{\text{o}}$$

(e.g., if the total pressure in each of the initial chamber is 1bar, and we mix 20% oxygen and 80% nitrogen – so the nitrogen chamber was 4 times bigger than the oxygen one -- then the partial pressure of oxygen after the mixture would be 0.2*1bar=0.2bar)

So the effect on the oxygen pressure would be that it was reduced by a factor of x_A.

We know that the chemical potential is then

$$\mu_A = \mu_A^{\text{o}} + RT\ \ln\left(\frac{P_A}{P^{\text{o}}}\right)$$

So

$$\mu_A - \mu_A^* = \mu_A - \mu_A^{\text{o}} = RT\ \ln\left(\frac{P_A}{P^{\text{o}}}\right) = RT\ \ln(x_A)$$

Therefore

$$\Delta G_{\text{mix}} = nRT\ (x_A\ \ln(x_A) + x_B\ \ln(x_B)) \quad \text{ideal gases}$$

and since $x_B < 1,\ \ \ln(x_B) < 0$, so

$$\Delta G_{\text{mix}} < 0 \quad \text{for ideal gases.}$$

9.4) Ideal Mixtures

So far the discussion was general. We'll now specifically deal with **ideal gases and solutions. An ideal mixture is one in which the A-A and B-B interactions are essentially the same as the A-B interactions.**

Examples:

- All vapors would be assumed ideal gases (since ideal gases molecules do not interact at all).
  For us, all gases are essentially ideal → so gas mixtures are mostly ideal mixtures.
- Similar molecules, e.g., Benzene and Toluene.
  Note: **Liquids are not individually ideal nor non-ideal. Mixtures of liquids are ideal or non-ideal. The same liquid would behave ideally when mixed with one compound, and non-ideally when mixed with another compound.**
- Later we'll discuss non-ideal mixtures in the limits $n_A \gg n_B$ or $n_A \ll n_B$. But ideal mixtures are easier – since we can treat for them any ratio $\frac{n_A}{n_B}$.

9.5) Raul's law, ideal mixtures, and non-ideal mixtures

The trick to getting information on solutions is to consider a **mixture (a liquid made from A and B) in equilibrium with its vapor, made from A and B.** Let's see what it gets us.

Ideal liquid Mixture: Raul's Law

A formal empirical observation by Raul on the vapor pressure in **an ideal** solution is (see figure):

$$P_A = x_A(l) \cdot P_A^*$$

Note that Raul's law obeys correctly the limits:

$$\text{When } x_A \to 1 \quad \text{then} \quad P_A \to P_A^*$$

$$\text{When } x_A \to 0 \quad \text{then} \quad P_A \to 0$$

Reasons for Raul's law: qualitative

Raul's law says that P_A (the **vapor** pressure) is proportional to the **liquid** mole fraction $x_A(l)$**.**

Think of it like that:

Equilibrium between vapor and liquid means that **the number of molecules leaving the liquid to the gas, equals the number entering the liquid from the gas.**

When $x_A(l)$, the concentration of A, is not 1 (i.e., A is not pure), then fewer A molecules leave the liquid (since there are fewer A molecules per unit area). In ideal mixtures the number leaving turns out to be proportional to $x_A(l)$.

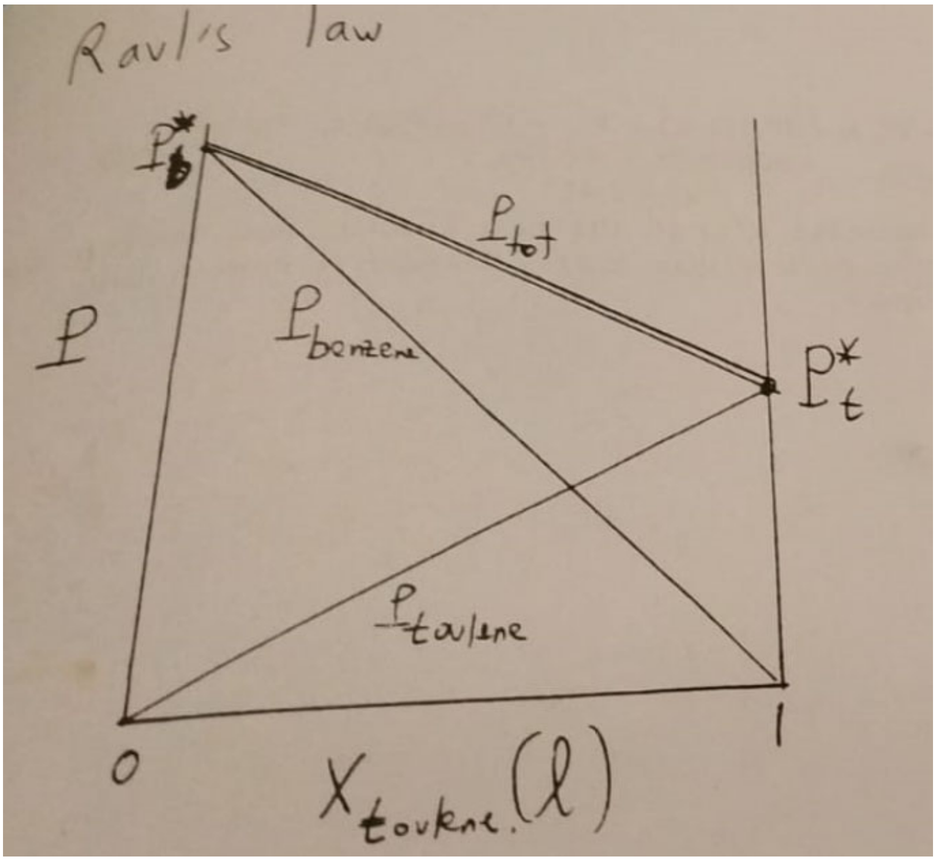
On the other hand the **number entering from the gas to the liquid** is proportional to the **pressure.**

So if $x_A(l)$, is, say, halved; then fewer molecules would leave the liquid, so the gas pressure required for equilibrium would be half as much.

In other words, P_A is proportional to $x_A(l)$, as mentioned.

The first figure below (important figure, we'll use it later) shows a diagram for a benzene-toluene ("b-t") mixture. The two liquid form together an ideal mixture, since the interactions are so similar.

The figure shows the **individual and total vapor** pressure vs. **the concentration of the toluene in the liquid.** The lines are straight, per Raul's law.



Numerical examples:

We'll measure pressure here in units of torr (750.06 Torr = 1bar).
Torr is also known as mmHg (roughly: you need 1torr to raise a liquid column of Hg by one mm in an old mercury thermometer).

(i) At 20 °C, **a liquid mixture of toluene and benzene has (I round the #'s):**

- $n_t(l)$ =10 moles of t =toluene (P_t^* =22 Torr at 20°C) with
- $n_b(l)$ =30 moles of b =benzene (P_b^* =75 Torr at 20°C)

The two compounds (benzene + toluene) are an ideal mixture, as we mentioned.

(i) Question: what's the vapor pressure of the mixture.

Answer: (#'s rounded)

$$x_t(l) = 0.25, \;\; x_b(l) = 0.75$$

$$\boldsymbol{P_{tot}} = P_t + P_b = x_t(l)P_t + x_b(l)P_b = 0.25 * 22 + 0.75 * 75 = 62 \text{ Torr}$$

(ii) Question: If $\boldsymbol{P_{tot} = 65}$Torr, what is $x_t(l)$, and is it the same as $x_t(v)$

Answer:

$$P_{tot} = P_t^* x_t(l) + P_b^* x_b(l) = P_t^* x_t(l) + P_b^*\big(1 - x_t(l)\big)$$

i.e.,

$$P_{tot} = P_b^* + (P_t^* - P_b^*)x_t(l)$$

Let's plug to get

$$65 = 75 + (22 - 75)x_t(l)$$

The solution of which is:

$$\boldsymbol{x_t(l) = 0.19}$$

Next: $x_t(v)$. We can easily determine $x_t(v)$ from what we know about gases. Within the vapor, the molar fraction of toluene in the vapor is the same as the pressure-fraction, i.e., the ratio of the toluene pressure to the total pressure, $x_t(v) = \frac{P_t}{P_{\text{tot}}}$. But

$$P_t = x_t(l)P_t^* = 0.19 * 22 = 4.2$$

so

$$\boldsymbol{x_t(v)} = \frac{\boldsymbol{P_t}}{\boldsymbol{P_{\text{tot}}}} = \frac{4.2}{65} = \boldsymbol{0.064 = 6.4\%}$$

Note that $x_t(v)$ "must" physically be less than $x_t(l)$. Toluene is less volatile than benzene, so it is less present in the vapor.

Next:

Non-ideal mixtures.

Two subparts:

"Solvent" limit

It turns out that even in non-ideal liquid mixture, Raul's law is obeyed for the **solvent**, i.e., when $x_A(l)$ close to 1. (In practice you can safely assume, in most context, that is it obeyed when the concentration of liquid A, $x_A(l)$, is bigger than 90%.). Put differently: **solvents are generally ideal.**

For example, for a non-ideal $A - B$ mixture, if the vapor pressure of pure A is $P_A^* = 0.020$ bar, then at $x_A(l) = 0.95$, the vapor pressure would be about

$$P_A = x_A(l) * P_A^* = 0.95 * 0.020 = 0.019 \text{ bar}$$

Question: in the same (non-ideal) mixture, if $x_A(l) = 0.6$, what will be P_A?
Answer: **we can't know**! $x_A(l) = 0.6$ is not big enough so we can't assume Raul's law.
If it would have been an ideal mixture, P_A would be $0.6 * 0.02 = 0.012$bar, but we are told it is not an ideal mixture.

Heuristically, the reason that Raul's law is valid for solvents is that the effect of the solute on the free energy (and therefore on the chemical potential, which determines the stability of the molecules in the liquid, and therefore the vapor pressure) is in two parts.

- First, **an enthalpy effect:** a small change in the enthalpy since a solvent molecule A interacts differently with B than with another A (for a general non-ideal mixture). But this is not a huge effect, since it only affects the very few solute molecules.
- Second **entropy effect**: Another, subtler but more important effect, is that the **presence of a solute molecule B** increases the entropy of the solvent, thereby making it more stable; and this effect is independent of the interaction of A and B.

> To exemplify the effect on entropy, consider 5 identical molecules A that are in a line, and what happens to the number of "system states" (i.e., how much disorder would be) if we replace one of the A molecules by a B molecule
>
> **Before: one state**. AAAAA

After: 5 possible states: AAAAB, AAABA, AABAA, ABAAA, BAAAA

More states mean more disorder --higher entropy –more stability.

For solvents the second, entropy, effect is the only important one, i.e., all solvents have the same general behavior (i.e., obey Raul's law) if their concentration is sufficiently close to 100% (i.e., say, above 90%).

“Solute” limit

For solutes (i.e., when $x_A \ll 1$) Raul's law is not obeyed when the solutions are not ideal. But we can still get a useful mathematical expression.

Specifically, when $x_A(l) = 0$ we'll have obviously $P_A = 0$ (i.e., pure B, no A in the liquid and therefore nor in the vapor).

So let's define $\boldsymbol{K_A}$ as the **slope of $\boldsymbol{P_A}$ vs. $\boldsymbol{x_A(l)}$ at $\boldsymbol{x_A \simeq 0}$.** (Note that **$\boldsymbol{K_A}$ depends on the identity of the solvent, *B***)

K_A is called Henry's "constant". That's a bad notation, since this "constant" really depends on the identity of both the solute and solvent. So it is not really a "constant", and it depends on "B", the solvent, not just "A". But this is the name that people use.

i.e., for **solutes:**

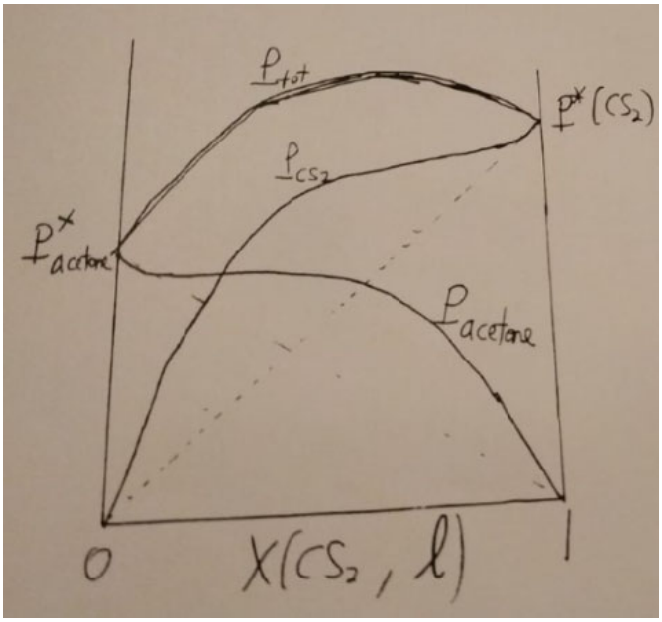
$$\boldsymbol{P_A = K_A \cdot x_A(l) \qquad x_A \ll 1}$$

Note that for ideal solutions, since $P_A = P_A^* \cdot x_A(l)$, then

$$K_A = P_A^* \quad (\text{ideal} - \text{solutions only})$$

Question:

In the figure below of CS_2 – acetone: is K_{CS_2} bigger or smaller than $P^*_{CS_2}$?



Answer:

$K_{\mathrm{CS_2}}$ is the **slope** of $P_{\mathrm{CS_2}}$ for small $x_{\mathrm{CS_2}}(l)$. **(**$P_{\mathrm{CS_2}} = x_{\mathrm{CS_2}}(l)K_{\mathrm{CS_2}}$ at low $x_{\mathrm{CS_2}}$)
$P^*_{\mathrm{CS_2}}$ is the **slope** of $P_{\mathrm{CS_2}}$ for **large** $x_{\mathrm{CS_2}}(l)$ **(**$P_{\mathrm{CS_2}} = x_{\mathrm{CS_2}}(l)P^*_{\mathrm{CS_2}}$ at high $x_{\mathrm{CS_2}}$)

For this mixture, the slope at low $x_{\mathrm{CS_2}}(l)$ is obviously HIGHER than the the slope at high concenrtations of CS_2.

Put differently, the slope of the vapor pressure of CS_2 in this mixture is larger when it is solute than when the same compound is a solvent.

Therefore, $K_{\mathrm{CS_2}} > P^*_{\mathrm{CS_2}}$ (for this CS_2 + acetone mixture).

Physically, $K_{\mathrm{CS_2}} > P^*_{\mathrm{CS_2}}$ means that the **CS_2 molecules interact with acetone less strongly than they would with other CS_2.**

I.e., at low concentrations of CS_2 its vapor pressure is higher than it would have been were they in an ideal mixture. **CS_2 likes to "leave" the liquid when it is a solute in acetone, more than the ideal-mixture** Raul's law would predict.

Of course, if the interactions of CS_2 with the solvent (acetone) were MUCH weaker (less binding, i.e., more "positive" energy) than the CS_2-CS_2 and acetone-acetone interactions, then the two liquids would not have mixed.

That's what happens in oil+water – the two liquids don't mix, since $\Delta H_{\mathrm{mix}} >> 0$, as we mentioned.

And, remember again, when a compound is a solvent, is always behaves ideally.

Ideal vs. non-ideal mixtures: qualitative reasoning

To understand ideal vs. non-ideal mixtures consider two examples.

Water and heavy/semiheavy water (D_2O, HDO) are an ideal mixture.

- Not because they do not interact – they actually interact very strongly (each molecule interacts very strongly with its neighboring molecules, whether they have D or H isotopes).
- But the interactions are the same. (The force that H_2O exerts on an HDO or D_2O molecule is the same as the force that it exerts on another H_2O molecule.)

Ethanol with water is a non-ideal mixture:

- The water molecules attract each other strongly;
- The ethanol molecules attract each other strongly;
- But water and ethanol molecules attract each other **very very strongly.** So the reactions are not the same as between each molecule, and the solution is non-ideal.

When you put ethanol and water together, the ethanol molecules get "between" the water molecules and attract them strongly – the water molecules cluster around the ethanol ions and therefore get close together.

As a heuristic example, consider what would happen if you put a group of timid people in

a party in a big room. They won't get too close to each other.
Now put into the room some small tables with good food and beer – the people will be drawn to the tables, and therefore to each other.

9.6) Conclusions – Chapter 9

In this chapter we studied:

- Partial molar quantities
$$V_A \equiv \frac{\partial V}{\partial n_A} .\quad \text{Often } V_A \neq V_A^*. \quad \text{Generally } V_A \text{ depends on } x_A, x_B, \ldots$$
where V^* indicates the volume of two separate compounds (n_A moles of A, n_B moles of B). And we proved
- $V = n_A V_A + n_B V_B \neq V^*(= n_A V_A^* + n_B V_B^*)$

Analogously

- $G = n_A \mu_A + n_B \mu_B \neq n_A \mu_A^* + n_B \mu_B^*$

In fact, the difference between the post-mixing and pre-mixing quantity is called the Mixing Free energy (or mixing enthalpy, mixing volume, etc.)

$$\boldsymbol{G_{\text{mix}} \equiv G - G^* = n\left(x_A(\mu_A - \mu_A^*) + x_B(\mu_B - \mu_B^*)\right)}$$

- For ideal gases, we proved that

$$G_{\text{mix}}(\text{ideal gases}) = nRT(x_A \ln(x_A) + x_B \ln(x_B)) < 0$$

- **Raul's law: valid** for ideal solutions at any concentration or for solvents in non-ideal solutions (i.e., when $x_A(l)$ is close to 1):
$$P_A = x_A(l) P_A^*$$
Henry's "law" for dilute solutes in non-ideal solution is
$$P_A = x_A(l) K_A$$
where K_A is solute-and-solvent-specific coefficient that simply describes the linear rise of the pressure from 0 when there's no "A".

XII. Multicomponent Phase Equilibrium

The overall question in this chapter is: how do non-reacting substances mix in solutions. Much of the theoretical foundation was laid in Chapter 9, and here we exemplify the theory through a few samples of the rich phenomena governed by thermodynamics.

This chapter as presented here is made of 3 parts (in the book one of these parts is in Chapter 9).

12.1) Phase diagram for 2 components

Here we consider 2 components in 2 phases; and both components can be present in both phases; this part is a continuation of the previous chapter.

Let's start with ideal mixtures (so we can derive quantitative expressions), where the two phases will be liquid and vapor.

We'll see that, for a given temperature, the vapor and liquid would in equilibrium over a **range of pressures.**

We'll also remind ourselves of the dependence of the concentrations on the pressure, $x_{Al}(P)$, $x_{Av}(P)$

We will then derive the lever rule relating the **total number of moles in the vapor and the liquid to the compositions.**

With the lever rule and the compositions-pressure relation we would be able to predict precisely, for any total n_A, n_B, how much of compound A would be in the vapor and how much in the liquid, and the same for B (and this means that we'll also know the concentration of A and B in each of the phases).

Another topic that will emerge from this general discussion is **distillation**, due to the difference in composition between one compound and another.

We'll then move to non-ideal liquids, still fully miscible but with **azeotropes**, i.e., (considering for example a fixed sea-level pressure) mixtures with a boiling temperature which, for some concentrations, is **lower even than that of the more volatile compound** (or **alternately: higher than that of the less volatile one**).

Finally, we'll move to **partially miscible liquids.** Mathematically, the discussion would not be very different: just like the case of a fully miscible liquid 2-component mixture in equilibrium with the associated 2-component vapor; Thus:

- There we also had 2 phases – liquid and vapor-- with fixed compositions in each phase (for a given P and T) but varying amounts of moles in each phase depending on the overall composition;
- Here (in the partially miscible case) we would again see that having 2 coexisting phases implies that their composition is fixed. All this behavior would be related to the phase rule.

Liquid-vapor phase diagram for ideal-solutions

Fix T. Recall that if we only had one compound A, then vapor and liquid could coexist at one (compound-dependent and T-dependent) pressure, i.e., when $P = P_A(T)$.

But for 2 components things will be different.

Definitions

First, recall some straightforward definitions. The total mole fraction of A is

$$x_A = \frac{n_A}{n_{\text{tot}}} = \frac{n_{Al} + n_{Av}}{n_{\text{tot}}}, \qquad n_{\text{tot}} \equiv n_A + n_B$$

The mole fraction of A in the vapor is

$$x_{Av} = \frac{n_{Av}}{n_v}$$

And of course $x_{Av} + x_{Bv} = 1,\ x_{Al} + x_{Bl} = 1,\ x_A + x_B = 1$.

Next:

Liquid-vapor coexistence curve

Recall that if there's equilibrium between liquid and vapor, the total pressure of the vapor would be, by Raul's law,

$$P = P_A + P_B = x_{Al}P_A^* + x_{Bl}P_B^*$$

So, since $x_{Bl} = 1 - x_{Al}$, $P = x_{Al}P_A^* + (1 - x_{Al})P_B^*$, i.e.,

$$P = P_B^* + x_{Al}(P_A^* - P_B^*).$$

We can rearrange to get the concentration of the liquid as a function of pressure

$$x_{Al} = \frac{P - P_B^*}{P_A^* - P_B^*}$$

At the same time, the vapor is still an ideal gas; so for example if the of A concentration in the vapor is 20%A (i.e., $x_{Av} = 0.2$), that means that the pressure of A would be 20% of the total pressure; so in general, $x_{Av} = \frac{P_A}{P}$, which implies

$$x_{Av} = \frac{x_{Al}P_A^*}{P}$$

Thus we can think of the **concentration of A in the liquid and the concentration of A in the vapor as both being functions of the pressure** (given P we determine x_{Al}; and then from P, x_{Al} we determine x_{Av}).

A plot of the two concentrations is given below. (It is clearest if you think of it as an inversion of the axis; the "y" axis is the "independent variable", the pressure, while the two "dependent" variables, x_{Al} and x_{Av}, are both along the "x" axis.)

Now we'll use an example to understand the phase diagram.

Say: A=benzene, B=toluene (bad notation, sorry!)

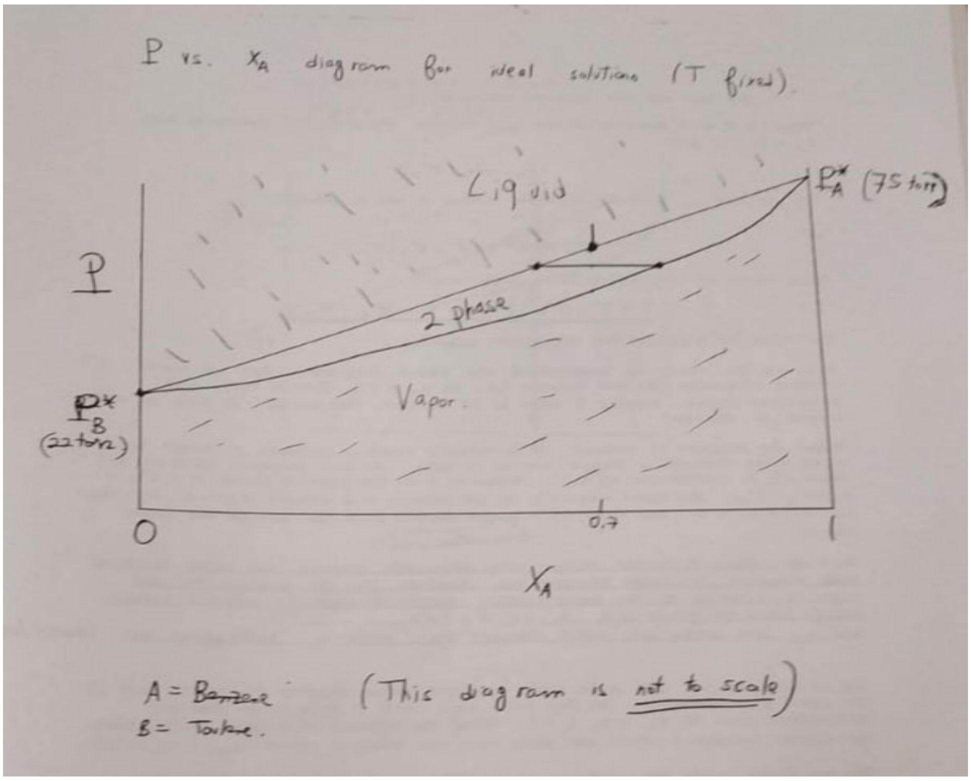
T=20°C, so
$P_A^* = 75$ torr, $P_B^* = 22$ torr (recall that 750 torr $\cong$ P°).

Also: assume $n_A = 7$ torr, $n_B = 3$ torr, so $x_A = 0.7$.

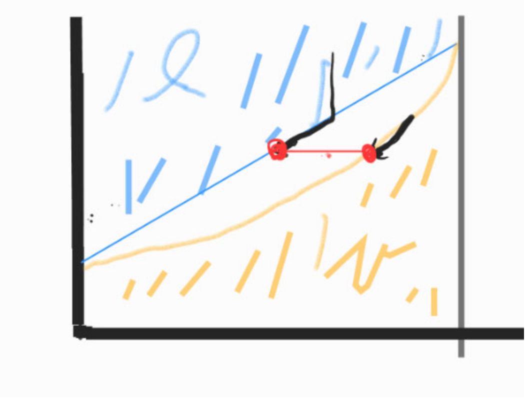
Now let's start at very high pressures, where only a liquid exists. Then lower the pressure (downward arrow in the figure).

When the pressure is reduced, we reach a pressure where some vapor starts forming, a minute amount at first. At that pressure, the liquid solution and vapor coexist, so x_{Al} is related to P by the equations above, $P = P_B^* + x_{Al}(P_A^* - P_B^*)$. But since at that point essentially all the mixute is still a solution (except for a minute amount of vapor), then $x_{Al} = x_A = 0.7$, and therefore at that point:

$$P = 22 + 0.7 * (75 - 22) = 58.9 \simeq 59 \text{ torr.}$$



In more cartoonish form (in the cartoons below the y-axis is always pressure, the x axis $x_A(l), x_A(v)$, where again “A” =benzene (not toluene!))

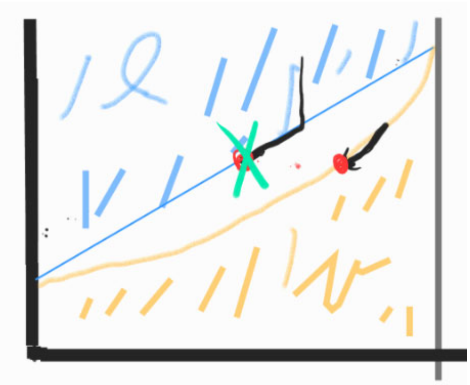


Now **reduce the pressure further. Notice what happens (gliding arrows along the two curves): the vapor becomes more abundant, the liquid less, and the two coexist.**
But at each pressure, the vapor is richer in A then the liquid, as A is the more volatile compound. I.e., <u>as long as both vapor and liquid coexist, x_{Al} will lie along the solid line</u>, while <u>x_{av} will lie along the curved line</u>, and they will fulfill:

$$x_{Al} \leq \quad x_A(= 0.7) \quad \leq x_{Av}$$

All of this goes on, with more vapor produced at the expense of the liquid, until almost all the liquid is consumed. At that point, only vapor is present, so that its composition must be $x_{Av} = x_A = 0.7$.

When the pressure is lowered even further, the mixture will remain a vapor, no liquid present; and since there's only one phase, $x_{Av} = x_A = 0.7$.



Determining P when we know $x_{Av} = 0.7$

The pressure at that point needs to be determined from the equation above,
$x_{Av} = \frac{P_A}{P} = x_{Al}\frac{P_A^*}{P}$.

It is possible to manipulate the expressions in the particular equation so that it reads as an equation for P in terms of x_{Av} only, but that's cumbersome. I personally like the "guessing" approach:

- Guess P
- Determine x_{Al} from P
- Determine x_{Av} from P and x_{Al}. If it is too high (higher than our target result, 0.7 here) reduce P, and vice-versa if it is too low.

For example:

$P = 54$ torr $\rightarrow x_{Al} = \frac{(P-P_B^*)}{P_A^*-P_B^*} = \frac{54-22}{75-22} = 0.615 \rightarrow x_{Av} = \frac{x_{Al}P_A^*}{P} = 0.615 * \frac{75}{54} = 0.85$: too high. Lower:

$P = 50$ torr $\rightarrow x_{Al} = \frac{(P-P_B^*)}{P_A^*-P_B^*} = \frac{50-22}{75-22} = 0.538 \rightarrow x_{Av} = \frac{x_{Al}P_A^*}{P} = 0.538 * \frac{75}{50} = 0.81$: Lower aggressively:

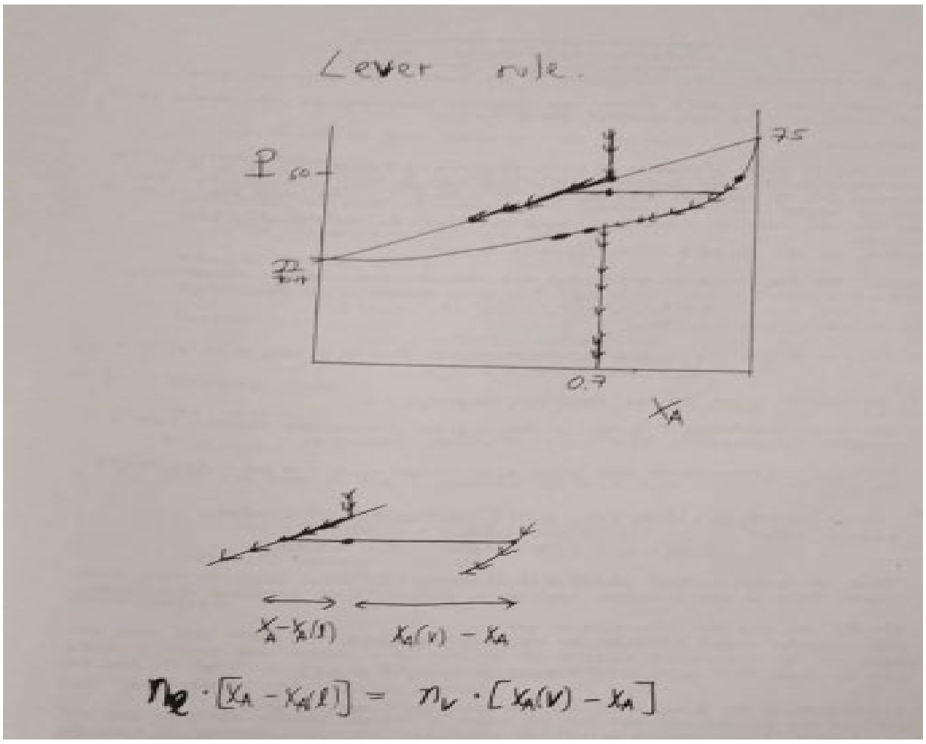
$P = 42$ torr $\rightarrow x_{Al} = \frac{(P-P_B^*)}{P_A^*-P_B^*} = \frac{42-22}{75-22} = 0.384 \rightarrow x_{Av} = \frac{x_{Al}P_A^*}{P} = 0.384 * \frac{75}{42} = 0.686$. Raise a little:

$P = 43$ torr $\rightarrow x_{Al} = \frac{(P-P_B^*)}{P_A^*-P_B^*} = \frac{42.5-22}{75-22} = 0.404 \rightarrow x_{Av} = \frac{x_{Al}P_A^*}{P} = 0.404 * \frac{75}{43} = 0.704$.

And by linear interpolation from the last two values we get $P = 42.7$.

Next we ask: **What are the distributions of vapor vs. liquid in between P=42.7 torr and P=59** (i.e., $n_l,\ n_v$) **when both phases coexist?** For this, we'll need

The lever rule



We'll get n_l, n_v by realizing that there are two ways to determine the total number of moles of A, i.e., n_A.

The first is from the overall concentration:

$$n_A = x_A \, n_{\text{tot}} = x_A \, (n_l + n_v)$$

The second is from the concentration in each phase:

$$n_A = n_{Al} + n_{Av} = x_{Al} n_l + x_{Av} n_v$$

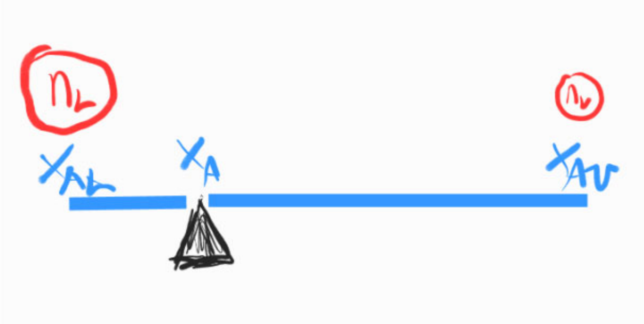
Equate these 2 equations and get

$$x_A \, (n_l + n_v) = x_{Al} n_l + x_{Av} n_v$$

Now move the terms so n_l is on only one side, and n_v on the other side, to yield

$$n_l(x_A - x_{Al}) = n_v(x_{Av} - x_A)$$

This is the lever rule. (It really should be called the **seesaw rule.**) See picture below:



In the picture above, the "weight" n_l times the "lever length" $(x_A - x_{Al})$ on one side should be the equal to the product of the weight and length on the other side. Like a seesaw!

Examples:

Mix 35 moles of benzene ("A) and 15 moles of toluene ("B") so $x_A = 0.7$

We're at 20°C, so $P_A^* = 75\text{ torr}, P_B^* = 22\text{ torr}$.

Question:

Find the total mass of A and B in the vapor and liquid for the following total pressures (all in torr):

(a) 60, (b) 50, (c) 43.8, (d) 30

Answer:

Recall from a few pages ago that we determined that the two-phase region is between 58.9 and 42.7 torr. Thus:

(a): Outside the two-phase region. All liquid, $x_A = x_{Al} = 0.7$. No vapor.

(**d**): Analogous, all vapor, $x_A = x_{Av} = 0.7$. No liquid.

(**b**): More interesting. In the 2-phase coexistence region. Vast majority of mixture is still liquid. Formally, the method is

$$P \to x_A(l), x_A(v) \to \text{Lever rule gives } n_v, n_l \ \to \text{get } n_A(v), n_A(l)$$

We've done the first stage a few pages ago, I reproduce the results (with more digits)

$$P = 50\text{ torr} \ \to \ x_{Al} = \frac{(P - P_B^*)}{P_A^* - P_B^*} = \frac{50 - 22}{75 - 22} = 0.538 \to \ x_{Av} = \frac{x_{Al} P_A^*}{P} = 0.538 * \frac{75}{50} = 0.807$$

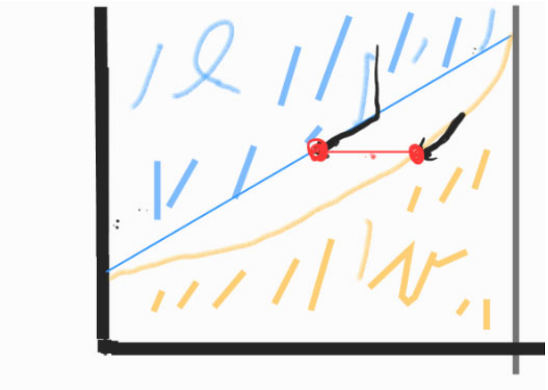
So the lever rule $n_l(x_A - x_{Al}) = n_v(x_{Av} - x_A)$ gives

$$n_l(0.7 - 0.538) = n_v(0.807 - 0.7) \ \to \frac{n_l}{n_v} = \frac{0.807 - 0.7}{0.7 - 0.538} = 0.660$$

Supplemented by $n_l + n_v = 50$ we can solve both equations to give:

$$n_l = 19.9, \ \ n_v = 30.1$$

And therefore, in the liquid there's $n_{Al} = n_l x_{Al} = 19.9 * 0.538 = 10.3$ moles of benzene; and in the vapor there will be $n_{Av} = n_A - n_{Al} = 35 - 10.3 = 24.7$ moles of Benzene.

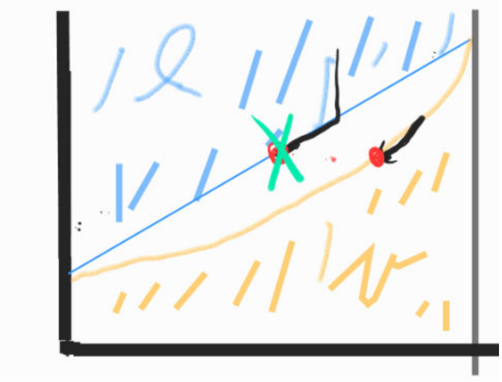


(c) Analogous, this time the vast majority is vapor and only a tiny bit of liquid. Do it yourself similar to (b). (See also the cartoon 2 pages ago).

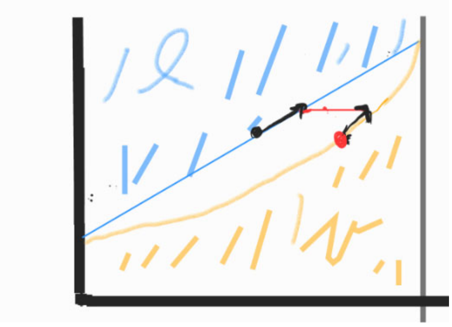
Distillation

We saw that when the pressure is in the range where there's some liquid and some vapor (for $x_A = 0.7$, for example, we saw that this happens for $P = 50$torr) the vapor would be much richer in the more volatile compound (here "A", i.e., benzene).

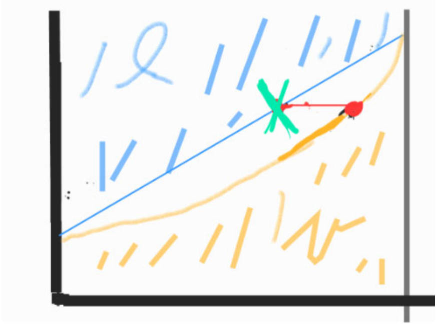
Thus, if we want to distill benzene, for example, we can then **remove the liquid, and** stay only with vapor. This will leave us with a much-more concentrated solution of "A" ($x_A = 0.807$ for this vapor-only part, compared with $x_A = 0.7$ before; with less moles (circa 30 vs. initially 50).



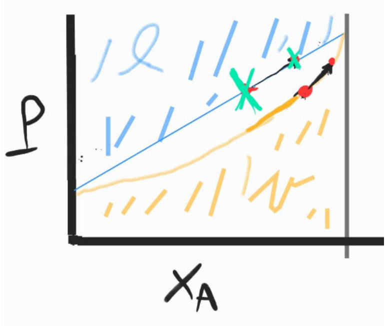
We can then **continue this cycle.** I.e., take the retained $x_A = 0.807$ vapor, and **increase the pressure on it** till about ½ of it liquifies – the remaining vapor (about 15 to 20 moles) would be at an even higher concentration of "A"!



We can continue this stage more and more, and at each time remain with less vapor, but a more concentrated one.



In practice 6-8 steps would be enough for an extremely highly purified "B".

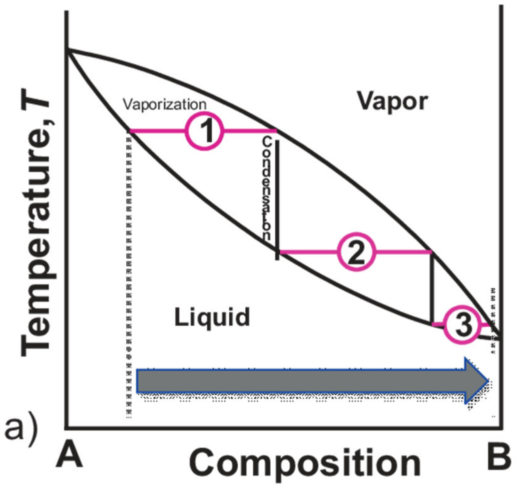


What about the “remainder”, i.e., all the liquid/vapor we removed along the way? The answer is simple: take that and pass it again through the same stages!

In this way, at least for the ideal liquids case, we can, after many steps, separate the compounds to almost-pure “A” and almost pure “B”. See pictures above.

Industrial distillation:

Usually done at fixed P, by changing T. See figure[6]



Non-ideal mixtures, Azeotropes

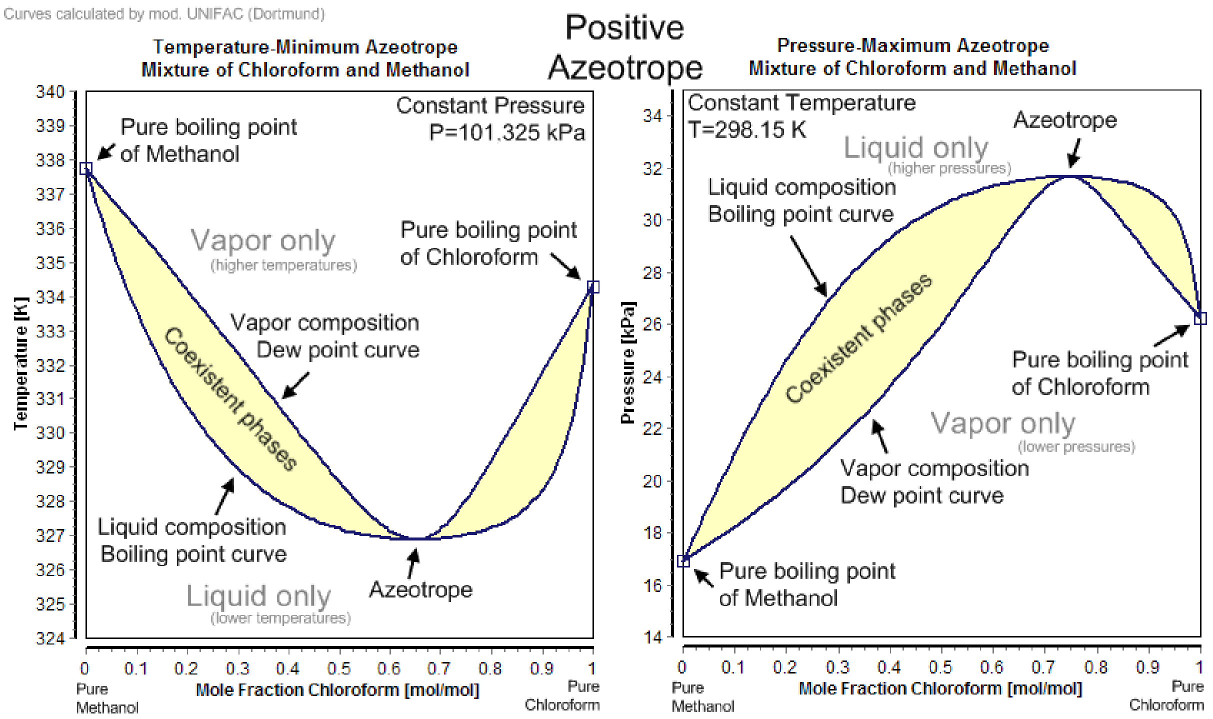
Most mixtures are non-ideal and exhibit interesting behavior. Especially interesting are “azeotropes”, defined when there’s either a minimum and/or a maximum in the vaporization temperature (at a fixed pressure) as a function of concentration, and that minimum is for a non-zero concentration of both compounds, see the figure for example:[7]

The most celebrated example of azeotropes is ethanol + water; at an ethanol molar concentration of 87% (or 96% by mass), the mixture vaporizes at 78.2°C, slightly less than pure ethanol which vaporizes at 78.4 °C.

---

[6] From https://www.tf.uni-kiel.de/matwis/amat/td_kin_ii/kap_1/backbone/r_se13.html

[7] From https://en.wikipedia.org/wiki/Azeotrope

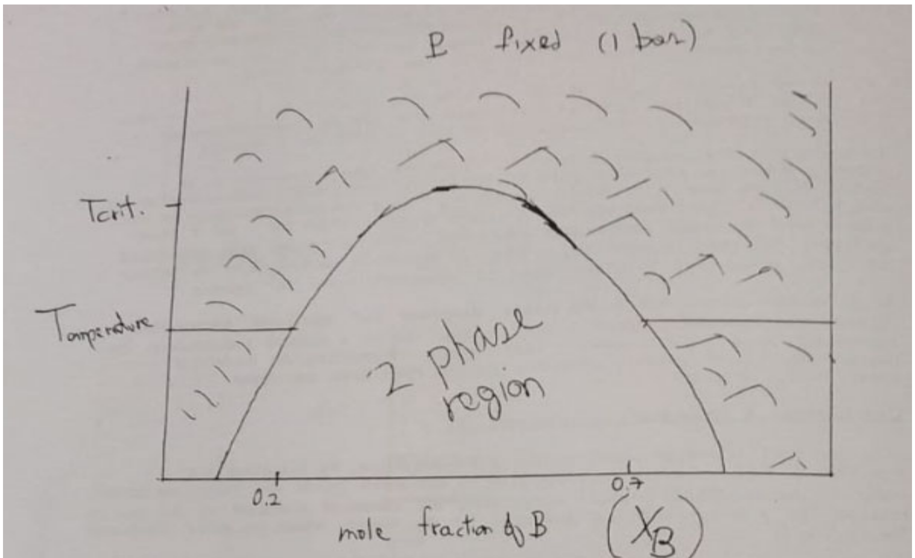


Such behavior (the mixture vaporizes at a lower temperature than either of the pure ingredients) is called a positive azeotrope (I am not sure why the name "positive").

It is physically due to the molecules of the mixture, at that concentration, liking each other a little bit less than the molecules <u>of either</u> of the pure compounds. So they are more volatile and vaporize at a lower temperature.

Note that **tied-knot** behavior. The reason it has to be is outlined in class and the discussion sections; basically, if it wasn't a tied knot, there would have been two vapors coexisting at a different concentration, which is impossible – they would have mixed.

Partially miscible liquids



Typical phase diagram for partially immiscible liquids

Previously, we dealt with fully miscible liquids (even H_2O+ethanol, though non-ideal, were fully miscible).

For partially miscible liquids, the phase behavior is as follows (**see the figure in this and next page)**.

Let's assume for presentation sake that the "A" molecules are red, and that "B" ones are blue. And assume that the color of the mixture just relates "linearly" to the concentration (B-heavy: bluish purple. A-heavy: reddish purple)

When you start with pure A and add B, then initially only one phase is present (A with some B; we'll call this the "Y" phase). The concentration in the Y phase becomes less and less A-heavy as we add "B". I.e., the "Y" phase, which started out red, would turn to be a reddish-purple as we add "B".

This is until you get to a certain composition (say $x_B = 0.2$, and this depends on compounds, temperature and pressure).

At that point suddenly the "Z" phase appears. That phase is, say, 30% A and 70% B, so since B is blue, it is a very bluish-purple

With adding even more "B" **the concentration of the two phases won't change**, so their color would be fixed – the "Z" phase would be 30% "A", and the "Y" phase 80% "A". But the "Y" phase would be consumed and the "Z" phase will grow.

Note how nonintuitive this result!!

Naively one would think (I did when I first studied this) that when we add more B, the Y and Z phases would become diluted with B, making each "bluer". **Wrong!**

What really happens is that when we add B there would be more grams of the Z phase, less grams of the Y phase, but as long as the Y phase is not completely consumed, the compositions of both the Z and Y phase would be fixed.

This is where thermodynamics excels: it does not tell us how the two phases are formed; only how does their composition vary.

The reason for the 2 **fixed-concentration phases** is the phase rule, $f = 2 + c - p$. Here $c = p = 2$, so $f = 2$, and these two variables are the pressure and temperature – which are fixed here. So no other degrees of freedom, i.e., **the concentrations in the two phases $\boldsymbol{Y}, \boldsymbol{Z}$ are set (for this case, $\boldsymbol{c} = \boldsymbol{f} = \mathbf{2}$, by the temperature and pressure, and cannot vary when we change the overall concentration.**

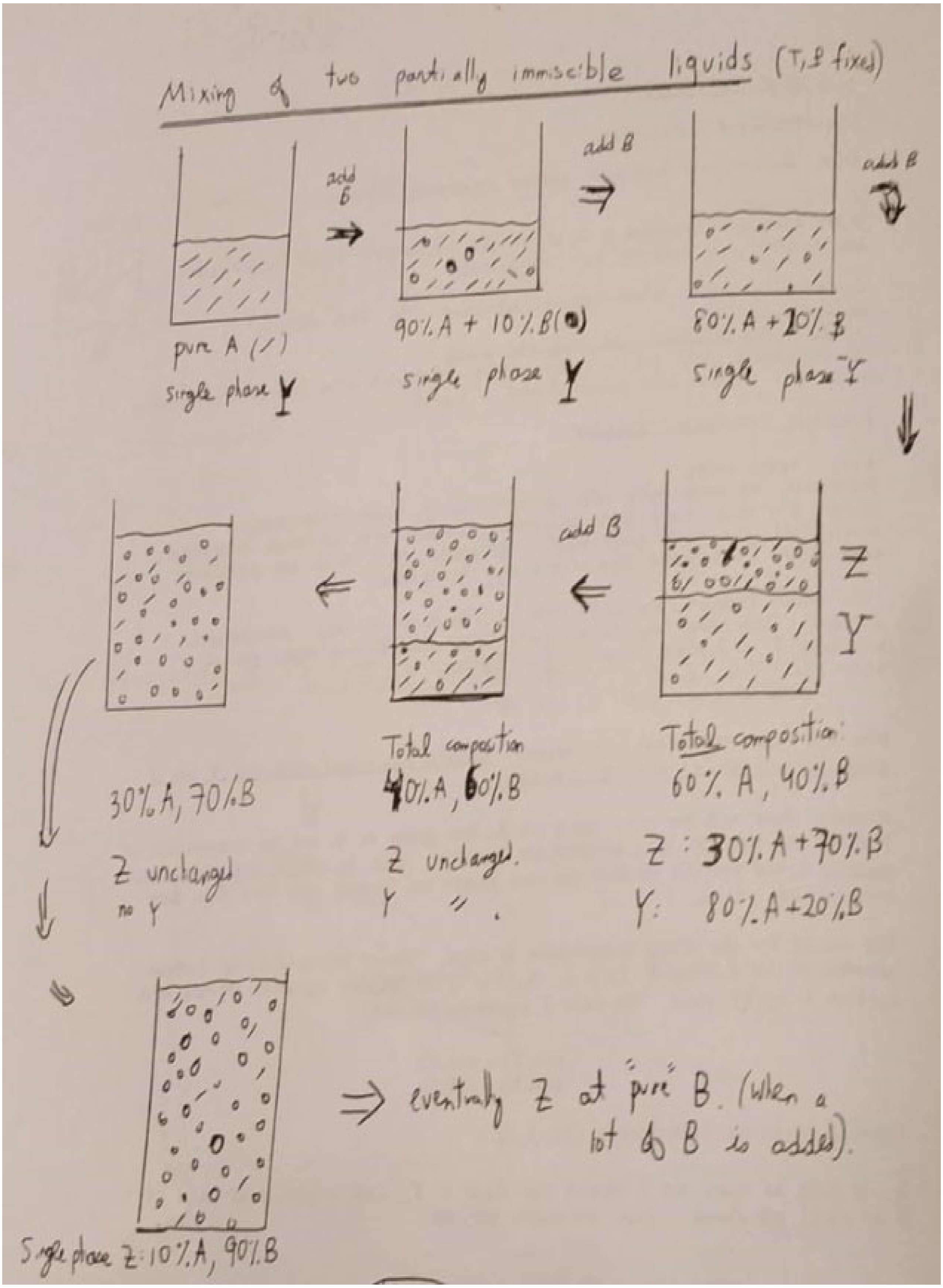
In more specific language, once T and P are fixed the remaining variables are $x_A(Y)$ and $x_A(Z)$ (the concentrations of B is set from that of A – if the concentration of A is 80% that of B would be 20%, etc.), and there are two equations for these variables,

$$\mu_A(Y) = \mu_A(Z), \qquad \mu_B(Y) = \mu_B(Z)$$

So 2 eqs. for two unknowns! I.e., the concentrations are set by these equations.

Next, continue adding "B" until there's so much "B" that all the "Y" phase is consumed, leaving only the "Z" phase; this happens of course at $x_B = 0.7$, i.e., when the overall concentration matches that of the "Z" phase.

When we add even more "B" the solution would turn bluer and bluer, i.e., all the solution would be at the Z phase and the concentration of "B" would rise (to 90%B, 95%B and eventually to almost 100%B).



Mixing of two partially immiscible liquids (T, P fixed)

pure A (/)
single phase Y

add B ⇒

90% A + 10% B (o)
single phase Y

add B ⇒

80% A + 20% B
single phase Y

add B ⇓

Total composition:
60% A, 40% B

Z : 30% A + 70% B
Y: 80% A + 20% B

add B ⇐

Total composition
40% A, 60% B

Z unchanged.
Y 〃 .

⇐

30% A, 70% B

Z unchanged
no Y

⇓

Single phase Z: 10% A, 90% B

⇒ eventually Z at "pure" B. (When a lot of B is added).

12.2) Chemical potential in liquid mixtures.

This part is from Chapter 9/10, but i moved it here to have continuity of subjects.

It is interesting that from the rules on vapor pressure, we can get the chemical potential μ_A of a liquid comound in a mixture, even when the total pressure is high enough that there's only a liquid, i.e., no vapor!

The trick is to recognize that the chemical potential of the liquid is nothing more than **the chemical potential of the vapor when the vapor is in equilibrium with the liquid.**

For example, say $T = 20$°C. We wrote that the vapor pressure of pure benzene is then 75 Torr = 0.1bar.

That means that the **chemical potential of pure liquid benzene** (at essentially any pressure) is **the chemical potential of benzene vapor at P_b^* =75Torr.** This chemical potential is denoted as $\mu_b^*(l)$ ("*" for pure). I.e., (now benzene is again "b")

$$\mu_b^*(l) = \mu_b(v, P_b^*)$$

Similarly, the **chemical potential of benzene in a mixture, denoted as $\mu_b\ (l)$, will be that of benzene vapor at P_b**

$$\mu_b(l) = \mu_b(v, P_b)$$

But we know the relation between the RHS of the two equations, since we know how the chemical potential of a vapor changes with pressure!

$$\mu_b(v, P_b) = \mu_b(v, P_b^*) + RT \ln\left(\frac{P_b}{P_b^*}\right)$$

Thus generally,

$$\mu_b(l) = \mu_b^*(l) + RT \ln\left(\frac{P_b}{P_b^*}\right) \qquad \textbf{any mixture}$$

This beautiful relation is valid of course for any compound, not just benzene. Note that while we need to know $\frac{P_b}{P_b^*}$, the relation **is valid at any pressure** (since the liquid chemical potential is essentially pressure-independent)

The chemical potential of ideal mixtures (and solvents):

Since Raul's law $P_A = x_A(l)P_A^*$ is valid in ideal mixtures and also for solvents, we can plug it into the last equation to get:

$$\mu_A(l) = \mu_A^* + RT \ln\big(x_A(l)\big) \qquad \text{ideal mixtures and / or solvents}$$

You see that the **chemical potential** in ideal mixtures and solvents is **lower than for a pure compound,** signifying **higher stability**

The chemical potential of solutes:

For solutes we will plug in Henry's law, $P_A = x_A(l)K_A$, to get:

$$\mu_A(l) = \mu_A^* + RT \ln\left(\frac{K_A}{P_A^*} x_A(l)\right) \qquad \text{for solutes,} \qquad x_A \ll 1$$

We now simplify by noting that the logarithm breaks to two parts

$$\ln\left(\frac{K_A}{P_A^*}x_A(l)\right) = \ln\left(\frac{K_A}{P_A^*}\right) + \ln\left(x_A(l)\right)$$

So we can write

$$\mu_A(l) = \mu_{A,\text{solute}}^{\text{reference}} + RT\ln\left(x_A(l)\right) \quad \text{for solutes,} \qquad x_A \ll 1$$

where we **defined the standard ("reference") state of the dilute solution to have a chemical potential:**

$$\mu_{A,\text{solute}}^{\text{reference}} = \mu_A^* + RT\ln\left(\frac{K_A}{P_A^*}\right)$$

Note that this reference **does not correspond to any real concentration.** Instead, think of it like this: the reference is **defined** so when the concentration of A, is say, 1 per million ($x_A = 10^{-6}$) then the chemical potential is

$$\mu_A(x_A = 10^{-6}) = \mu_{A,\text{solute}}^{\text{reference}} + RT\ln(10^{-6})$$

I.e., we can **measure** the chemical potential at this tiny concentration ($\mu_A(x_A = 10^{-6})$ then we can **define**

$$\mu_{A,\text{solute}}^{\text{reference}} = \mu_A(x_A = 10^{-6}) - RT\ln(10^{-6}) = \ \mu_A(x_A = 10^{-6}) + 13.81 * RT$$

Think of the reference chemical potential for non-ideal solutes as what WOULD have been the chemical potential if we could have continued Henry's law up to a concentration of 100%.

> **Important:** for solutes in water: $x_A(l) = \frac{n_A}{n_A + n_{\text{water}}} \cong \frac{n_A}{n_{\text{water}}}$. In practice most chemists use the molar density of the solute $[A] = \frac{n_A}{V}$, and in water solution you know how to transform from one to other.
>
> So for most chemist, the reference pressure and concentration of solutes refer, in actual experiment, usually not to a molar concentration of 100% but to a molar density, $[A] = \frac{n_A}{V}$ of $1\frac{\text{mol}}{\text{L}}$.
>
> That means the expressions and definitions in some text books and in the literature are slightly different than mine.

Activity coefficients.

Remember that when we derived the rate law ($K = e^{-\Delta G^o/RT}$) we defined K to be the appropriate product of powers of activities, and we defined the activity to be

$$\mu_A(l) = \mu_A^{\text{reference}} + RT\ln a_A$$

Looking at the definitions above, we find that for solutions we can write:

$$a_A(\text{in solution}) = x_A(l) \qquad \textbf{ideal}\text{ solutions, }\textbf{or}\text{ any }\textbf{solvent}\text{, }\textbf{or}\text{ any }\textbf{dilute}-\textbf{solute}.$$

To account for deviations from these three limits, yet another coefficient is introduced, **the activity coefficient, γ_A, which is 1 for ideal solutions, for solvents, or for an extremely dilute solute.** Then

$$a_A(\text{in solution}) = \gamma_A\, x_A(l)$$

Any deviation from these limits implies that γ_A will not be exactly 1.

Note: In polar solutions, and especially for batteries, **the values of γ_A could be significantly different than 1** due to the strong long-range Coulomb interactions (which implies that, for example, solute molecules see each other even when there are very few of those).

12.3) Overview of colligative properties part

The last, easier, part deals with **colligative properties** (the effects of adding a little "salt:, i.e., a non-volatile solid or liquid, to a solvent), when the **solute is not present in one or more of the phases of the solvent.**

Colligative properties are ones which depend on the number of solute particles present, not their identity, and the concept is relevant for **dilute solutions.**

In this part (only) **A denotes the solvent, B the solute.**

Usually, the solvent will be water, and by "salt" solute we'll refer to any substances that don't mix into ice and do not vaporize, i.e., are only present in the liquid aqueous solution.

Then, due to the presence of the solute molecule, the liquid solvent is stabilized, and therefore the **boiling point increases, and the freezing point decreases**.

Basically: salty water boils at >100°C and freezes at <0°C.

A similar-in-spirit phenomena is osmotic pressure, where a solute-solvent mixture in again in equilibrium with a phase in which the solute is missing. But this time the 2nd phase is a solvent separated by a membrane, and the effect of the contact is to **increase the pressure in the solvent-solute mixture**.

The one key feature that enables an analytic treatment of boiling point elevation and freezing point depression is that they are governed by **equilibrium conditions for the solvent, and every solvent (not solute!!) is almost ideal** – i.e., obeys Raul's law.

Colligative properties: Freezing point depression and boiling point elevation

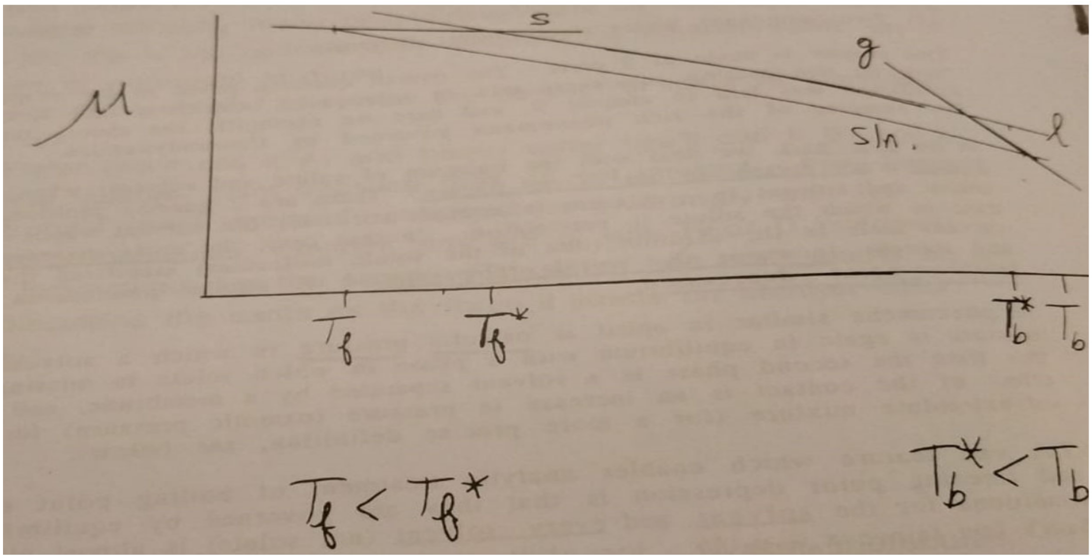
Assume the solvent is water, and the **solute (B)** is involatile, and can't penetrate to ice. (Example of such a solute: NaCl, or sugar). It only mixes with the liquid water.

The **chemical potential of the liquid water is then reduced by the presence of the solute – the extra disorder raises that water entropy,** so the liquid water becomes more stable, while the chemical potential of the ice and vapor forms don't change.

This causes (see figure):

$$T_f < T_f^* \quad \text{freezing point depression}$$

$$T_b^* < T_b \quad \text{boiling point elevation}$$



Freezing point depression: Quantitative

Consider solid (ice) vs. liquid water (both at 1bar). Water is the solvent, so it will be designated as A. All the discussion will be for 1 bar.

When there's a solvent, B, the chemical potential of the liquid is lowered (see figure) so the equilibrium freezing temperature, T_f will now be when the new chemical potential of the liquid matches that of the solid

$$\mu_A^*(s,T_f) = \mu_A(l,T_f)$$

Note that since the ice has no solute, it remains pure, so we keep the "*" in it.

We learned also that the liquid chemical potential for solvents

$$\mu_A(l,T_f) = \mu_A^*(l,T_f) + RT_f \ln x_A$$

Plugging in the last eq. to the one above gives

$$\mu_A^*(s,T_f) = \mu_A^*(l,T_f) + RT_f \ln x_A$$

which we can rearrange to give

$$RT_f \ln x_A = -\left(\mu_A^*(l,T_f) - \mu_A^*(s,T_f)\right) = \Delta G(T_f)$$

where we know that the chemical potential of pure compounds equals their molar Gibbs free energy (relating to A), so their difference is the "fusion" (or "melting") free energy, which I denote by $\Delta G(T)$ (avoiding further labels and subscripts).

A simple way to get the freezing temperature from this relation is to note that **at T_f^*, the freezing free energy difference (relating to the pure water case) <u>vanishes!</u>** $\Delta G(T_f^*) = 0$.

Therefore, at other temperatures, we can approximate

$$-RT_f \ln x_A = \Delta G(T_f) = \Delta G(T_f^*) + (T_f - T_f^*) \cdot \frac{d(\Delta G)}{dT} = 0 - \Delta S \cdot (T_f - T_f^*)$$

Note: we used the relation we learned in the 1st, math chapter:

$$f(x) = f(x^*) + (x - x^*) \cdot \frac{df}{dx}$$

Now

$$\Delta S = \frac{\Delta H}{T_f^*}$$

As we once derived.

> This is because the Gibbs free energy vanishes at the pure-compound melting temperature $0 = \Delta G(T_f^*) = \Delta S - T_f^* \Delta H$

So plugging to the Green equation above gives

$$RT_f \ln x_A = \frac{\Delta H}{T_f^*} \cdot \boldsymbol{(T_f - T_f^*)}$$

The difference, $T_f - T_f^*$, is called the **freezing point depression.**

To further simplify we note that $x_A + x_B$ (the mole fractions of A and B add up to 1), so

$$\boldsymbol{\ln x_A = \ln(1 - x_B) \simeq -x_B}$$

where the 2nd equality is a mathematical approximation (i.e., a Taylor expansion) valid for small x_B.

> Example: $x_A = 0.95, x_B = 0.05;$
>
> $\ln x_A = \ln 0.95 = -0.05129,$
>
> i.e., $\ln x_A$ is very close to $-0.05 = -x_B$ as predicted.

So:

$$T_f - T_f^* = \frac{R}{\Delta H} T_f T_f^* \ln x_A \simeq -\frac{R}{\Delta H} T_f T_f^* x_B$$

Finally, since in absolute magnitude the freezing temperature with and without salt are not that different percentage wise (for water one is 273K, the other may be at most 18K lower, i.e., 255K, i.e., at most 6% lower), then the product $T_f T_f^* \sim (T_f^*)^2$ we get

$$T_f - T_f^* \cong -\frac{R}{\Delta H} T_f^2 \, x_B$$

Thus, as long as the solute concentration is not too high (say <10%) then **the freezing point depression is proportional to the mole concentration of the solute, $\boldsymbol{x_B}$, and is independent of the nature of B (as long as it does not incorporate to the solid).**

> **Example**: **find the freezing temperature of an aqueous solution with $x_B = 5\%$.**
>
> **Answer:** Recall that the melting free energy is $\Delta H_{\text{fusion}} = 6 \frac{\text{kJ}}{\text{mol}}$.
>
> Thus:
>
> $$T_f - T_f^* = -\frac{8.3 \frac{\text{J}}{\text{K mol}}}{6000 \frac{\text{J}}{\text{mol}}} \cdot (273\text{K})^2 \cdot 0.05 \simeq -5\text{K}$$
>
> i.e., for such water the freezing point will be -5°C.

Another example:

Say that the solute was **NaCl**, and we pour in about 16% NaCl by weight of water. How will the result above change.

Answer: the molar concertation of NaCl will be about 5%

$$x_{\mathrm{NaCl}} = \frac{M_{\mathrm{H_2O}}}{M_{\mathrm{NaCl}}} * 0.16 = \frac{18}{58.4} * 0.16 \sim 0.05$$

However, in water NaCl breaks to $\mathrm{Na}^+, \mathrm{Cl}^-$, so the amount of solute moles doubles; i.e.,

$$\boldsymbol{x_B = x_{N_a^+} + x_{Cl^-} = 0.05 + 0.05 = 0.1}$$

And therefore, since x_B doubles compared with the previous example, the freezing point depression doubles, i.e.,

$$T_f - T_f^* = -10\mathrm{K} \rightarrow \;\; T_f = -10℃.$$

Boiling point elevation

Similar – see figure earlier, in the opposite direction, since when we add a solute the liquid is more stable, it will vaporize a little later.

Since $\Delta H_{\mathrm{vap}} \gg \Delta H_{\mathrm{fus}}$, and since the change in phase-transition temperature is proportional to $\frac{1}{\Delta H}$, it follows that boiling point elevation will be much smaller than the freezing point depression, but it can reach a few degrees for water with lots of solvent.

Colligative properties: Osmotic pressure

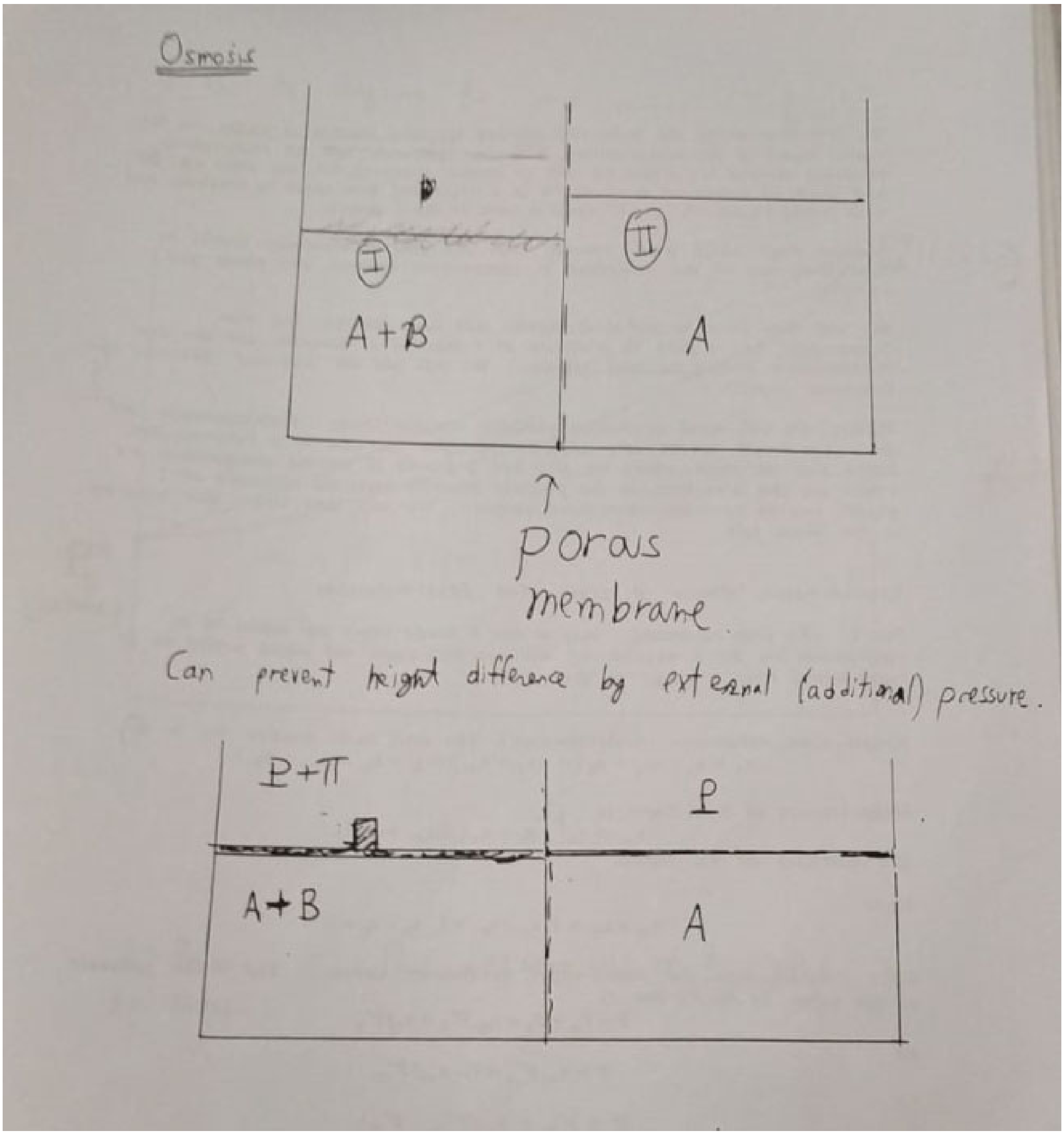
Let's look at the figure below. We have liquid in a container divided to two parts, labeled I and II, and separated by a membrane which only allows water to go through, not solutes.

Part I has water (solvent, "A") and a solute ("B"), while Part II has only water.

Because the membrane allows water to go through, it will flow to the region where it has the lowest chemical potential. But we know that the chemical potential of water when it is a solvent is less than that of pure water, so that means that water will flow from II to I.

The flow is terminated once the pressure in Part II will be high enough due to the extra pileup of liquid there (this causes an extra pressure, labeled Π). (Alternately, we can just impose a higher pressure on the water in Part II, as in the lower part of the figure).

The reason that the flow stops is that the chemical potential of water does change a little bit with pressure. This is an effect we usually ignored for liquids and solids but it is crucial here.



Can prevent height difference by external (additional) pressure.

Note: in practice we often will use the same height, but push the water on part II with that extra pressure, Π, see the figure.

Let's compare a point at the top of the water in region I. (See lower figure)

Once equilibrium is established then since the chemical potential at part II will be that of pure water, at atmospheric pressure, the chemical potential will be $\mu_A^*(P^o)$

Now label the extra pressure on the left region by Π. Then the chemical potential of the water solvent at that point (**which has to equal the chemical potential on the right)** will be

$$\mu_A(P^0+\Pi, x_A) = \mu_A^*(P^o+\Pi) + RT\ln x_A = \boldsymbol{\mu_A^*(P^0) + V_m\Pi + RT\ln x_A}$$

Reminder: the last equality follows since we learned earlier that upon a pressure change $d\mu = V_m dP$, so

$$\mu_A^*(P^0+\Pi) = \mu_A^*(P^0) + \int_{P^0}^{P^0+\Pi} V_m\, dP \simeq \mu_A^*(P^0) + V_m\Pi$$

The equality of the last two blue expressions becomes

$$\mu_A^*(P^o) = \mu_A^*(P^0) + V_m\Pi + RT\ln x_A$$

i.e.,

$$0 = V_m\Pi + RT\ln x_A$$

Since we learned that $\ln x_A = \ln(1 - x_B) \simeq -x_B$, we get

$$V_m\Pi = x_B RT$$

(also, $V_m = 18\frac{\text{cm}^3}{\text{mol}}$ is the molar volume of the solvent, water).

By measuring the extra pressure we can therefore find x_B, and therefore the number of moles of B. For a given, known solute mass we can therefore find the molar mass (mass per moles) of the solute. This is the basis of **osmometry,** which is used to find the molar mass of macromolecules.

> Incidentally, the ΠV_m term measures how much **work** a cell must do to transport minerals across a membrane.
>
> And note that this last yellow equation looks **so much like the ideal gas equation of state.** This is the only time we get an ideal-gas-looking equation for something involving liquids, even though of course there are no gases here.

Osmometry

The equation above, $\Pi V_m = x_B RT$, is the basis of osmometry, which is used to find the molar mass of macromolecules (and this could be important for identifying them).

Since V_m refers to "A" i.e., water (so it is simply 18cm^3/mol), then by measuring Π and T accurately we can extract x_B, the molar concentration of the solute macromolecule.

Therefore, if we pre-measure the absolute mass of the sample of macromolecule that we disperse in water, we can determine from that and from its measured molar concentration, x_B, the mass per mole, which **will help identify what the solute is!**

Of course one has to be careful; for example, if the macromolecule has for some reason attached salts that dissolve in water (or is acidic so it releases a few hydrogens), then x_B would be larger (possibly much larger) than the molar concentration of the macromolecules, since for every macromolecule there will be several salt ions dissociated.

12.4) Conclusions: Chapter 12

In this chapter we studied:

In the 1st part (continuing Chapter 9):

- For two ideal liquids (A and B), mixed, the key was that when there are two phases (liquid and vapor) the concentration would be different in each, $x_A(l) \neq x_A(v)$. The important equations were Raul's law, $P_A = x_A(l)P_A^*$ that gave
$$P = P_B^* + x_A(l)(P_A^* - P_B^*)$$
and
$$x_{Av} = \frac{P_A}{P} = \frac{x_A(l)P_A^*}{P}$$
combined with the:

- Lever-rule (for two species in two phases)

  $$n_l(x_A - x_{Al}) = n_v(x_{Av} - x_A)$$

  We saw how this leads to quantitative description of the equilibrium concentrations and mole-numbers in the two phases

  Further, the lever rule is valid always, not just for ideal mixtures, and we can use it, e.g., to analyze partially-miscible liquids.

- We also learned distillation, azeotropes (and tied-knots), and fixed-composition phases for two partially miscible liquids.

In the 2nd part (from Chapter 9):

- **Chemical potential of mixtures:** using the trick of considering a liquid-vapor equilibrium to find the chemical potential of the liquid, we found that in general

  $$\mu_A(l) = \mu_A^* + RT\ln\left(\frac{P_A}{P_A^*}\right) \quad \boldsymbol{generally}$$

  And this expression was further simplified for ideal mixtures and/or solvents, and for solutes.

- **Activities:** we defined the reference state for solutes, and managed to relate the activity that appears in the rate law to the concentration for solutes, ideal solutions, and solvents: $a_A = \gamma_A x_A(l)$.

In the 3rd part: We learned about

- Freezing point depression, recalling that for $P = 1\text{bar}$ and $T = T_f^*$ (the no-salt pure freezing temperature) the chemical potential of the **pure** liquid and vapor are equal, while once we add salt, at the modified (lower) freezing temperature, the chemical potential of the gas is balanced by a lower chemical potential for the liquid, which is more disordered. With a few lines of math we got

  $$\text{freezing} - \text{temperature change} = dT_f = -x_B R\frac{\left(T_f^*\right)^2}{\Delta H}$$

  which indicated that when the heat-of-phase-change is small, the temperature change is big (and that's why the freezing-temperature change is much larger than the boiling one)
- We applied a similar methodology to obtain the equations for osmotic pressure:

  $$\mu_A^*(P) = \mu_A(P + \Pi, x_A) = \mu_A^*(P) + \Pi V_m - RTx_B \quad \rightarrow \quad \Pi V_m = RTx_B$$

That's it for Thermodynamics!