20B notes: Prof. Daniel Neuhauser

Partially based on notes by Prof. Peter Felker.

Parts written by Christopher Arntsen and Arunima Coomar.

IMPORTANT: ABOUT 20% of these notes are "INSERTS", derivations which will not be covered in class but you'll be <u>expected to study and know everything in the notes, including the inserts, for the exam.</u>

Course overview:

This is a course about how molecules behave in aggregate – interact, form solutions and phases, and react with useful results (heat and electricity). Along the way we'll learn a lot of chemistry and physics, and at times gloss over some proofs, leaving the details to Chem. 110A (thermodynamics)

<u>Brief outline:</u>

1. Gases
2. Interacting systems (liquids, solids, phases)
3. Phases
4. Solutions
5. Thermodynamics: The 1st law
6. Thermodynamics: 2nd law: disorder increases in world.
7. Thermodynamics: Free energy – minimum in reactions.
8. From free energy to mass reaction law, chemical equilibrium
9. Mass reaction law and LeChatelier's principle
10. Acids and bases; mass reaction law in acids and bases; titrations.
11. Electrochemistry
12. Kinetics
13. (Time permitting:) Raul's law, physical properties of solutions, colligative properties.

Part 1: Units and Ideal-Gases (Gas-law, Kinetics):

- Units, Avogadro's number.
- PV=nRT – experiments, temperature scale.
- PV=nRT – theoretical proof (kinetic).
- Maxwell's velocity distribution
- Boltzmann factor – application to vibrations.

PRELUDE (NOT COVERED IN CLASS): Review from 20A

Units, Avogadro's numbers and moles

in practice it is difficult to deal with big # of molecules, so we measure it in terms' of moles. A "mol" of things means it contains

Avogadro's' #: $N_{Avogadro} = 6.02*10^{23}$

[We call $N_{Avogadro}$ interchangeably N_A]

(Note that the concept of "mol" is analogous to "dozen"; dozen molecules are 12 molecules, and a mole of molecules is $6.02*10^{23}$ molecules).

N_A was adjusted to be almost exactly the number of hydrogen atoms in one gram of hydrogen atoms. However, we have to be careful when we say that, since hydrogen is made of separate individual H atoms only at very high temperatures (above, say, 2000-3000 degrees).
At room temperature, hydrogen is a diatomic molecule H_2; each H_2 molecule weighs twice as much as one individual hydrogen atom, so at room temperature a mole of hydrogen molecules (H_2) will weigh <u>two</u> grams.
(A dozen hydrogen molecules weigh twice as much as a dozen hydrogen atoms, so a mole of hydrogen molecules weighs twice as much as a mole of hydrogen atoms).

The mass of a hydrogen atom is almost exactly

Mass(H atom)~ 1gram/ N_A = 1gram/ $(6.02*10^{23})$ = $1.66*10^{-24}$ gram

Example: a mole of H_2O will weigh about 18gram; proof:

Mass(O atom) ~ 16 Mass(H atom)
[ignoring isotopes, and other even smaller effects]

Mass(H_2 molecule) = 2 Mass(H atom)

So

Mass(H_2O molecule) = 18 Mass(H atoms)

So

Mass(mole H_2O molecules) = 18 Mass (mole H atoms)= 18g

We therefore say

Molecular mass(H_2O) = 18gram/mole

(Exercise – give the mass in gram of a <u>single</u> H_2O molecule based on this!)

A reminder from 20A: Chemists like to change things, so they decided that the mass of hydrogen atom will not be used as the basic definition, but rather they say that:

1 Atomic Mass Unit (AMU) = 1/12 * mass of the ^{12}C isotope

but those are almost the same, since

Mass(H atom) = 1.00794 * Mass (^{12}C)/12 = 1.00794 AMU

Energy and Units

<u>Reminder, scientists found that in nature energy (labeled by "E" or at times by "U") is conserved.</u>

Energy of atoms is made of two parts. The first is the kinetic energy (K.E.), relating to how fast each atom moves (what's its speed, v) and what's its mass (m),

K.E.(one atom)= $mv^2/2$

(I won't prove this equation; you learned it or will learn in the physics series).

A side note on energy units.

Note: energy = (mass)* (speed)^2 = mass *distance^2 / time^2
so energy is measured in units of (mass* distance^2 / time^2)

Energy units reminder: two sets (one called CGS and the other MKS) are commonly used; MKS is more prevalent. The energy units get special name in each unit system:

1 erg = 1 g cm^2 / sec^2 (CGS units)

1 J = 1kg m^2 / sec (MKS units)

End of side note

Say that we have "N" atoms (N will be of course N_{Avog} if we have a mole of atoms, but we take the general case). Let's consider the "j'th atom, i.e., we consider either the 1st atom (in which case j=1), or the 2nd (then j=2), or the 3rd, etc.

The K.E. of the "j'th atom will be therefore

K.E.(jth atom)= $m_j v_j^2/2$

So the total kinetic energy will be the sum over all "j" atoms where j will range from "1" (the first atom) to "N" (the Nth atom) will be:

Kinetic energy for N atom: K.E. = $\frac{1}{2} \sum_{j=1,\ldots,N} m_j v_j^2$

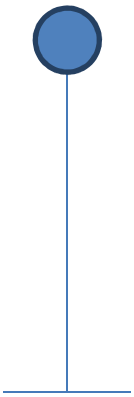
(The strange symbol, Σ , means "sum", it is the capitalized form of the Greek letter sigma; we'll encounter more Greek letters below).

The total energy, E, has, in addition to the kinetic energy, a 2nd part called potential energy, defined as:

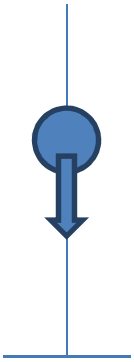
Potential energy: energy that can turn to K.E.

E.g., when we raise an iron bar up, we increase its potential energy; as we let it go, it will fall, and while it falls it acquires kinetic energy and its potential energy will decrease, its total energy will be conserved (will actually slightly decrease, due to friction, i.e., transfer of energy from the iron bar to the air molecules).

Example for Potential energy and Kinetic Energy—a mass falling;



K.E.=0
Pot.E.=10 J
Total E=10J



K.E.=3J
Pot.E.=7 J
Total E=10J

Densities

There are several types of densities we will deal with. Densities in general are defined as something/volume.

The most common type of densities are mass-density and molar density.

Mass density is defined as :

Mass density = Mass/Volume, and has units of g/cm^3 or g/L or kg/L.

Molar density is:

Molar density = # moles/Volume = n/V ;
So for example the molar density of water =1mol/(18 cm^3)

Pressure and Units

From now on we'll use MKS units.

To remind you: from above, energy is in units of Joule (labeled henceforth as J), and Energy is Mass*velocity^2, i.e.,

$J = kg * m^2/s^2$

But

F=Force = Energy/distance→

So

F will be measured by = $J/m = (kg* m^2/ s^2)/m = kg* m/ s^2$

This force unit, J/m, has been given a special name, Newton, labeled as N
(don't confuse this "N" with "N" the number of particles from above!)

Newton = J/m

END OF PRELUDE ON UNITS

Next: pressure (to be covered in class):

P=Pressure = Force/Area , and labeling the force as "F" and the area as "A",

$$P = \frac{F}{A}$$

P is measured in its own unit in MKS, which has been given a special name:

$$\text{Pascal} = \frac{\text{Newton}}{m^2}$$

Multiply by m (meter) both numerator and denom.:

$$\text{Pascal} = \frac{\text{Newton} * m}{m^3} = \frac{J}{m^3}$$

(i.e., PRESSURE = ENERGY/VOLUME!)

However, 1 Newton is really a weak force in daily life (it is about the force exerted by a quarter-pound object – e.g., a small pear – on your hand when you hold it so it does not fall) , and a meter squared is a large area, so 1 Pascal is actually a very weak pressure.

Ambient atmospheric pressure, i.e., pressure near sea level, is much higher than 1 Pascal

1 atmosphere $\sim 1.02 * 10^5$ Pascal.

One atmosphere is denoted as P^0

It is a coincidence of nature that 1 Atmosphere is so close to a power of ten (here 100,000) times Pascal; so to use this fact, scientists introduced another pressure, called a bar, **defined as**

1bar = exactly 10^5 Pascal

So

$P^0 = 1.02$ bar$\sim$1bar.

A secret: since we are a little higher than sea level, the pressure at UCLA is actually lower than P^0 and is closer to a bar (and fluctuates daily with weather). So for me, in this course, we'll just approximate that $P^0 \text{ " = " } 1bar$

and we'll ignore the 1atm vs. 1bar difference (don't do it in other courses or labs or you will lose points there…)

Useful: Note that

1bar = 100,000 J/m^3, and m^3=1000L (L means Liter),

1bar = 100,000J/(1000L)

1bar = 100 J/L

Useful later.

The Gas Law , Temperature scale

This section is only relevant for gases.

We'll see how experimentally the gas law, PV=nRT, was derived, where:

P: pressure
V: volume
T: temperature
N: number of moles
R: constant ("gas constant", R=8.3 J / (K mol))

Historical route:

Separate experiments on gases by Charles and Boyle and Avogadro.

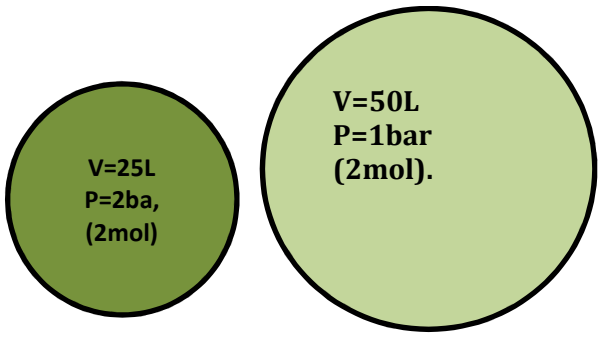
Take an amount of gas put in a piston that can move but is sealed to other gases (see picture) so the gas inside cannot leak.

1nd : If T fixed, P*V will be proportional to the amount of material (and will be therefore unchanged if the amount of material is unchanged, and T is fixed) (e.g., P→ P/2 when V→ 2*V, but only when T and amt. of material are fixed!).

An example is in the picture below.

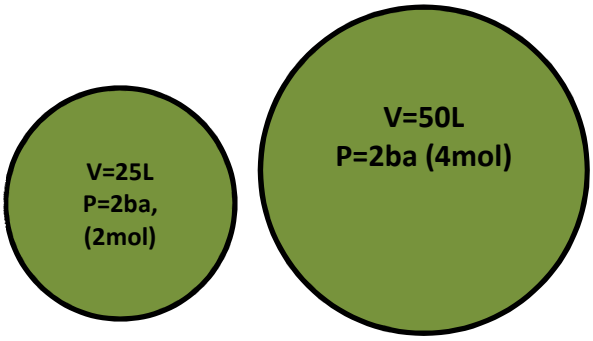
We have two balloons at the same temperature (say, 300K) and with the same amount of material (say, 2mol). In one Balloon, V=25L, and the pressure is 2bar; in the other, the volume and pressure are different (50L and 1bar), but their product is the same as in the 1st balloon (since 25*2=50*1).

Example for PV=n*const. at fixed T=25°C and fixed for ideal gases: V doubled, P halved.



Further, if we fix T and P, and double the amount of material, then, the volume needs to double (that's almost obvious!), i.e., in our example:

Example for
PV=n*const.
at fixed T
for ideal gases:
Double volume and n while P and T fixed.



So: mathematically we write these observations as:

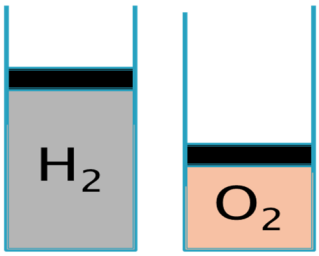
P*V=n*function(T)

However, so far this "function(T)" could depend on the material; the next experiment proves it does not depend on the material, i.e., "function(T)" has universal characteristics!

2nd experimental observation: for same T, and P, the ratios of the volumes between 2 different gases = ratio of the numbers of moles;

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

If the final gases kept at same P and T, $V(H_2)=2V(O_2)$
Proves that V proportional to n.



E.g., consider making hydrogen and oxygen gases

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$$

The outcome of this reaction is twice as many hydrogen moles as oxygen moles

$$n_{H2} = 2\, n_{O2}$$

The observation is that if we collect the hydrogen in one container and the oxygen in the other, and both containers have the same P and T, then

$$V_{H2} = 2V_{O2} \qquad \text{so:}$$

$$\frac{PV_{H2}}{n_{H2}} = \frac{PV_{O2}}{n_{O2}}$$

And we'll find this for any reaction, **i.e., 'function(T)' above is universal,** i.e.,

$$PV = nf(T)$$

where $f(T)$ is a function of temperature.

Note on raising volumes without reactions:

The gas laws tells us that if we were to increase the temperature at a fixed pressure, then two gases that have initially the same volume will continue having the same volume.

(Example:, say we have a gas of hydrogen and a gas of bromine, all in 1 bar, and that initially, when each is at the same initial temperature T each occupies 100L then if at another temperature, T', one gas occupies, say, 160L , the other gas will also occupy 160L at that temperature).

Next Defining the temperature in Kelvin, based on the Gas Law.

So far we avoided the question of what temperature scale to actually use. An example: we intuitively "know" that the temperature of boiling water is higher than the temperature of ice-water; but we can label the two as being 100 and 0 (as in the Celsius scale) or 212 and 32 (as in the Fahrenheit scale), or other arbitrary designations.

Clearly, it will be best to use a temperature definition that is based on a physical law, rather than being completely arbitrary. The simplest way for that is to use directly the gas law, i.e., we **define**:

$$RT = PV/n$$

R: constant used to match T to more historical definitions.

The T that's defined above is called: T in Kelvin.

The numerical value of R was adjusted so that:
The difference in Kelvin ("K") between boiling point of water and freezing point, when measured at the pressure near sea level, will be 100 (i.e., 100K), just like it is in Celsius.

Experimentally: put a sealed balloon filled with air in boiling water, at P=1bar, and find that V is, say, 50.000 L. When the same balloon is then put into ice water, we'll find that V=36.601 L.

We find (experimentally!)

$$\frac{\mathrm{P\ V\ (at\ T_{boil})}}{\mathrm{P\ V\ (at\ T_{Freeze})}} = \frac{1\mathrm{bar}*50.000\mathrm{L}}{1\mathrm{bar}*36.601\mathrm{L}} = 1.36609 \quad \rightarrow \quad \frac{nRT_{\mathrm{BOIL}}}{nRT_{FREEZE}} = \frac{T_{\mathrm{BOIL}}}{T_{FREEZE}} = 1.36609$$

This equation is then combined with our desire to have

$$\mathrm{T_{BOIL}} - \mathrm{T}_{FREEZE} = 100K$$

To yield:

$$100K = \mathrm{T_{BOIL}} - \mathrm{T}_{FREEZE} = 1.36609 \cdot \mathrm{T}_{FREEZE} - \mathrm{T}_{FREEZE} = 0.36609 \cdot \mathrm{T}_{FREEZE}$$

i.e.,

$$\mathrm{T}_{FREEZE} = \frac{100\mathrm{K}}{0.36609}$$

i.e.,

$$\mathrm{T}_{FREEZE} = 273.16\mathrm{K} \sim 273\mathrm{K}$$

and

$$\mathrm{T_{BOIL}} = \mathrm{T}_{FREEZE} + 100\mathrm{K} = 373.16\mathrm{K}$$

Further, we can get R from this:

Say we were able to determine that in this experiment n=1.61mol (for example, we can weigh the air in the balloon somehow and divide by the average molecular weight of air, including the ~80% contribution of N_2, ~20% O_2, etc.). Then:

$$R = \frac{PV}{nT} = \frac{1\text{bar} * 50.00\text{L}}{1.61\ \text{mol} * 373.16\ \text{K}} = \frac{0.0831\ \text{bar} * \text{L}}{\text{mol K}}$$

But recall that we learned that

1bar * L = 100 J (where J=Joule),

So

$$\text{R} = 8.3\ \frac{\text{J}}{\text{K mol}}$$

You don't need to memorize this number (I'll give it to you in the exams), but with time you'll remember it naturally.

Room temperature, and R T(room):

Officially people define, for reference, room temperature as

T(room) = 25Celisus = 298 K ;

I'll round in this course T(room)~300K

Note: **RT(room) = 8.3 J/(K mol) * 300K ~2500J/mol**

WORD OF CAUTION ON THE IDEAL GAS LAW,

PV=nRT is only valid for "ideal" gases, i.e., ones in which the distances are so large that the molecules barely meet each other once in a while. At high pressures (e.g., bigger than say, 30bar and definitely for more than100 bar) we have to start worrying about corrections to the ideal gas law.

But for most gases the ideal gas law is extremely accurate at room pressures.

We'll study shortly deviations from ideal gas laws and how they teach us about the forces that hold the atoms together in solids and liquids.

IMPORTANT: never apply the ideal gas law to liquids and solids!

Physical derivation of the Ideal Gas Law: kinetics

Overview

Now we'll derive the ideal gas law; our derivation will be kinetic, i.e., based on the properties of the motion of individual molecules. We'll ignore on the beigning factors of ~2.

Imagine a cubical container with a 1 mole of gas.

Assume very simplistically that:

½the molecules move to the left with a characteristic speed: u,

Another ½ move to the right with the same speed, u

(This is a very simplistic assumption, since molecules have a range of speeds; further, they also move in different directions, not just left and right. We'll remedy this assumption later, one by one).

Further, our goal in this derivation is to be very simplistic, so we will sometimes forget about factors of 2 (which will miraculously cancel out in the final relation, i.e., our approximate derivation will give the correct result).

Before we start, several reminders:

(i) the mass density equals

$$mass\ denity = \frac{M}{V_m}$$

where n is the number of moles, M is the molar mass of the molecules, and V is the molar volume.

(ii) momentum is defined as mass* velocity.

(iii) Force is defined as change in momentum per time

(iv) kinetic energy is defined as (up to factors of 2) mass*velocity^2

Now to the pressure calculation: we imagine a container with unit cross sectional area in the left wall (e.g., if we use cgs units, the area will be A=1 cm^2, etc.); the force on that area will be the pressure.

$$P = F(on\ unit\ area)$$

But the force exerted by the molecules on the left walls the same as the force exerted on the molecules; the latter is, as mentioned, simply the rate of change in momentum of the molecules that hit the wall,

$$P = Force(unit\ area) = \frac{change\ in\ momentum}{\tau}$$

where "τ" is a short time; and since the momentum equals mass*velocity, we can write the pressure as

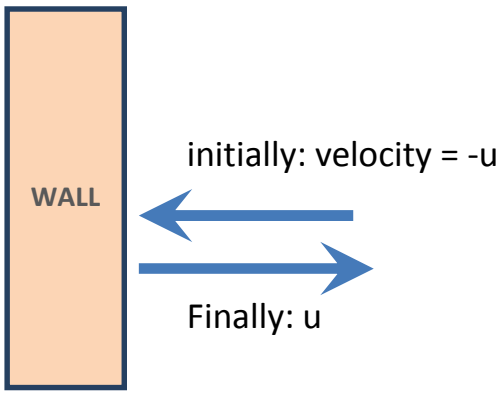
$$P = \frac{(mass\ of\ particles\ that\ hit\ \ wall\ in\ time\ \tau)\ *\ (change\ in\ velocity\ when\ molec.\ hit\ wall\ )}{\tau}$$

Let's then calculate the term.

The velocity will change because when a particle hits the left wall it will bounce back, so its velocity change will be (see figure)

$$change\ in\ veolcity = 2u \sim u$$

where we ignored a factor of 2, as promised.



So we are only left with the need to calculate what's the mass that hits the wall in a short time τ.

Now we know that in a time τ, only particles that are within a distance $u\tau$ from the wall can hit the wall; particles that are further way simply wont make it in time. (See figure)

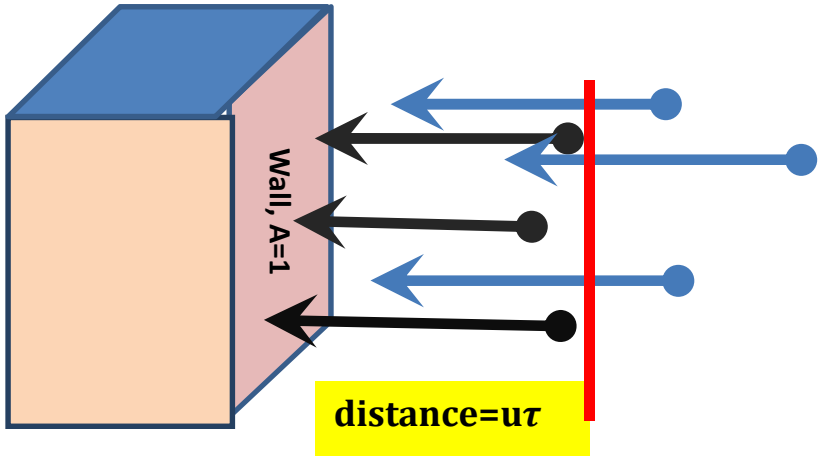


Figure: Only molecules that are within a distance $u\tau$ from the wall will hit it in time τ (molecules in black, that start to the left of the imaginary "red line" at a distance of $u\tau$ from the wall); molecules which are further away (blue in figure) will not hit the wall in time τ.

Therefore, the volume from which particles that hit the wall come is its cross-section area (1) times its length ($u\tau$), i.e., it will be $u\tau$

Therefore, the mass of particles (within a unit area) that hit the wall will be *the **mass density times the volume from which the particles come.***

i.e.,

$$(mass\ of\ particles\ that\ hit\ the\ unit-area\ wall\ in\ time\ \tau)$$

$$= mass\ density * (volume\ from\ which\ the\ particles\ that\ hit\ in\ \tau\ arrive)$$

$$= \frac{M}{V_m} * u\tau$$

So collecting it all we get, using the eq. we derived:

$$P = \frac{(mass\ of\ particles\ that\ hit\ the\ wall\ in\ time\ \tau) * (change\ in\ velocity\ when\ molec.hit\ the\ wall\ )}{\tau}$$

we get that:

$$P = \frac{\left(\frac{M}{V_m} * u\tau\right)u}{\tau}$$

i.e.,

$$P = \frac{M}{V_m}u^2$$

It turns out that this equation has the correct numerical factor, i.e., factors of 2 that we ignored earlier canceled each other out. From now on we will not ignore any more factors.

The kinetic energy per mole, E_m, is the molar mass (M) times the velocity squred, times $3/2$,

$$E_m = \frac{3}{2}Mu^2$$

(You recognize the $1/2$ as always appearing in kinetic energy; the "3" is because u is the velocity in the "x" direction, and we need to add the contribution of the y and the z directions.. that gives a 3).

Merging together the last 2 equations gives

$$PV_m = \frac{2}{3}E_m$$

(Also note that up to $2/3$, this is the same equation we "derived" from unit analysis earlier!)

So if we **define** the temperature as proportional to the kinetic energy per mole, i.e.., define T to be:

$$RT \equiv \frac{2}{3} E_m$$

Then by plugging the last equation into the one before it, we get the ideal gas law,

$$PV_m = RT!$$

(Note that as a bonus, we get from the definition of RT the "result" – really just a definition – $E_m = 3\,RT/2$, which we will need later)

Note: this derivation makes it clear that T cannot be negative, since it is proportional to kinetic energy, which is always positive.

ALSO Note: this is a mathematically involved derivation, but I'll expect you to be able to redeliver it!

Finally, note that **E_m is NOT THE TOTAL ENERGY,** but is instead the kinetic energy associated with center of mass motion. For atoms that are far from each other, there is no other energy, so $E_m = 3RT/2$ is the energy of atomic gases (e.g., He, Ar, , etc.); for molecules, we have to supplement this energy by intermolecular kinetic and potential energy, so

$$\text{Molar Energy(molecules)} > E_m = 3RT/2.$$

Maxwell's Velocity Distribution:

The derivation above was approximate as it assumed that all molecules have the same speed in the x direction (with ½ going left, ½ right). Typically such approximate derivations give results that are accurate within an order of magnitude, i.e., have mistakes of order of 0.3 - 3.0. However, in this case we were lucky and even the final factors were correct (so PV=nRT is correct exactly for an ideal gas).

One issue we ignored in our derivation is that molecules do not have a fixed speed; if we want to really know what molecules behave like, they have distribution of speeds.

Let's use "u" to denote the total speed. This is different from the previous section, where u denoted the speed along x; here it denotes the total speed.

Further, u will be variable, so different molecules (or even the same molecule at different times) will have a different u.

Since u is a continuous variable, we define the fraction of particles within a range between u and u+du, i.e., with speeds around u but within a range du,

$$\mathrm{F}(u, u+du) = \text{FRACTION OF } molec.with\ u < speed < u+du$$

For example, a gas can have a temperature where, say, 0.03% of its molecules have speeds between 50 and 50.1 m/s; in that case,

F(50 m/s, 50.1 m/s) = 0.03% = 0.0003

Next, note that if du is small, F(u,u+du) is proportional to du:

$$\mathrm{F}(u, u+du) \propto du$$

(where the symbol $\propto$ means: proportional to).

E.g., if u is, say, 50m/s, then the number of particles that have speeds between say 50 and 50.2 m/s will be about twice as large as the number of particles between 50 and 50.1 m/s

$$\mathrm{F}\left(50\frac{m}{s}, 50.2\frac{m}{s}\right) \cong 2 * \mathrm{F}\left(50\frac{m}{s}, 50.1\frac{m}{s}\right)$$

And in our example it will equal to 2*0.03%, i.e., 0.06%.

If you are not clear about the fact that $F(u, u+du)$ will be proportional to du, think of an example from your daily life. The fraction of students with SAT score between 1100 and 1108 is about twice as high as the fraction of students with scores between 1100 and 1104; i.e., the fraction of students within a small range of scores is proportional to the size of the range.

Therefore, we can talk about probability densities, which will be **defined** as:

$$f(u) \equiv \frac{\mathrm{F}(u, u+du)}{du}$$

i.e., $f(u)$ is the fraction of molecules per unit speed, i.e., **per m/s.** The advantage of using "$f(u)$" rather than $F(u, u+du)$, is that as long as du is not too big, f is independent of du [the size of the range], and depends only on u., so instead of depending on two variables (u and du) f depends only on one (u).

This is similar to the definition of derivatives, for those who know calculus.

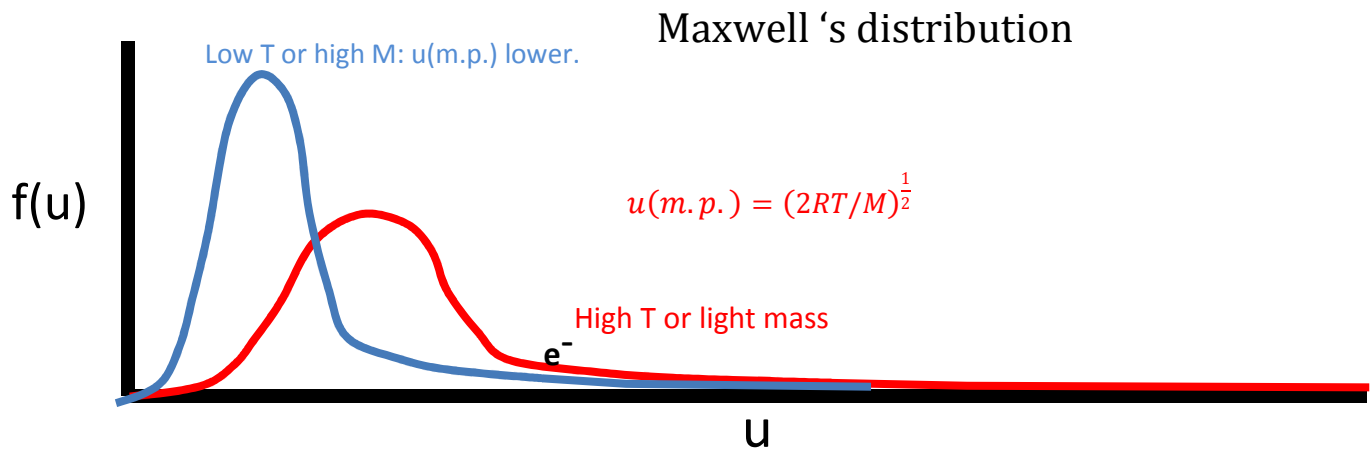
For molecules, $f(u)$ is called: Maxwell distribution.

It has units of 1/speed, i.e., 1/(m/s)= s/m.

(in the previous example, where F(50 m/s, 50.1m/s)=0.0003, we get f(50 m/s)= 0.0003/[0.1m/s] = 0.003 s/m)

Turns out (see Chem. 110B), that for ideal gases f(u) has a general universal form, called the Maxwell equation, which equals (don't be scared!)

$$\boldsymbol{f(u) = \frac{1}{\left(\frac{\pi}{2}\frac{RT}{M}\right)^{3/2}} u^2 \exp\left(-\frac{Mu^2}{2RT}\right)}$$



M is the molar mass of the molecule, as we saw earlier.

We'll come back later to the most important part, which is the exponential term, $\exp\left(-\frac{Mu^2}{2RT}\right)$; it is called the BOLTZMANN FACTOR.

Maxwell distribution Properties:

Most prevalent (m.p.) speed: where f(u) peaks.

From calculus (if you know it)

df/du=0 at $u_{m.p.}$ →(after a short derivation)

$$u_{m.p.} = \sqrt{\frac{2RT}{M}}$$

Important alternative to calculus: deriving the probable distribution approximately from unit analysis:

We can find out the important factor $\sqrt{\frac{RT}{M}}$ in $u_{m.p.}$ by "unit analysis", also called dimensional analysis, as $\sqrt{\frac{RT}{M}}$ **is the only quantity with units of speed that we can make out of RT (energy) and M (mass!)**

(since velocity^2=Energy/Mass, velocity=square root of (Energy/mass)).

Note that the dimensional analysis did not give us the $\sqrt{2}$ factor, but that's typical of dimensional analysis.

Understanding the different parts in the Maxwell distribution.

The Maxwell distribution looks very scary, but let's see that it makes sense. I'll rewrite it as product of 4 terms

$$f(u) = \frac{4}{\sqrt{\pi}} \frac{1}{u_{m.p.}{}^3} u^2 \exp\left(-\frac{K.E.}{RT}\right)$$

Where we'll understand the terms by going right to left:

- The 4th term, $\exp\left(-\frac{K.E.}{RT}\right)$, is the Boltzmann factor, which is, as mentioned, very prevalent (we'll see it later): K.E. is the kinetic energy of a mole of particles with molar mass M and speed u:

  $$K.E. = \frac{1}{2}Mu^2$$

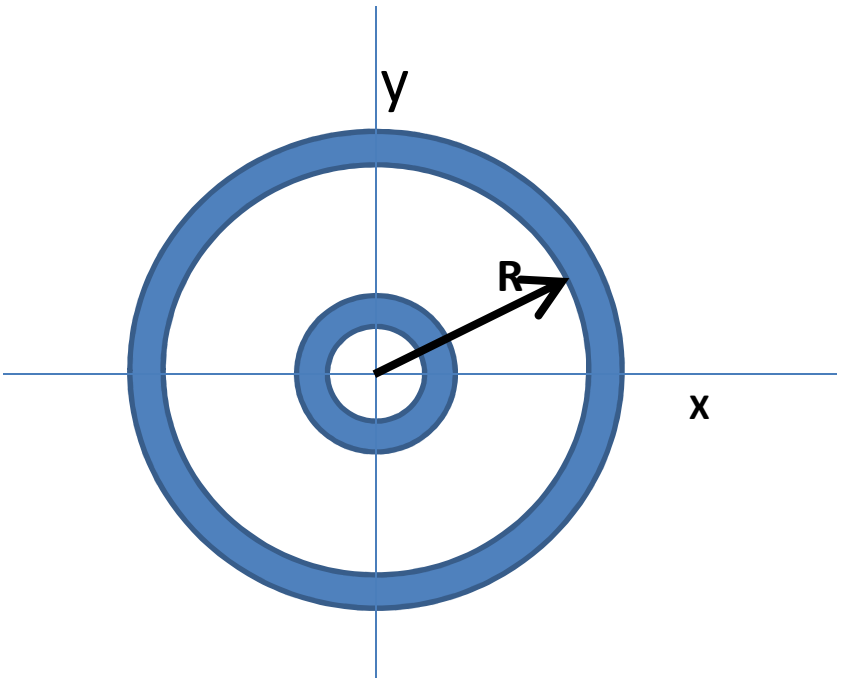
  So the Boltzmann factor discriminates against particles with high energies – in this case, high kinetic energies, but later, when we talk about particles also with potential energies, it will discriminate against other high energies (total energies; or potential energies; depending on the circumstance).

- The 3rd part is an interesting part. It actually discriminates against particles with low speeds. It turns out it is a geometric factor; which accounts for the following:

  The higher the speed, the more possibilities there are to get the same speed u from different u_x, u_y, u_z: i.e., if the speed is small, then that can happen only if u_x, u_y and u_z are all small; but if the speed is high then there are many different combinations – u_x can be high, or u_y can be high, or bot could be intermeidnate, etc.

  To see a close analogy, consider what happens when we throw darts at a circular board:

  DARTS: Much higher possibility to hit the outer rim (unless it is too far out) since it has a much larger area due to its larger circumference.



The same argument applies for molecules, except that then we have to replace "x" by "v_x" , y by " v_y", R by "u" and in 3D include also v_z.

If space was 2D, the rim analysis tells us that that the geometrical factor would have been the "circumference", which in velocity space is 2πu;

But space is 3D, so the geometrical factor is $4\pi u^2$, i.e., the surface area of a sphere in 2D

And in general we can summarize it as : the geometrical factor is up to an overall constant $\mathbf{u^{d-1}}$, where d is the **dimensionality** of our space.

- The second term in the Boltzmann distribution is the units factor

$$\frac{1}{u_{m.p.}{}^3}$$

This term ensures the correct units of f(u); i.e., since f(u)du is a probability, i.e., a number with no units, f(u) has to have units of 1/speed.

Specifically, the geometrical factor has units of $(\text{speed})^2$ (in 3D) so the units-factor has to be of the form of $(1/\text{speed})^3$, so when multiplied together, we will get the correct (1/speed) unit for f(u)

- The left most part, $\frac{4}{\sqrt{\pi}}$, is a numerical factor which ensures that overall $\int_0^\infty f(u)du = 1$, i.e., that the fraction of molecules between 0 and inifitte speed is 100%, as it should be. This constant is the least important to remember, and anyway it is not very far from 1 (it is ~2.5)

Physical properties of the Maxwell distribution:

Note: T rises or M lower: $u_{m.p.}$ higher

Examples: H_2 molecules at room temp.

$$u_{m.p.} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \cdot 8.3 \frac{\text{J}}{\text{K mol}} \cdot 300\text{K}}{\frac{2\text{g}}{\text{mol}}}} = \sqrt{2500 \frac{\text{J}}{\text{g}}} = 50\sqrt{\frac{\text{J}}{\text{g}}}$$

But:

$$1\text{J} = 1\text{kg} * (\text{m/s})2$$

So

$$u_{m.p.} = 50\sqrt{\frac{\text{J}}{\text{g}}} = 50\sqrt{\frac{\text{kg}\left(\frac{\text{m}}{\text{s}}\right)^2}{10^{-3}\text{kg}}} = \frac{50}{\sqrt{10^{-3}}}\frac{\text{m}}{\text{s}} = 1600\frac{\text{m}}{\text{s}}$$

Another example: Air. We don't have to repeat the calculation. First, let's approximate air as essentially all N_2 since air is 80% N_2.
The mass of N_2 is 18 times higher than H_2 so we need to divide u_{mp} that we got for hydrogen by 1/sqrt(18) to get the result for air, at the same (room) temperature, i.e.,

$$u_{m.p.}(Air) = \sqrt{\frac{2RT}{M(N_2)}} = \sqrt{\frac{M(H_2)}{M(N_2)}}\sqrt{\frac{2RT}{M(H_2)}} = \sqrt{\frac{1}{18}}\frac{1600m}{s}$$

So

$$u_{m.p.}(Air) \sim 370\frac{m}{s}$$

Average speed; Since f(u) has a significant "tail" at high speeds → $u_{average} > u_{m.p.}$ (by about 15%).

Analogous to earnings – a few people with really high salary increase the average wage (~$50K) above the most likely wage (~$40k). Similarly, the

average speed is higher than the most likely speed, due to the contribution of those very few molecules that have very high speeds.

Other implications of the average speed and the speed distribution: diffusion – we'll see later.

High energy tail (from Boltzmann Factor) : Explains why atmosphere does not contain light particles (no hydrogen or helium).

Example:

A particle with speed 11km/s can escape the earth atmosphere and run out to space. Let's estimate the Boltzmann factor, which is the most important part determining the probability that a particle can have speeds close to this "escape velocity". Let's do it for two different molecules, hydrogen and oxygen. Specifically:

Answer:

First, note that the temperature high up in the atmosphere, where the particles can escape, could be quite high. Let's say it is 1500K, although it varies.

u~11km/s = 11,000 m/s (we converted to MKS units, since we need to use a consistent set of units in the calculations.

(i) For H_2

$$\exp\left(-\frac{Mu^2}{2RT}\right)$$

$$= \exp\left(-\frac{\frac{0.002\text{kg}}{\text{mol}}\left(\frac{11{,}000\text{m}}{\text{s}}\right)^2}{\frac{8.3\text{ J}}{\text{mol K}} * 1500\text{K}}\right) \sim \exp(-10) \sim 0.001$$

[Note that since a Joule is in MKS units, which use kg and not grams, i.e.,

$$\text{J} = \text{kg}\left(\frac{\text{m}}{\text{s}}\right)^2$$

so we converted the molecular mass to kg/mol, i.e., wrote

$$M = molar\ mass(H_2) = 0.002\,\frac{\text{kg}}{\text{mol}}$$

This conversion from g/mol to kg/mol was essential so we can cancel the mass units in the expressions.]

Since earth exists for so long (more than 4 billion years) molecules have a chance to reach, once in a while, the escape speed (11 km/s) and then to run away from earth.

In contrast O_2 is heavier so the Boltzmann factor is too small for anything to escape.

Specifically, raising M by a factor of 16 (from H_2 to M_2) raises (for the same speed), the kinetic energy by a factor of 16, so the $\exp\left(-\frac{Mu^2}{2RT}\right)$ factor, which was before exp(-10), now becomes exp(-160)~ 10^{-70} , i.e., utterly negligible.

Therefore, the Boltzmann factor ensures that the probability for an oxygen molecule to leave earth it utterly negligible, but hydrogen can leave, so our atmosphere has lots of oxygen (and nitrogen) and little helium or hydrogen.

Boltzmann Factor: Consequences

As we mentioned, $\frac{Mu^2}{2}$ is a kinetic energy, labeled E, so the expoential term in the Maxwell distribution has the form

$$\exp\left(-\frac{Mu^2}{2RT}\right) = \exp\left(-\frac{E}{RT}\right)$$

This exponential term is very important in science and got the name "Boltzmann Distribution" or "Boltzmann factor".

In general, for a quantum mechanical system with different states (which are labeled by a subscript j, then:

$$P(state\ j) = C\ exp\left(-\frac{E_j}{RT}\right)$$

Where:

- P stands for "probability", <u>don't confuse it</u> with P for pressure.
- C is an overall constant which will depend on temperature but not on the specific energy.
- E_j is the energy of state j

Note that if we have several states with the same energy, then

$$P(E) = C\ N(E) exp\left(-\frac{E}{RT}\right)$$

Where "N(E)" is the number of states with energy E.
We encountered something similar to that when we considered the geometrical factor, u^2, which essentially counts the number of "available states".

A useful formulation of the Boltzmann factor which does not have the constant is when we divide the probabilities for two different energies, E and E'; then

$$\frac{P(E')}{P(E)} = \frac{C\ N(E') exp\left(-\frac{E'}{RT}\right)}{C\ N(E) exp\left(-\frac{E}{RT}\right)} = \frac{N(E)}{N(E')}\exp\left(-\frac{E'-E}{RT}\right)$$

i.e., the ratio of the probabilities of be at an energy E vs. and energy E' is an exponential of minus the energy difference scaled by RT, times the ratio of the number of states of each energy.

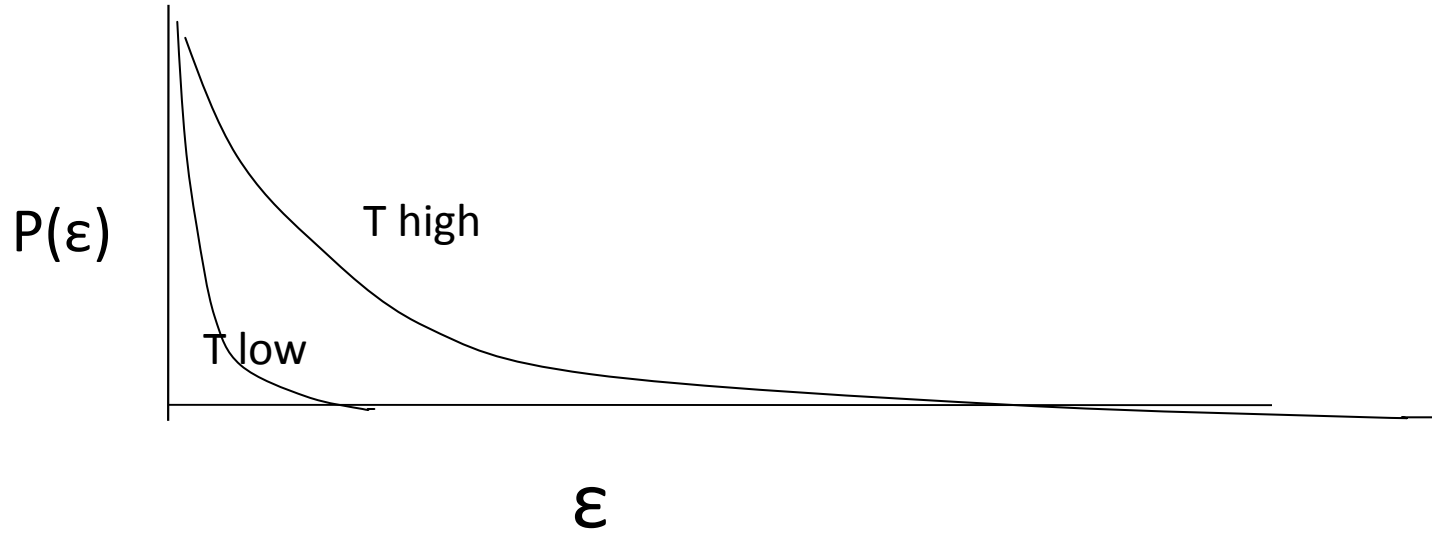
The Boltzmann factor is prevalent in science!

Note: If E >> R T then P(E)<<1

P(E) is exp(-E/(RT)). For E=0, P(E) is exp(-0)=1, But when E is higher, P will be smaller.

How much higher?

Well, if E, say, equals RT then P will equal exp(-RT/(RT))=exp(-1)~0.4, i.e., significantly less than 1. So we see that if the temperature is low, then the energy at which P starts becoming small will be lower.)



So basically: If an excitation energy > RT, the probability for it is very small!

Example for the Boltzmann factor: vibrations of diatoms.

Just like you learned in 20A that energy levels of electrons are discretized , so are vibrations;

i.e., to excite a non-vibrating molecule to vibrate even a little, you need a non-zero amount of energy, which is

$$E(single\ vibrational\ excitation) = h f$$

where f is the vibrational frequency of the diatom, and h is Planck's constant ($h=6.62*10^{-34}$ J s)

Since a molecule can be excited none, once, or twice, etc., the energies of the states are (ignoring something called "zero point energy", not relevant here but important elsewhere):

$$E = 0, hf, 2hf, 3hf, \ldots$$

Further, each state has a different energy, so N(E)=1

Specific example: O_2 at room temperature:

$f(vibration, O_2) = 4.7 * 10^{13}$Hz (an IR frequency) (recall that 1Hz=1/s)

$$E(1st\ vibration, O_2) = h f = 6.62 * 10^{-34}\ \text{J s} * 4.7 * 10^{13}\ (\text{s}^{-1})$$

$$= 3.1 * 10^{-20}\ \text{J}$$

(and using $1= N_{AVOG}$ /mol = $6.02*10^{23}$ /mol)

$$h f = 3.1 * 10^{-20}\ \text{J} * \frac{6.02 * 10^{23}}{\text{mol}}$$

$$= 19 * \frac{10^3 \text{J}}{\text{mol}} = 19 \frac{\text{kJ}}{\text{mol}}$$

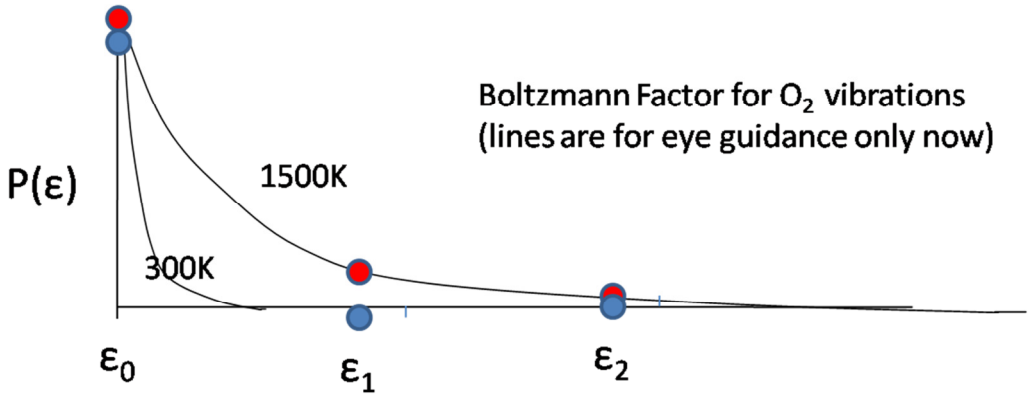
Also, for room temperature

$$RT = 8.3 \frac{\text{J}}{\text{mol K}} * 300\text{K} \sim 2500 \frac{\text{J}}{\text{mol}} = 2.5 \frac{\text{kJ}}{\text{mol}}:$$

And therefore the probability that oxygen is vibrationally excited to the first level, i.e., the probability that its energy is higher than the ground-state by $E_{vib\ excitation} = hf$, is:

$$\frac{P(E = hf)}{P(E = 0)} = \exp(-hf/RT)$$
$$= exp\left(-\frac{19\text{kJ/mol}}{2.5\ \text{kJ/mol}}\right) = exp\left(-\frac{19}{2.5}\right) = 5 * 10^{-4} = 1/2000$$

This is a small number; only 1 in 2000 oxygen molecules is vibrationally excited.



In order to get a significant probability for vibrating, we need to have temperatures which are >> 1000K, so that the Boltzmann exponential will be much larger. See the picture above.

(If you ever saw it – note that we ignored something called "zero point energy", it is not essential for this discussion).

INSERT (read at home, required material)

Another example for the Boltzmann factor: Barometric pressure dropoff with height

There are several ways to determine the falloff of the air pressure above earth with height; for our purposes, it is interesting to see that we can get it from stat. mech.

The potential energy of a molecule above earth is

$$U(h) = M\bar{g}h$$

Where h is the height, M is the molar mass, and $\bar{g}$ is the gravitational constant ($\bar{g} = 9.8\frac{\text{Newtons}}{\text{kg}} = 9.8\frac{\text{J}}{\text{kg m}}$, since Newton $= \frac{\text{J}}{\text{m}}$.) Also, I use a "bar" so we don't confuse $\bar{g}$ with g for gram)

The "state" of the molecule is its height, h; further, it turns up that the N(E) factor is constant in this case.

Therefore, the Boltzmann distribution tells us then that the ratio of the probability of having a molecule near a height "h" compared with another height, say, "0", is

$$\frac{P_{prob}(h)}{P_{prob}(0)} = \exp\left(-\frac{M\bar{g}(h-0)}{RT}\right) = \exp\left(-\frac{M\bar{g}h}{RT}\right)$$

The ratio of probabilities is, quite intuitively, the same as the ratio of molar densities at height h vs. sea level,

$$\frac{n(h)}{n(0)} = \frac{P_{prob}(h)}{P_{prob}(0)}$$

; but since the molar density is proportional to the pressure, the equation above also is the same as the ratio of pressures; i.e., we can interpret the equation above as if "P" is also the pressure, i.e.,

$$\frac{P_{pressure}(h)}{P_{pressure}(0)} = \frac{n(h)}{n(0)} = \frac{P_{prob}(h)}{P_{prob}(0)} = \exp\left(-\frac{M\bar{g}h}{RT}\right)$$

(this is the only place in the course where it is allowed to confuse "P" for probability with "P" for pressure!)

If you plug in the numbers you see that, for example for oxygen (O_2, M~32g/mol), when h=2km=2000m, and T=300K (so RT=2500J/mol) then

$$\frac{P(h = 2000\text{m})}{P(0)} = \exp\left(-\frac{M\bar{g}h}{RT}\right) = \exp\left(-\frac{\frac{32\text{g}}{\text{mol}} \cdot 9.8\frac{\text{J}}{\text{kg m}} \cdot 2000\text{m}}{\frac{2500\text{J}}{\text{mol}}}\right)$$

$$= \exp\left(-251\frac{\text{g}}{\text{kg}}\right) \sim \exp(-0.25) = 0.78$$

i.e., at 2km above sea level (about 6600 ft. above sea level, so above Denver but below Mexico City), the pressure is about 0.78 atmosphere.

END OF INSERT

Part 2: Real Gases, Solids, Liquids

Overview:

- Gas and Liquid volumes, distances
- Attraction and repulsions, Z=PV/nRT,
- Potential energy of interactions.
- Physical Properties: compressibility, thermal expansion coeff., discussion, surface tension
- Intermolecular forces: Columbic and dipole:
  Ion-dipole, dipole-dipole, induced forces, fluctuation-induced (vdW) forces, exchange-repulsion.
- Boiling points and hydrogen bonds

Gas Volume

Gas volumes—practical numbers

For T(room) and P^o , the volume of one mole, labeled molar volume, V_m is:

$$V_m = \frac{RT}{P} = \frac{8.3J}{K\,mol} * \frac{300K}{100\frac{J}{L}} = 25\frac{L}{mol}$$

i.e., One mole of ideal gas occupies 25L at room pressure and temperature.

Distance between gas molecules--estimate:

Let's estimate the distance between each molecule.

For this, let's first in our mind (i.e., doing a "thought experiment") take a mole of molecules in a gas, and do a snap shot of all the molecules in that volume at a single instant of time. Then, divide space to imaginary cells, such that each cell contains exactly one molecule.

Now some of these cells will be very small, as will happen if a molecule happens to be close to a few others; a cell could also be big, if the molecule it contains happens to be far from the other molecules.

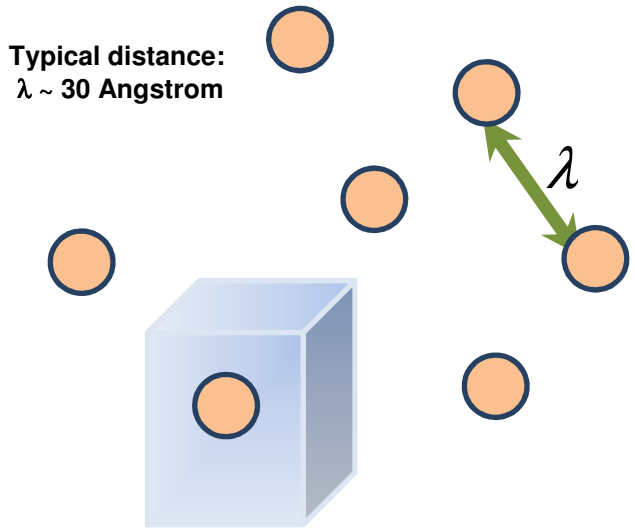
But the average size of these cells is very simple to calculate – it will be the total volume (V_m) divided by the number of atoms, i.e.,

$$V_{cell} = V_m/N_{avog}$$

And for room temperature and pressure, where V_m=25L,

$$V_{cell} = 25L/6*10^{23} = \frac{25\square 10^{3}\,cm^{3}}{6\square 10^{23}} \sim 4\square 10^{-20}\,cm^{3}$$

Further, let's imagine that the "average" cell is cubic in shape (we could have imagined a different shape, but that will not change our conclusions).



Next let's estimate the average distance between the molecules. IF they were all ordered, then the average distance between each molecule (λ) would have equaled the length of the edge of the cube (see picture above to believe me).

Therefore, the volume of that average single-molecule cell will equal λ^3, so.

$$\lambda^3 = V_{cell} = 4\square 10^{-20}\,cm^{3} \quad \text{(for room temperature and pressure),}$$

So: $$\lambda = \left(4\square 10^{-20}\,cm^{3}\right)^{1/3} \sim 3\bullet 10^{-7}\,cm = 30\bullet 10^{-8}\,cm = 30\ \text{Angstrom}$$

(recall that 1Angstrom is defined as 10^{-8} cm)

<u>Liquid volumes</u>:

Unlike ideal gases, liquid volumes are dependent on the material;

Also, in general liquids are much denser than gases.

Let's see an example: <u>molar volume of liquid water</u>; this example will then allow us to estimate the volume of each water molecule.

We know one mole of liquid water weights 18 g, and its mass density (mass/volume) is

$$\text{mass density (liquid } H_2O) = 1 g/cm^3$$

(that is of course not a coincidence but was used to define the gram when the meter was adopted by French scientists more than 200 years ago),

So

Volume(one mole liquid H_2O)
=(mass of one mole)/ (mass/volume)
= (mass of one mole)/density

Now, the molar mass of water, as we saw is 18g/mol;
so the mass of one mol=18(g/mol)*1mol = 18g,

And further, the density of water is $1 g/cm^3$, so

$$\text{Volume(one mole liquid } H_2O) = 18g/(1 g/cm^3) = 18 cm^3 = 18*10^{-3} L$$

Compare this number to gases, which at one bar and room temperature have a molar volume of 25L!

<u>i.e., Liquid water is more than 1000 times denser than ideal gases at room temperature and pressure!</u>

Molecular Volumes

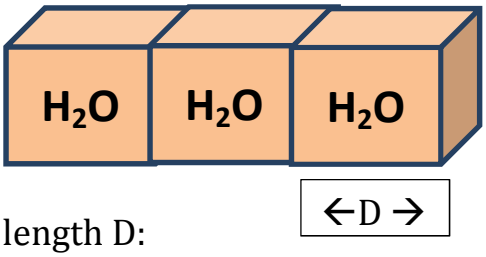
Now let's use this to estimate the volume and size of each molecule!

If we imagine that the molecules of the liquids are little cubes (they aren't, but we are just interested in qualitative calculations), and arranged fully stacked, then the volume of a single molecule will be just the volume of the whole liquid divided by the number of molecules;

Taking one mole of water, the volume occupied by one water molecule is:

V(one molecule)
= V(one mole)/ $N_{avogadro}$
= 18 cm^3 / $6.02*10^{23}$

$=3*10^{-23}$ cm^3



If we imagine each volume as being of a cube of length D:

$V(1 \text{ one water molecule }) = D^3$

So: $D^3 = 3*10^{-23}$ cm^3

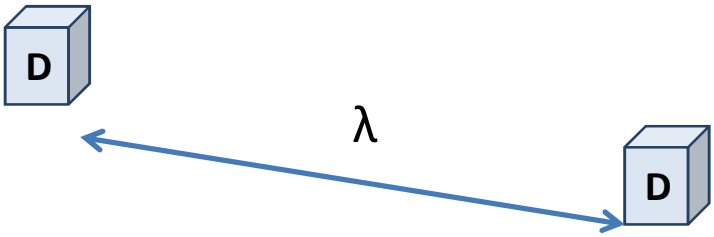
$D= (3*10^{-23})^{1/3}$ cm

$D \sim 3.2*10^{-8}$ cm$\sim$ $3*10^{-8}$cm = 3 Angstrom

Note: in gases the distances between atoms (λ that we calculated earlier) are ~ 10 times more than in liquids!

Attraction and repulsions

The ideal gas law. PV=nRT , is valid only when λ, the distance between particles, is much larger than their diameter, D



Note: λ>>D → ideal behavior (molecules rarely "meet" each other).

This is true for simple molecules at room pressures temperatures, since:

D~ 3Angstrom,

and for gases at room T and P^0, as we saw earlier:

λ~30Angstrom >> D.

That explains why gases at room pressure are ideal.

<u>But if P is much higher</u> → λ smaller → interactions important.

Inter-atomic interactions are important not just for higher pressure applications but because they teach us about forces between molecules – the same forces that hold molecules together in solids and liquids!

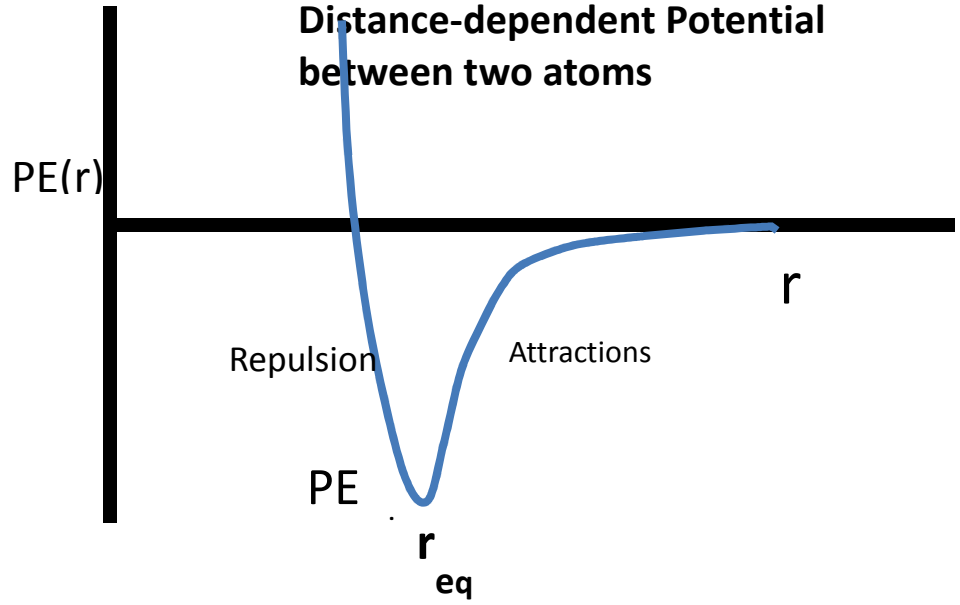
Molecules interact with a distance-dependent potential (and therefore a distance dependent force).

A generic potential energy (or briefly just: potential) of interaction between different molecules is depicted below.

The potential is minimum at a distance we call r_{eq}, because the molecules will like to be at that distance if possible; that's the lowest energy point.

The value of the potential at r_{eq} is labeled as PE_{min}

If the distance is larger than r_{eq}, the molecules attract; if the distance is smaller, they repel – just like a spring would want to contract if you were to stretch it, and to expand if you were to compress it



The most important parameters characterizing the potential (the equilibrium distance and r_{eq} and the minimum potential, $P.E._{min}$) depend on the type of interactions as we'll see later, but the shape is fairly universal.

Typically r_{eq} ranges from below 1 up to 4 angstrom (stronger bonds and smaller molecules are associated with shorter equilibrium distances).

$P.E._{min}$ ranges from:

9eV (about 900 kJ/mole) for N_2

to 0.002eV or lower for weakly interacting helium atoms.

In general:

At far away distances (typically above $2r_{eq}$, i.e., at above 5-8 Angstrom) , the particles barely interact.

What happens at closer distances? Recall that particles will like to get to regions with low potential (nature loves "negative energy", i.e., lowering the potential.)

So for $r_{eq}<r$ the particles will like to get together, to lower their distance to req, therefore they attract;

For $r<r_{eq}$ they strongly repel (particles cannot interpenetrate too much).

Therefore: if the pressure is increased but not too large (typically tens and hundreds of bars), particles get closer to each other, attract each other, and since they "like each other", the volume will fall below the ideal gas law prediction.

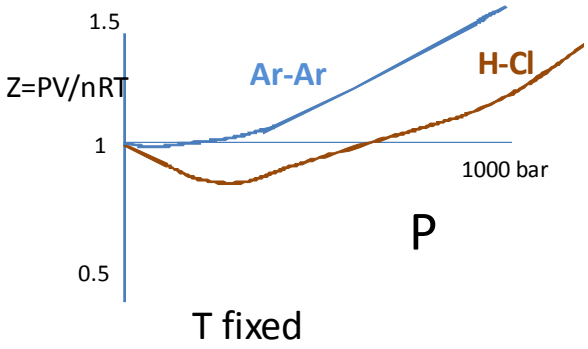
When the pressures are very high (hundreds or thousands of bars and more) particles push each other away, so the volume is increased beyond what the ideal gas law predicts.

Real gases – experiments:

define: $Z = PV/nRT = PV_m/RT$ (see graph, not to scale).

For ideal gases, Z=1. Any deviation from 1 indicates that the gas is not ideal.

Z is a function of P, and T; typically it is plotted as a function of P at one value of T (but remember that Z looks different when a different T is used!)



T fixed

For real (not ideal) gases: when P rises, but is still not very large, the distances between the particles are reduced → attractions between the particles are significant → the volume shrinks, so Z<1

For strongly interacting particles (e.g., HCl molecules, which interact strongly with each other, as we will learn later), the lowering of Z below 1 is a strong effect.

But eventually at very high P→ particles repel each other (they cannot interpenetrate), so the distance between them cannot shrink too much; therefore, the volume will not decrease much. Therefore, the true volume will be much higher than the ideal gas prediction ($V_{m,\ ideal} = nRT/P$, which is very small when P is high since it involves dividing by a high pressure), so $Z=PV_m/(RT)$ will be much larger than 1

So: Z<1 → an indication that attractions dominate

Z>1 → repulsion dominate

Z=1 for ideal gas

Note: when Z isn't close to 1, the ideal gas equation of state is not correct.

Solids, Liquids, gases: physical properties.

Solids and liquids: packed together, together labeled as "condensed phases"

Forces: balanced repulsion + attraction.

We saw: equilibrium distances 2-5 Angstroms;

Distances in gases we saw ~ 30 Angstroms.

Compressibility

κ (kappa) = fractional change in volume per pressure change, when T is fixed.

Gases:

In an ideal gas, κ is large [1]

For example if the initial gas pressure is 1bar, and at fixed T we reduce the pressure by 1%to 0.99bar, then, since PV will be fixed (PV=nRT which does not change), V will increase by about 1%

So κ for a gas (at P^0) = (fractional change of volume)/ (pressure change) ~ 1%/0.01atm =1/atm.

i.e., κ(gases) = 1/P = 1/atm (for standard conditions, P=1 atm)

But for Solids and Liquids

κ(solid/liq.)~ 10^{-4}/atm, much smaller than for gases;

Example: in a diving pool, for each 1 meter we lower ourselves, the pressure on us rises by about 0.1 bar; but our volume barely changes even when we dive!

---

[1] we say ideal gas, but remember that for pressures that are typically encountered in a lab, below 10 bar, real gases are essentially ideal, so below we will refer to real gases as if they were ideal and just call them all gases; of course, as you saw in the discussion of Z, at high pressures the real vs. ideal gases distinction is very important.

Reason that κ(solid/liq.) is small : In liquids and solids, the positions are generally near the equilibrium distances; we need very large pressures for r to decrease significantly from $r=r_{eq}$ to lower value.

Thermal expansion

The thermal expansion coefficient measures the percent change in volume when we raise the temperature:

α (alpha) = fractional change in volume / temperature change

For gases: α is big, since V is proportional to T;

$$V = \frac{nRT}{P}$$

So, if P is fixed, then if we change the temperature by 1% then the volume will change by 1%, i.e., a big change.

But for condensed phases(i.e., solids or liquids) this isn't true; α is much smaller.

E.g., when the temperature changes by 3% (9 degrees Celsius, around 16 Fahrenheit) a car does not change its volume much.

The thermal expansion coefficient for solids and liquids is about 1/1000 times lower than for gases, just like the compressibility.

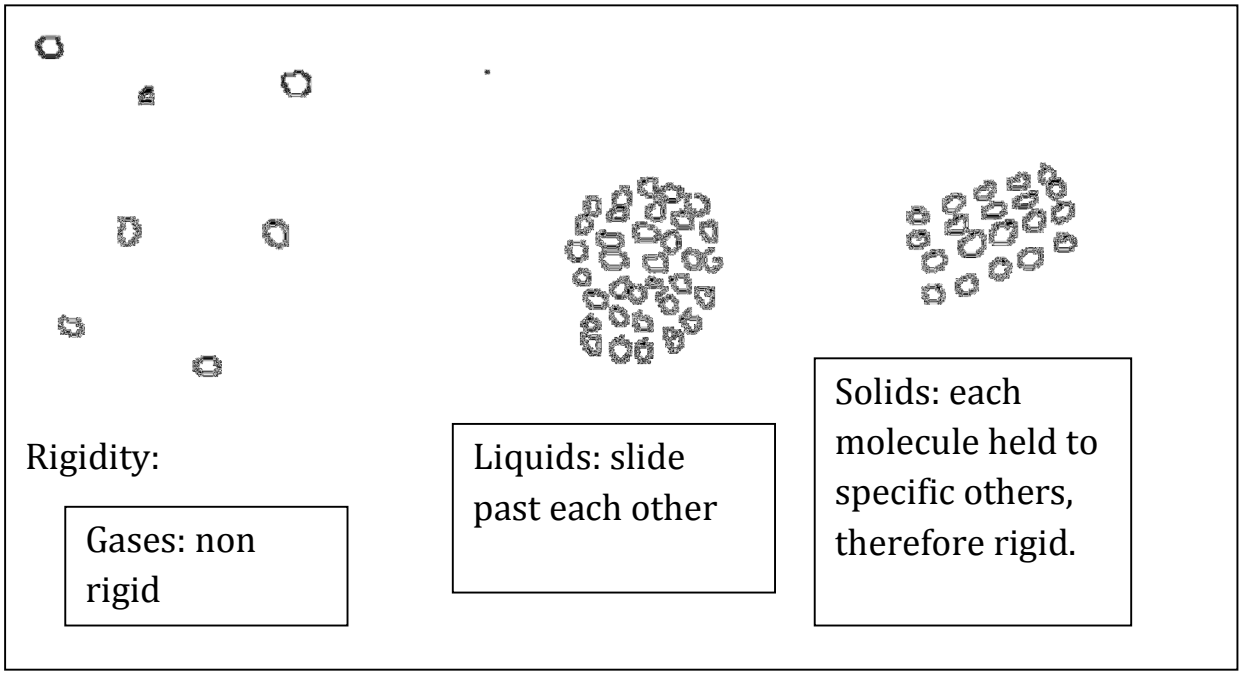
Other Physical properties of materials

Bulk properties:

Fluidity and rigidity: degree to which bulk sample retains shape upon externally applied force.

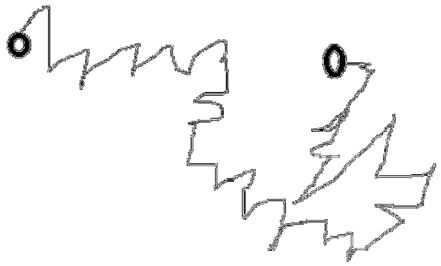
Gases more fluid than liquids;

Liquids more fluid than solids.



Diffusion:

<u>Diffusion is the process of mixing of different substances when brought in contact.</u>



DIFFUSION OF PARTICLES – ATOMIC IN ORIGIN. PARTICLE CONTINUIOSLY HIT BY OTHER MOLECULES, SO HAS "RUGGED" TRAJECTORY.

Diffusion is molecular in origin.

Diffusion is fast in gases as there is little to impede motion.

Side Note: classic example you must have heard about is perfume diffusion (you open a perfume bottle in one side of the room and smell in the other).

HOWEVER: A note of heresy: when you plug in the numbers you discover that the spread of perfume smell cannot be through diffusion – diffusion is too slow beyond a distance of a few cm!

The spread of perfume smell really has to do with weak air-streams that push the molecules around, and not much with diffusion.

In Liquids: diffusion slow. Lack of space impedes motion.

In solids: diffusion is very slow.

T-dependence:

<u>In gases diffusion slows gradually when T rises</u>, since there are more molecular collisions which change the direction of motion.

On the other hand: <u>in liquid as T rises, diffusion is dramatically faster</u> since particles can jump to new places with higher energy. (Tat low temperatures they are almost "locked"

Biology relevance: In small living cells (with size below about 1 micron) diffusion is a mechanism for transport; in bigger or more developed cells other mechanisms (transport along "chains") dominate.

Surface Tension:

Molecules in liquids love to have several neighbors (we'll learn the details of the molecular interactions in a few pages).

But molecules on the surface of liquids cannot interact with many neighbors (for example, in water-air interface, a water molecule on the surface does not have molecules above it, except for an occasional air (N_2) molecule arriving rarely).

Therefore → liquids try to minimize their liquid-air (or generally liquid-gas) surface area, to have as few molecules on the surface as possible.

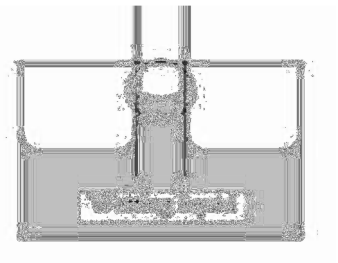
The strength of this "surface tension" effect depends on the type of the liquid.

Figure: Minimization of surface area ("surface tension") causes coalescences of liquid drops to minimize area; causes liquid drops to resist breaking down

Weakly interacting liquids (e.g., He-Ar, Ar-Ar at very low temperatures, where they are liquids) have weaker surface tension, i.e., they "do not mind" having a large surface.

Note: sometimes (e.g., water near wood) the interactions with another surface are actually quite favorable, e.g.., a water molecule likes the surface of some other materials even more than it likes other water molecules. This leads to the opposite of surface tension, a phenomena which is called <u>capillary action:</u>

Capillary action leads to the rise of liquid in a narrow confine (the water climbs to "wet" more of the surface area of the wood)→ capillary action is responsible for delivery of water to and within leaves (water rises within the leaves against the force of the gravity).



Intermolecular forces: Columbic and dipole

Inter means "between different things". Intermolecular forces are the forces between different molecules; this is the opposite of intramolecular forces, which are the forces within a molecule.

Intermolecular forces control chemical and biological behavior, since they are weaker than chemical bonds (i.e., weaker than intramolecular forces, which are so strong that bonds are usually fixed; so it is almost paradoxical that the strongest bonds are not that important biologically—as they don't change!).

Intermolecular forces are mostly electronic (due to attractions between different charges), and are caused less by quantum mechanics (QM) (except for some aspects of van-der-Waals forces, as we'll see later).

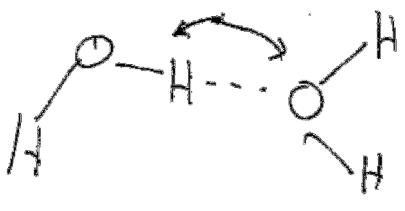
Contrast this with the important role that QM plays in covalent bonds.

Inter- vs. Intra- molecular forces comparison:

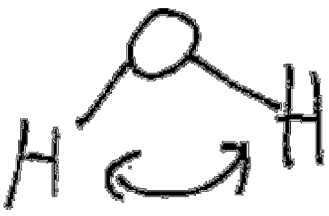
Intermolecular interactions: typically 1-50 kJ/mol
vs. Intramolecular forces (covalent, ionic): 200-900 kJ/mol.

> Side note: Contrast this with RT~2.5kJ/mol;
>
> So we see that the intermolecular interactions are not much larger than RT, which is a measure of the thermal energy;
> But RT<< strength of intramolecular forces, so temperature barely affects strength of intra molecular bonds..

Intermolecular forces: slower fall-off, Intermolecular forces: less directed:



Little energy to rotate around molecules



But :Within a molecule (intra-): a lot of energy to rotate bond

Types of interactions:

Ion-Ion :

Na^+ ---Cl^-

Ca^{2+} ---- SO_4^{2-}

Cl^- --Ca^{2+}--Cl^-

Na^+--Na^-

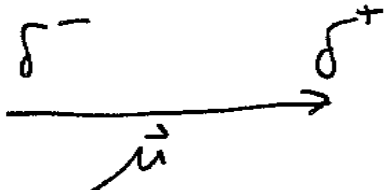
- "Columbic", i.e., due to attraction between opposite charges
- Long range
- Non-directed (does not depend on relative orientation, only on distance, unlike covalent interactions)
- Strong (the same strength as covalent interactions)
- Present in intra-molecular bonds and inter-mol. bonds ; e.g., Na-Cl molecules and Na-Cl crystals.

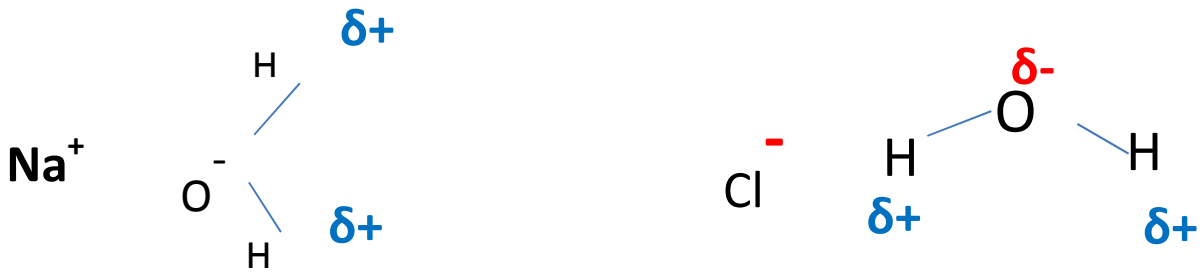
Difficult to even decide if intermolecular or intramolecular!

Ion-dipole:

A molecule with a dipole is a molecule where the positive charge and the negative charge are offset; for example, water, see picture below.

For simplicity, we often replace a molecule with a dipole by a single line, called the dipole moment, where one side is positive and the other negative.





Take an ion in a solution (i.e., "solvated" in a solution), where the solution molecules have dipoles. A positive ion attracts the negative side of the solvent molecule.

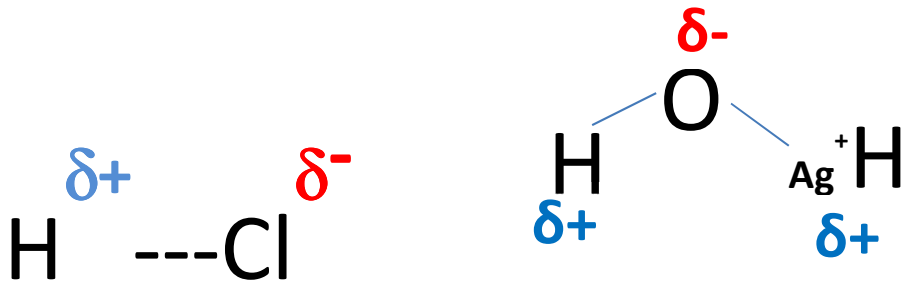
The attraction between the ion and the molecules that have dipole is called "ion-dipole interaction".

Ion-dipole interaction is :

- Stronger than dipole-dipole, weaker than ionic.
- Long range ~ $1/R^2$
- Directional (a rotation of the dipole by 180 degrees turns the interaction from attractive to repulsive, or vice versa).

Dipole-dipole

Water-Water, HCl-water, etc.



The dipole-dipole interaction is directed; see picture below.

On the left side we show two parallel dipoles. The positive charges are closer to each other than the positive-negative distance, so repulsion is stronger than attraction, and the molecules repel each other.

On the right side – dipoles in opposite direction – so there is attraction.

When the dipoles are on the same line and pointing in the same direction, the dipoles will attract.

Dipole-dipole interaction properties:

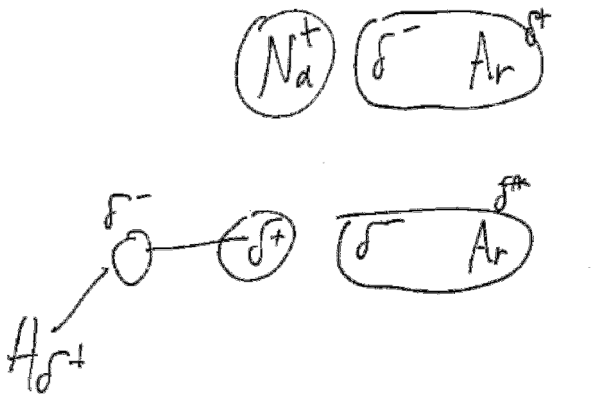
- P.E.: long range ($1/R^3$) but not as long-range ion-ion or ion-dipole
- Directional
- Relatively strong: ~ 5-50 kJ/mol

Induced forces

Several:

Ion -- induced dipole (see fig.)

Dipole -- induced dipole (see fig.)

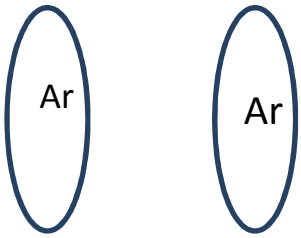


Induced dipole means: Distortion of charge cloud due to other charges.

Another induced force is:

Induced dipole-induced dipole; (Van-der-Walls potential)

Imagine, e.g., Ar-Ar.

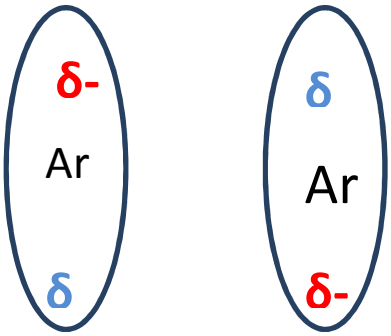


QM says there are fluctuations, i.e., times when the electrons are not in a spherically symmetric shape. For example, there will be times when the fluctuation will look like this (electrons move to right):

Fluctuation

Each fluctuation will induce a dipole in the other molecule, e.g.:

Alternately, a fluctuation along the "y" axis in one atom will induce a dipole in the –y direction in the other atom:



Properties of the vdW (van-der-Waals) interaction:

- Always attractive., so it is not very directional (i.e., even for molecules, the interaction does not depend much on the relative orientation of the molecule). Contrast this with the interaction between two molecules with permanent dipoles, which will attract or repel each other depending on direction.
- Very short-range, $1/R^6$
- Since always attractive, adds up. Can be significant for large surfaces – causes two regions with large surface area that are placed near each other to stick together.

Finally we get from attraction (or mild repulsion) to strong repulsions when atoms get too close:

Exchange Interaction: Repulsive

Due to Pauli principle – not more than 2 electrons can be in the same orbitals.

When we bring two molecules together, the orbitals of each atom start overlapping the core orbitals of the other atoms;

There is no space in these core orbitals for more electrons (they are filled up already), so, due to the Pauli principle, the electrons from the other atom need to be bumped up in energy to high energy orbitals,.

That increases the energy, and higher energy is less "desirable", i.e., the potential energy increases so that there is repulsion

Higher energy → repulsion..

Exchange interaction is VERY SHORT RANGE. It is modeled as if it is a strongly increasing function when R is smaller; typically, it is modeled as proportional to $1/R^{12}$ (note that we decrease the distance by a factor of, $1/R^{12}$ increases by a factor of 2^{12}, i.e., by a factor of 4000!).

Manifestation of Inter-Molecular forces: Boiling Points, Hydrogen bonds.

As T rises, K.E. (kinetic energy)rises.

When T rises, the higher K.E. eventually overwhelms the attraction; so the avg. molecule has enough K.E. to escape from its neighboring molecules,

I.e. if the initial material is a liquid then as T rises, eventually the molecules will have enough kinetic energy to run away, and then the material "boils", i.e., converts to gas..

Therefore:

Larger attractive forces → need higher K.E. to escape → Boiling T (T_B) higher.

Examples:

- The strongest bonds: ionic materials

  T_B(NaCl) = 1686 K ion-ion interactions, very strong).

- The weakest bonds: small molecules interacting by vdW forces

$T_B(N_2) \sim 77K$,

T_B(He)~4K

Both are low temperatures since nitrogen and helium interact through very weak vdW potentials (i.e., vdW liquids –an abbreviation for liquids interacting mainly by vdW forces --- have low boiling temperatures unless the molecules are really big). The boiling temperature is much lower for helium since it has much less "fluctuation", i.e., its electrons are held tightly and are not "polarizable".

Contrast this with the **higher boiling temperatures of some hydrides**:

$T_B(H_2S) \sim 220K$,

$T_B(H_20)$~373K (100 Celsius) :

These hydrides have higher boiling point due to:
permanent dipole- permanent dipole interaction, and in some cases due to H bonds (covalent sharing of H electrons across two bonds; see below).

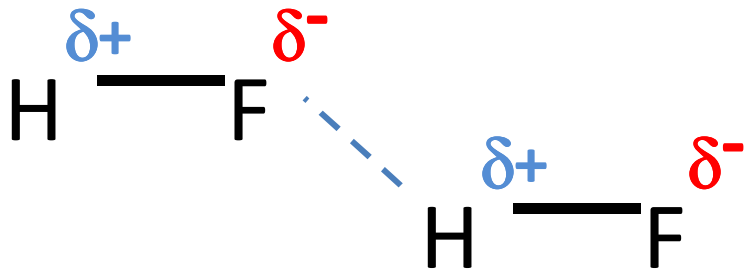
Generally: down a column, vdW interactions increase, and therefore the boiling point of pure materials usually increase down a column.

But there are exceptions, mainly due to **Hydrogen bonds**

Thus: **$T_B(H_2O) > T_B(H_2S)$ (373K vs. 220K) even though S is lower** in the periodic table, and in the same column as O (which implies that the van-der-Waals interactions are stronger in H_2S than in H_2O).

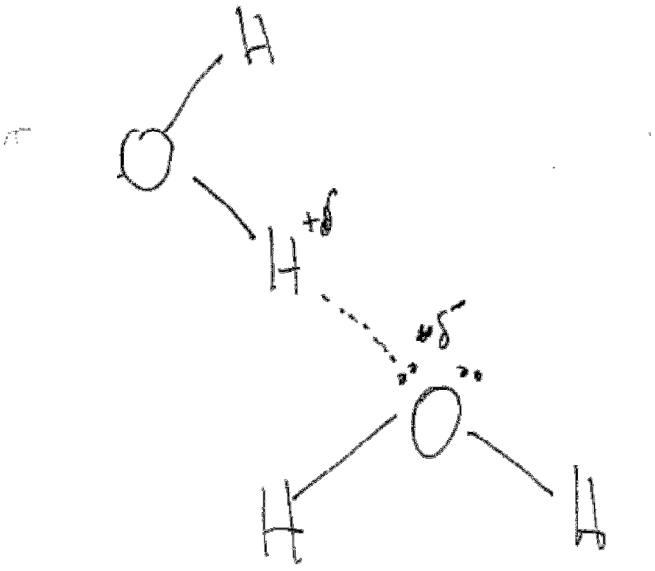
Reason: This is because of hydrogen bonds.

Hydrogen Bonds occur for highly electronegative atoms (F, O N, and somewhat in Cl), so in compounds such as: H_2O, HF, NH_3. See below:



H is partially ionized, so its electron cloud is very small. Therefore, H can bond with a lone pair of a heavy atom in another molecule; see above for HF and below for H_2O:

Water has unique properties due to a high # of H bonds, leading to unique properties:



H-bonds in H_2O are responsible for several properties:

- High T_B
- "Strange" density vs. T behavior (we'll see later) -- not dense, especially ice.
- Larger dielectric constant (response to electricity and E.M. waves).

Part 3: Phases and Phase equilibrium:

Overview:

- **Phases**
- **Phase transitions**
- **Gas-liquid isotherms**
- **H_2O phase diagram**
- **The Solid-Liquid boundary**

Samples that are homogenous in chemical comp. and physical state are called phases.

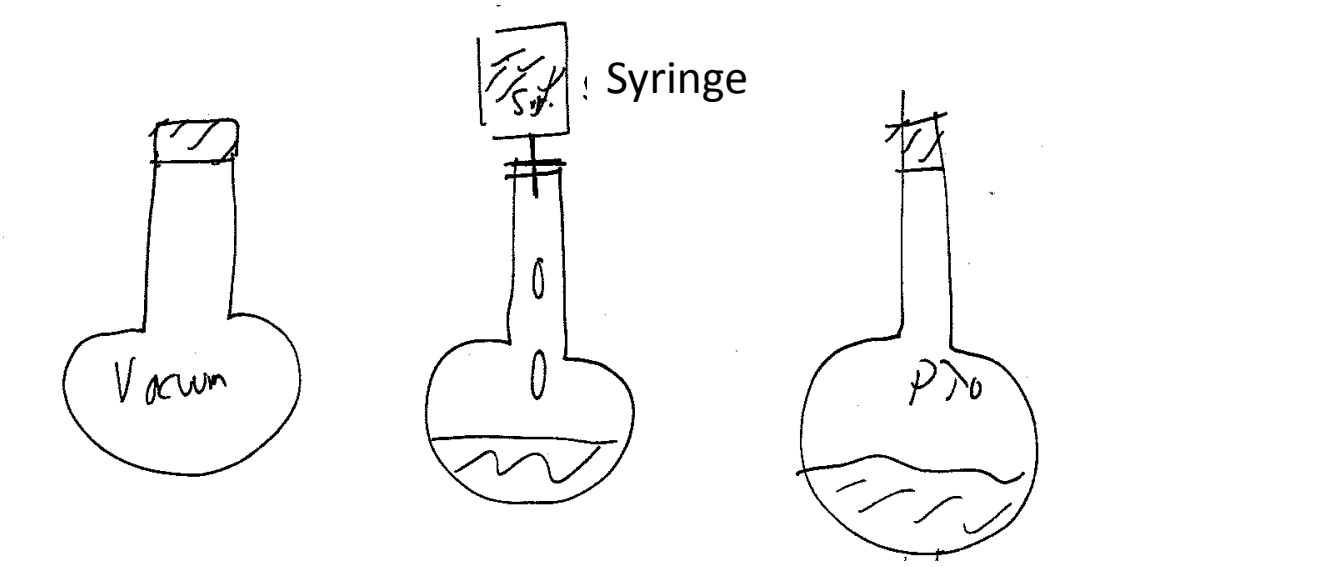
There can be 2 or more phases present at the same time (coexist); e.g., ice-water.

Another example: liquid-vapor transition:

Simplest: closed laundry room (with wet cloths) or closed pool "feeling very humid".

In experiments:

- Evacuate flask
- Introduce liquid that does not fill up volume
- Monitor P



Initially empty

Then: Inject liquid with syringe

Later on: some fluid spontaneously evaporates, Non-zero pressure.

P_{eq}: " vapor pressure": (E.g., $P_{H2O}(T_{room})$ = 0.035 bar; I.e., in an enclosed pool, with 100% humidity, 3.5% of molecules are water.)

Also note:

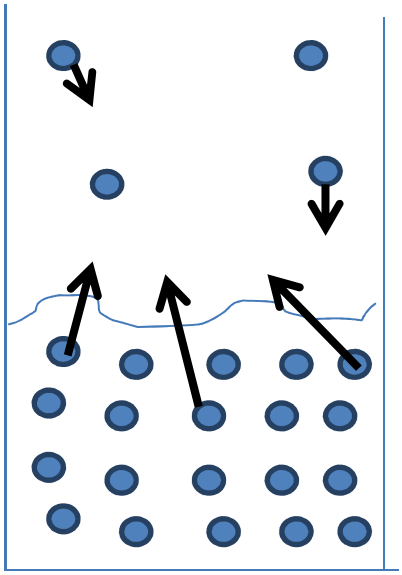
T ↑ P_{vapor} ↑

Microscopic picture:

At any time some molecules get through collisions enough E to leave liquid

Also: gas molecule collide back & trapped in liquid.

So: Equilibrium results when $P=P_{eq}(T)$



Phase eq.: dynamic, molecules leave and join;
In <u>average</u> the number of molecule in liq. and gas is fixed in equilibrium.

Since: the rates of gas-to-liquid conversion and liquid-to-gas conversion will be equal in equilibrium, the number of molecules in each phase is unchanged.

Note:

Our description was for the case that initially the flask contained only liquid (no vapor initially), so we schematically write:

$$H_2O(Liq.) \rightarrow H_2O(\ Liq.).$$

If initially there's no liq., and we instead pump vapor in, then the gas will liquefy:

$$H_2O(Gas) \rightarrow H_2O(\ Liq.).$$

Finally: **what happens if another gas, e.g., air is present?**

Answer: nothing really changes as far as the water vapor and pressures!

The air pressure simply adds up with the water pressure to give the total pressure

$P_{total} = P_{eq\ H2O}(T) + P_{air}$

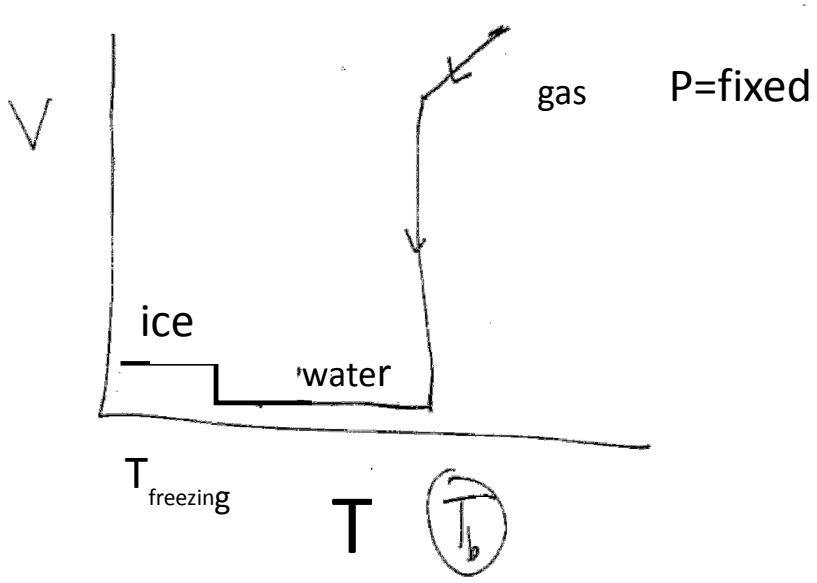
So for example at room temperature, if we have 100% humidity (e.g., water in a balloon), then $P_{eq,\ H2O}(T=298K) \sim 0.035\ P^0$, so if the total pressure is P^0 (sea level), then $P_{air} \sim 0.965 P^0$.

Phase Diagrams

Simplest way to achieve phase transition: Change T at fixed P

Take H_2O at fixed P and, say, 200 ^{0}C → pure vapor.
Now: Reduce T (i.e., remove energy), keeping P fixed→Volume decreases.

At a particular T labeled "boiling temperature" (100 ^{0}C if P=P^0) liquid appears.



After liq. start appearing then (only if P remains fixed!) as we remove energy, T will be fixed until last drop of vapor liquefies.

After cooling to about 0 Celsius, solid appears, resulting at a 2nd phase transition, liq.→ solid.

Note: Reason for bubbles.

If external P is fixed, and T is raised to $T_{boiling}$ or above
(e.g., for water, 100 Celsius for P=1bar, 80 Celsius for P=0.5bar, etc.),
then, at that T, $P_{vapor}(T)=P_{external}$.

At that point, as we continue heating, liq. spontaneously turns at local "hot spots" to have slightly higher temperature, so $P_{vapor}>P_{external}$ at those points so vapor is formed and pushes away the air around it ("boiling").

Note: If we have a fixed volume and slowly raise T (so P is raised at the same time) no boiling will happen! The pressure of the vapor will simply rise.

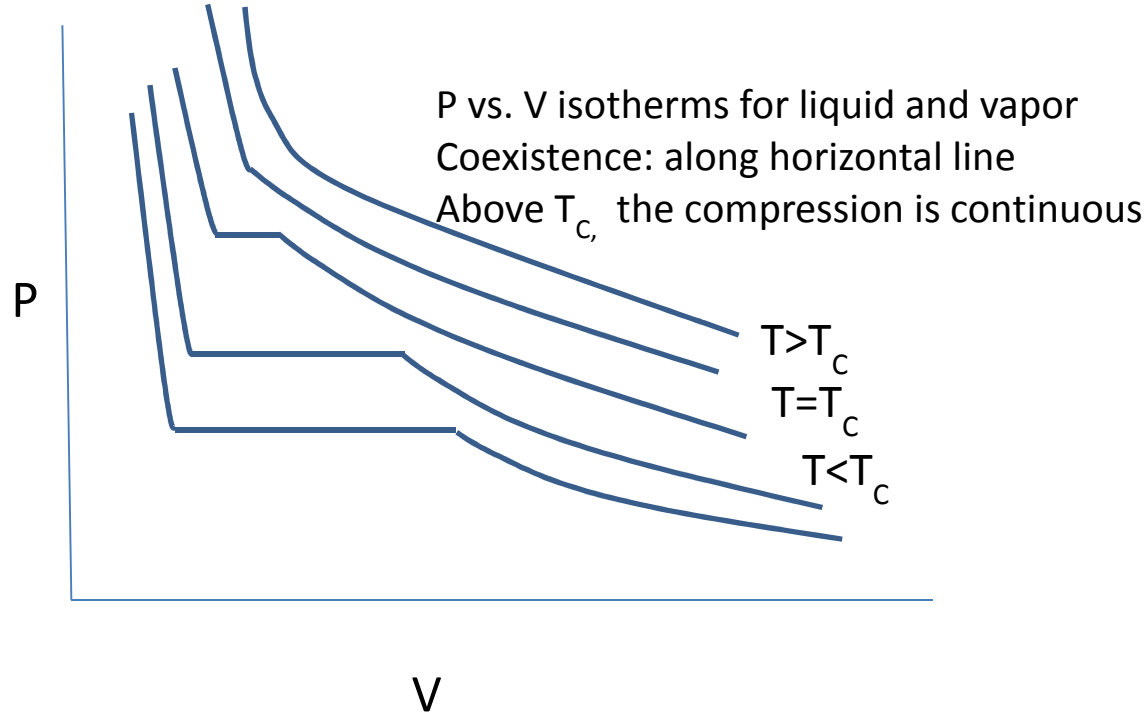
Another way to achieve phase-transition: change P at a fixed T.
Fix T, and P↑

At $P=P_{eq}(T)$ condensation; above $P_{eq}(T)$, vapor turns to liquid.

(At very high pressure: liquid solidifies.)

Another way to look at phase transitions:

Gas Liquid Isotherms: (i.e., lines of constant temperature:)



Compression at const. T. will be different if $T<T_C$, or $T>T_c$. .

(For H_2O, for example, T_c=374celsius=647K, and P_c=220 P^0).

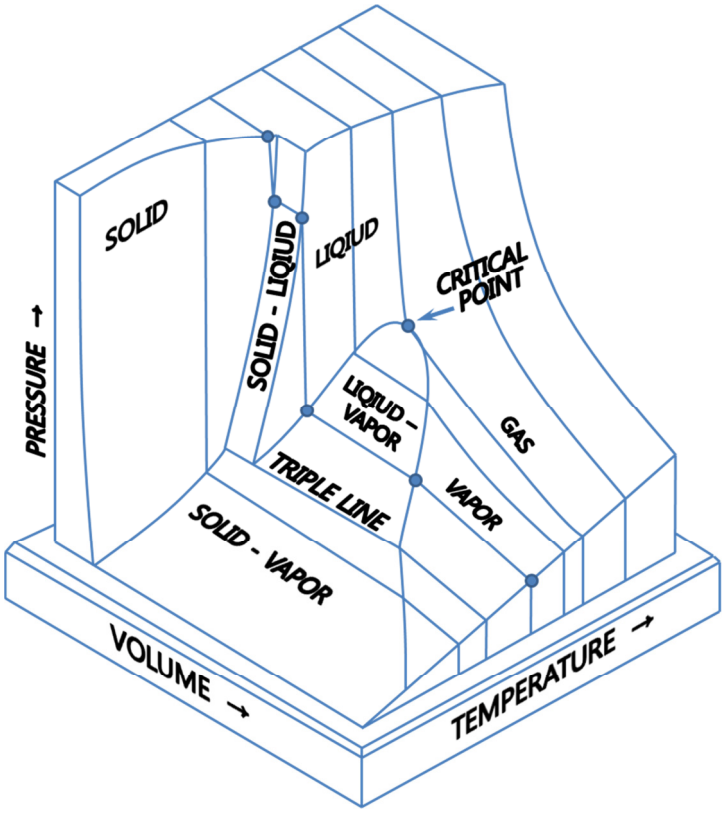
If $T<T_c$, gas liquefies at a T-dependent Pressure ($P=P_{eq}(T)$) ; volume changes then from gas volume to liq. volume as both coexist. P will be fixed for a whole volume range (from volume when pure gas to volume where pure liquid).

This is what happens to water at room pressure P^0 at 100 Celsius; then, as we lower the volume it will change, for one mole, from about 31L (idea gas molar volume for temperature of 100 Celsius), to about 0.02Liter for pure liquid, all the while P being kept at one bar.

But for $T>T_c$: g→ liq. continuously without a phase change when T (and therefore thermal energy) is high enough to overcome binding.

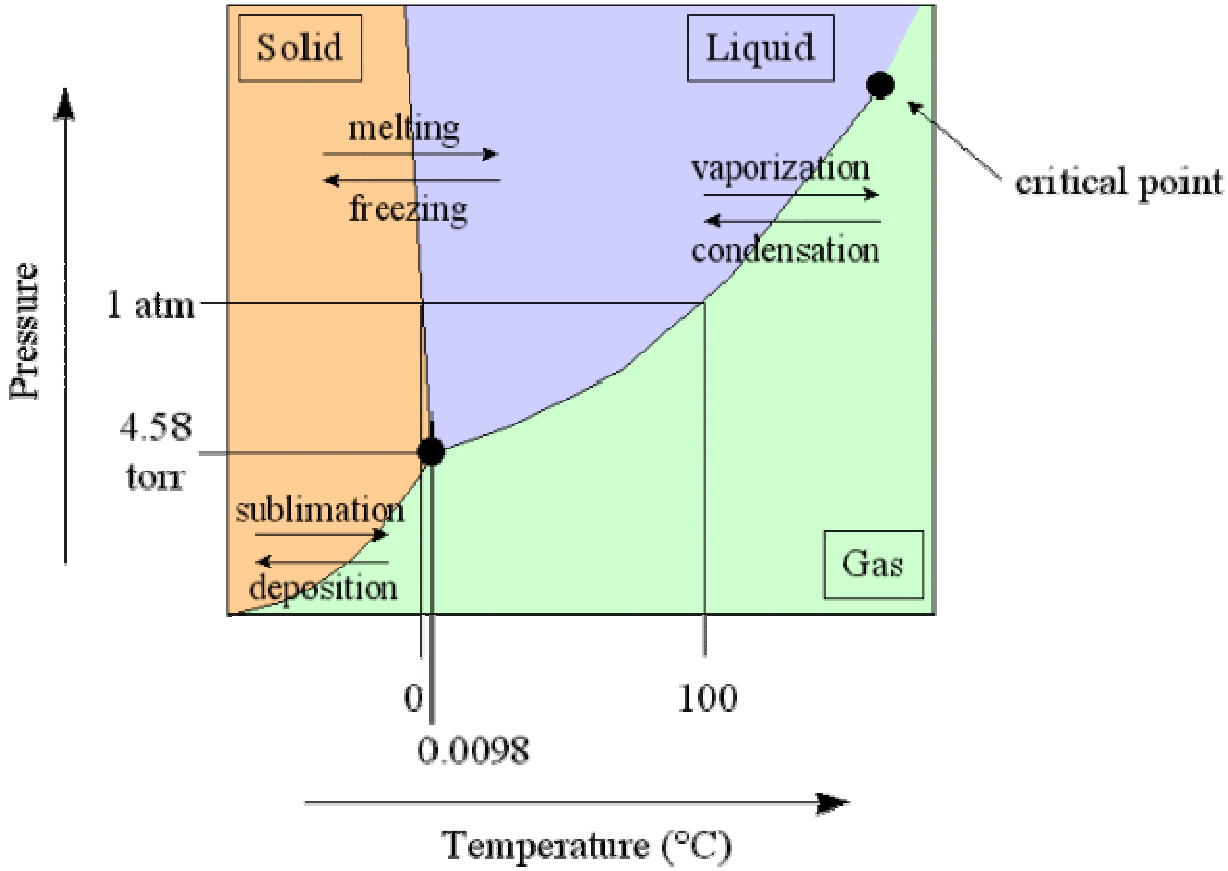
Note: we use g (gas) and v (vapor) interchangeably!!!

Phase diagrams in "3D" (pressure, volume, temperature):



Note how the 2D diagrams we discussed before are much more transparent in this 3D picture – they are projections of this graph.

Phase Diagrams for H_2O: (taken from gi.alska.edu)



In this figure:

m.p. = normal meting point: T(s→l) at 1atm (273K)

b.p. = normal boiling point: T(l→v) at 1atm, 373K (100 celsius)

t.p. = triple point; P,T at which l, v, s coexist
(for H_2O: 0.001Celsius, 0.006 bar)

T_c, P_c: above which there are no l/v phase transitions, just gradual transition; called "supercritical region;
In the supercritical region it isn't possible to uniquely say "liq." or "vap." .

(Note that At high pressures,2000 bar and afovee, other (more compressed) solid phases appear, different from the "usual" ice).

Phase diagrams: the S/L boundary

Water and few other substances: V(solid)>V(liq.)
(E.g., water bottle crack in freezer as water→ice).

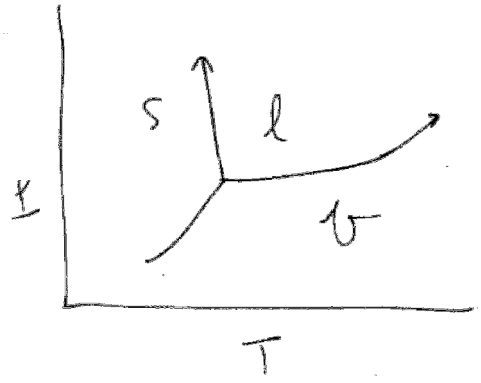
For these substance, as P increases, substances prefer to be more liquid like (lower V)→ so at the same pressure liquid preferred.

Therefore, for water & few others:

$P \uparrow$, $T_{melting}(H_2O) \downarrow$

(This effect is very weak however! Need huge P increases to change $T_{melting}$ by 1K!)

H_2O, few other substances



For most substances, the opposite behavior, since usually:

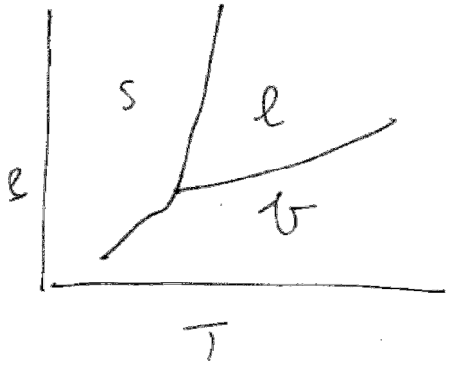
V(solid) <V(liquid),

so

$P \uparrow$ $T_{melting} \downarrow$ (most substances)

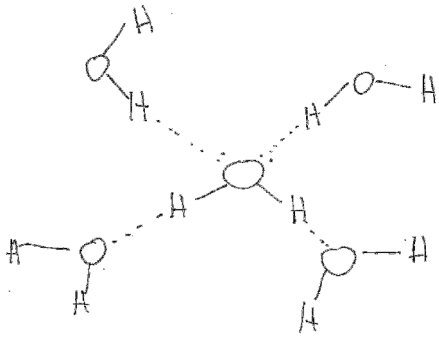
(again, a weak effect).

Most substances



The special behavior of water is called:
"Anomalous" dependence of the S/L boundary on pressure.

It is due to hydrogen bonds, due to which ice has a big volume:



Part 4: Solutions

Topics:

- Mole fractions, molarity, molality
- Molality.
- Macroscopic nature of dissolved species.
- Solution reaction stoichiometry

Solution is : A "homogenous system with 2 or more substances" (usually liquids or gases)

Composition measures:

Mole fraction of a substance "i"

$$X_i = \frac{n_i}{n_{tot}}$$

Sum of the mole fractions is 1:

$$\sum_i X_i = \sum_i \frac{n_i}{n_{tot}} = \frac{1}{n_{tot}} \sum_i n_i = \frac{n_{tot}}{n_{tot}} = 1$$

$$\sum_i X_i = 1$$

(e.g., salty water could be 5% salt and 95% water, together 100%).

Other measures beyond mole fraction:

Molarity:

$molarity = \frac{\text{moles of solute}}{\text{Liters of solvent}}$ (mol/L)

Measure: M = (definition): mol/L.

Example:
0.2 mole of NaOH in 20 Liter of H_2O: molarity = 0.2 mol/20L = 0.01 M

Another measure is: Molality:

$$molality = \frac{\text{moles of solute}}{\text{Kg of solvent}} \text{ (mol/Kg)}$$

Molarity will change with T if V changes; Molality won't change with T, so it is easier to use.

INSERT (as always, required): Different composition measures can be related:

E.g., take the example of a binary solution:

$$\frac{X_A}{X_B} = \frac{\frac{n_A}{n_{tot}}}{\frac{n_B}{n_{tot}}} = \frac{n_A}{n_B}$$

i.e., (since $X_A + X_B = 1$)

$$\frac{X_A}{1 - X_A} = \frac{n_A}{n_B}$$

So, if B is solvent (e.g., water) and A is solute, then, we define

$$\text{Molality} \equiv \frac{n_A}{mass(B)}$$

$$= \frac{n_A}{n_B * \ mol.mass(B)}$$

$$= \frac{1}{mol.mass(B)} \frac{n_A}{n_B} = \text{(using the Eq. above:)}$$

$$\text{Molality} \ = \frac{1}{mol.mass(B)} \frac{X_A}{1 - X_A}$$

END OF INSERT

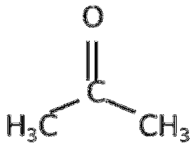
Macroscopic Nature of Dissolved Species

Dissociation of a species (the "solute") in a solution (i.e., in a "solvent"), is caused by combination of 3 effects

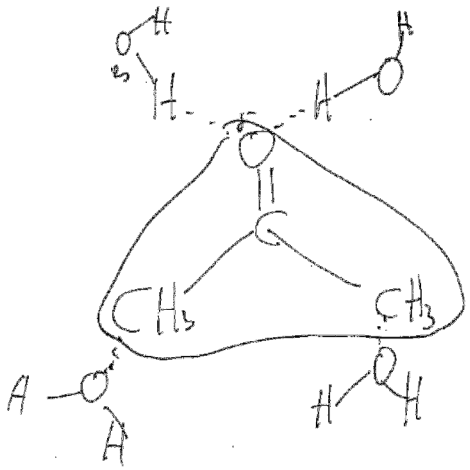
1. Solute-solute bonds break (loss of attraction, not favorable)
2. New I.M. bonds form between solute and solvent (gain of attraction, favorable)
3. There is much more "disorder", which increases the possibilities for dissociating (favorable); we'll study this later.

Dissolved species appear in solution in several forms:

- **Intact solvation** (e.g., acetone, CH_3COCH_3)



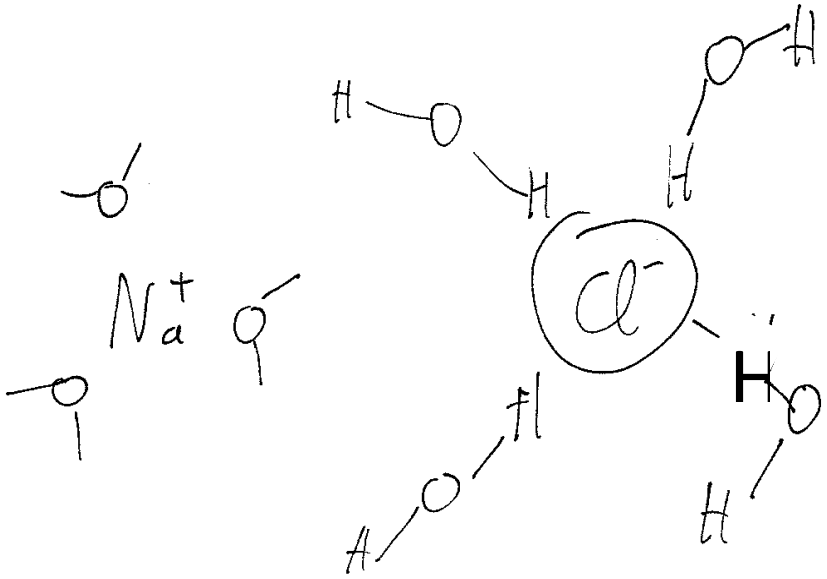
which dissociates like this:



(In this example: solvation using dipole-dipole interactions and H bonds.)

Break completely: e.g., NaCl.

(Here: solvation due to ion-dipole interaction)



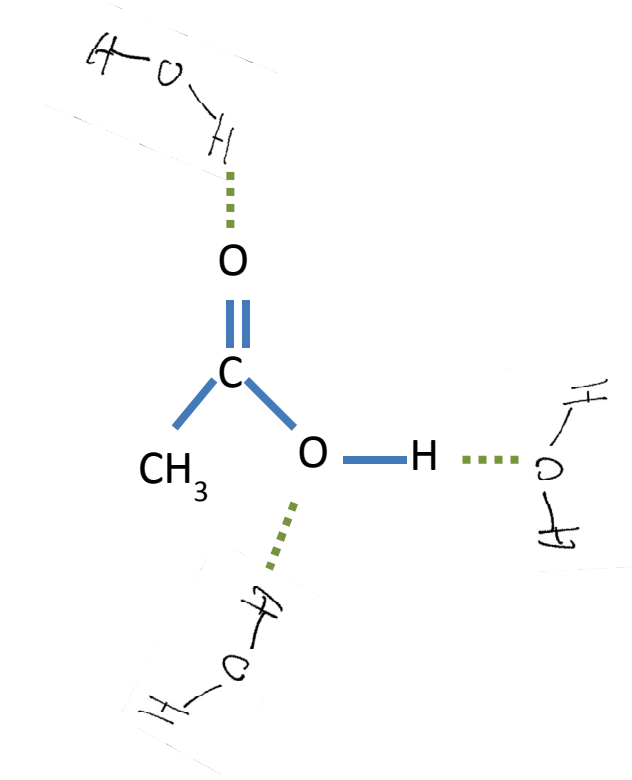
Mixture:

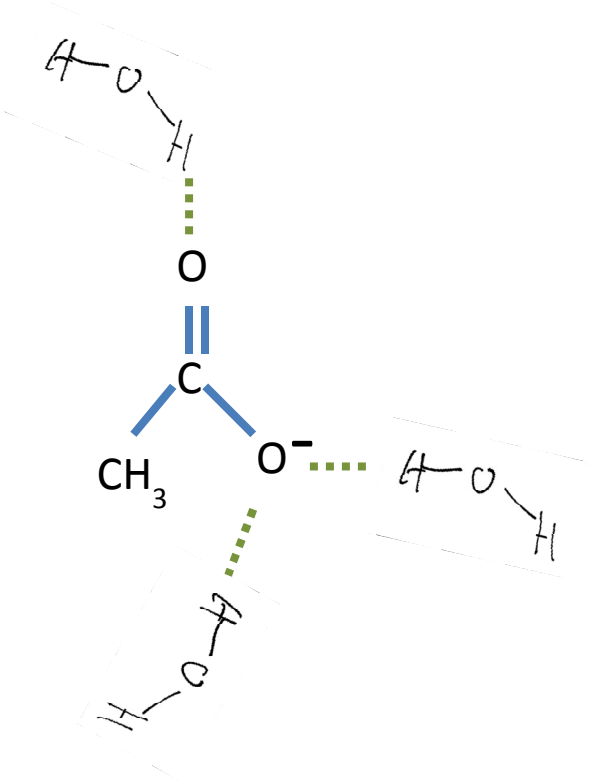
Other solutes (weak detergents) exist in solution as **mix of intact molecules and ions.;**

E.g.,: acetic acid

$$CH_3CHOOH(s) \rightarrow$$

$$CH_3COOHH(aq) \leftrightarrow CH_3COO^-(aq.) + H^+(aq.)$$


O
C
CH3
O
H


O
C
CH3
O⁻

INSERT: Solutions rxn. Stoichiometry (not covered in class, but you will need to know this!)

Vast majority of chem. rxns. happen in solution.

Need to convert stoichiometry of rxns. to eqns. for concentrations rxns.

Schematically, 3 steps are needed:

- Concentrations of reactants → Volumes and Molar quantities
- Volumes and Molar quantities → # moles of products
- # moles of products → concentrations of reactants

Example:

$$2Br^{-}(aq.) + Cl_2(aq.) \rightarrow 2Cl^{-}(aq.) + Br_2(aq.)$$

Question: Say we have 75mL of 0.08M solution of NaBr. (M means: mol/L)

1) What's the Volume of 0.03M Cl_2 solution that's needed to react completely with Br^{-} ?

2) What's the conc. of Cl^{-} in resulting solution.

Answer:

First: note that NaBr essentially breaks completely to Na^{+}, Br^{-}

We know the Volume → get # of moles of reactants

moles Br^{-} = Vol.(L) * conc.(M) = 0.075L * 0.08 M

$=6 * 10^{-3}\ mol$ [Remember: M = mol/L].

To learn from this about the products, we'll use:

RXN. Stoichiometry:

1mol. Cl_2 reacts with 2 mol of Br- →
$3 * 10^{-3}\ mol$ of Cl_2 reacts with $6 * 10^{-3}\ mol$ of Br-

So: The answer to (1), i.e., the volume of the Cl_2 necessary to react with Br^{-}:

$$V(\mathrm{Cl_2}\ solution) = \frac{\#mol}{conc.\left(\frac{mol}{V}\right)} = \frac{3 * 10^{-3}\ mol}{3 * 10^{-2}\ mol/L} = 0.1L = \mathbf{100}\boldsymbol{mL}$$

Note that when mixing 75mL of 0.08 M NaBr with 100mL of 0.03 M Cl_2 , final volume is about 175mL (not exactly, since molecules in solution rearrange to have smaller or higher volume, but we'll approximate that the rearrangement effect is small and does not change the total volume appreciably).

So assuming rxn. goes completely to products (recalling that for every Cl_2 mole we produce 2 moles of Cl^- , so $3*10^{-3}$ mol of Cl_2 will give $6*10^{-3}$ moles of the ion):

$$Conc.of\ Cl^- = \frac{\#mol\ of\ Cl-}{Vol} = \frac{6 * 10^{-3}\ mol}{0.175L} = 3.4 * 10^{-2}\,\frac{mol}{L} = 0.034\ M$$

i.e.,

$$[\boldsymbol{Cl^-}] = \mathbf{0.034}\boldsymbol{M}$$

END OF INSERT

Parts 5-7: Thermodynamics

Overall Aim in chemistry:

- What reacts?
- How far reactions goes?
- T, P effects on rxn.
- Energy liberated or absorbed.
- How to optimize rxn.

Along the way, study lots of physics (engines, efficiency, energies, etc.)

Part 5: The first law.

Overview:

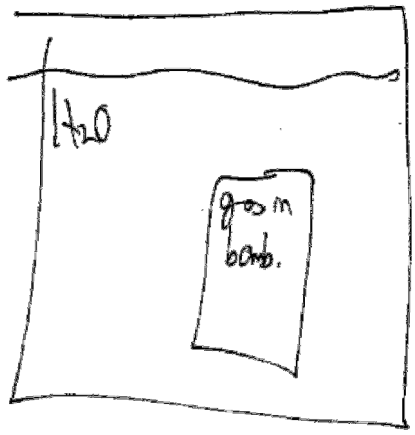
- Reversible, irrev. processes, energy
- Work and Heat
- First law
- q, w and U in specific cases
- Enthalpy
- Heat capacity

Reversible, irrev. processes, energy

Definitions:

System: part we care about. Depends on what goal is.

Example: Bomb calorimeter. Device to measure energy release in rxn. from the rise in the water's T..



System can be:

Gas in "bomb";

or: Gas in "bomb" + water.

The description will change depending on what we define as system!

Some definitions:

Extensive properties: Proportional to system size..

Intensive properties: Independent of system size (T,P, $V_m = V/n$).

Thermodynamic state: Macroscopic condition in which P,T,V are well defined.

Equilibrium: Thermodynamic state where nothing changes.

Eqn. of state: a relation between P,V,T

Note: PV=nRT is an eqn. of state but it only applies for rarefied ("ideal") gases.
Never apply PV=nRT for liquids or solids! It is not true for them!

For example: for liquids, e.g., water, when P rises and T is fixed, V barely decreases! While for gases, when P rises and T is fixed, V shrinks!

Reversible processes: a type of transition between states which proceeds through continuous series of thermodynamic states, and can be reversed at any stage

Irreversible: Otherwise.

EXAMPLE: Start piston at P_1, V_1, T_1, and n; End at P_2,V_2,T_2, and same n. ($P_2>P_1$, $V_2<V_1$)

If the transition between 1 and 2 is through gradual slow increase of pressure and compression of the volume, then the transition is reversible;

But if the transition happens by placing a large mass on top of the piston and suddenly letting it go, then the process will be irreversible (the piston will compress and expand back and forth until eventually it will settle down at the new volume); i.e., throughout, P may not even be defined, only at the end.

Work and Heat, 1st Law, path dependent (q, w) vs. path independent quantities. Work as area.

There are two different types of energy transfer.

Heat: E transfer by thermal contact

Work: Ordered transfer (mechanical pushing or electron current).

Heat example:

Throw an iron bar with a hot T (T_{iron}) to water at a colder temp., T_{water}; there will be a transfer of thermal energy from the hotter object (the bar) to the colder one (water) and the eventual systems will be iron+water at a temperature T_f which is in between T_{iron} and T_{water}.

This energy transfer is called "heat", denoted by q, and has energy units.

Work derivation and example

First and foremost we'll consider mechanical work ("pushing") (electrical work will be considered much later, in the context of batteries).

Work= energy transfer. (units: J)

Work derivation: We'll derive the machnical work in a piston (piston pushed or expands)

Small amount of work will be denoted as dw (as in calculus, "d" denotes small).

Recall that change in energy = force*distance

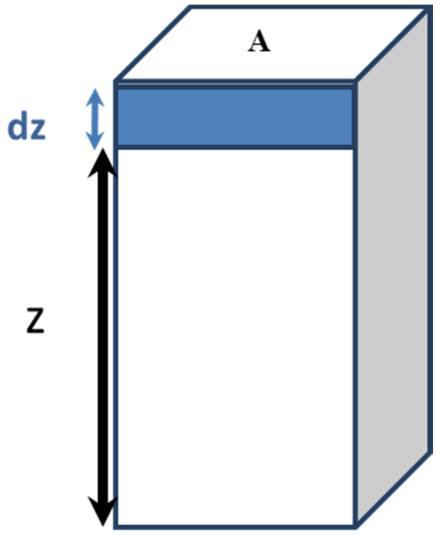
$$dw = -F * dz$$

(the negative sign in –F is there since work is done by the piston on the environment, i.e., when the piston expands and dz>0, the piston's gas, which pushed to expand the gas, lost energy, so dw<0).

Recall that

$$F = P_{ext}\, A$$

where A is cross sectional area of piston.



So:

$$dw = -P_{ext} A\, dz$$

But (see figure!)

$$A * dz = dV = volume\ change$$

So:

$$dw = -F\, dz = -P_{ext} A\, dz$$

which implies:

$$dw = -P_{ext} dV$$

We derived **dw=-P_{ext} dV** for a specific geometry, but this is a general equation for the mechanical energy for any compression or expansion (i.e., valid for general shapes!)

Note:

As mentioned, dw<0 if dV>0 → if piston expands, it loses energy since it does work on surrounding.

Relevant pressure – always the external. E.g., if there is no external pressure, and the piston expands, it does not lose any energy. (Similar to weight lifting if the weight you lift is very light – you won't spend any energy then!)

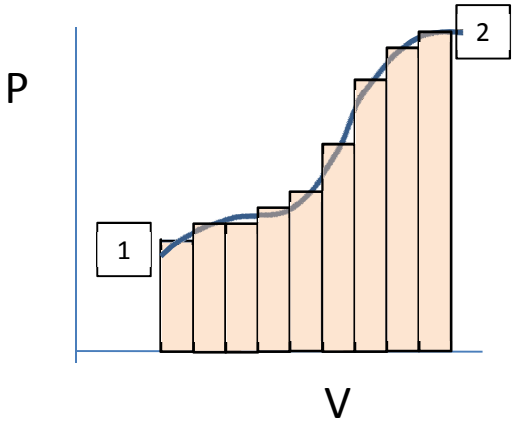
<u>For reversible process: simplification</u>; P_{ext} has to be almost equal to P (as otherwise piston will expand or compress quickly and not reversibly), so:

Reverisble processes : $dw = -PdV$

INTEGRAL FORM: $\boldsymbol{w_{reversible} = -\int PdV}$

So far: the "differential" form of the work. What happens if we take a finite, long path? See picture.

Then: each column's area is hieght*base, i.e., P*dV, i.e., -dw;



So the sum of the areas is

$$w = sum(dw) = \int dw = -\int PdV$$

i.e.,

$$-w = \int PdV = area\ under\ trajectory\ if\ P,V\ used\ to\ characterize\ it.$$

DIGRESSION ON CALCULUS (not covered in class, but required).

We need to calculate summation over small changes; for example, the amount of work spent in a process is

$$\omega = \sum d\omega$$

Where the sum is over all the steps, i.e., we expand (or compress) from the initial to the final volume, the expansion is done in little steps, in each step the work is $-PdV$ (where P is the pressure at each step), and add that up.

If you learned calculus, you know that this operation of summing over the contribution of many small steps is called an integral, and is denoted by a stretched-S (i.e., a stretched **S**um):

$$\omega = \int_{\text{initial volume}}^{\text{final volume}} d\omega = \int_{1}^{2} d\omega$$

where we denote by *"2"* and *"1"* the final and initial states.

The two integrals you need to know are:

$$\int_1^2 dx = x_2 - x_1$$

(This is obvious – the sum of volume changes is the difference between the final and initial volume), and

$$\int_1^2 \frac{dx}{x} = \ln\left(\frac{x_2}{x_1}\right).$$

(If you never saw this, accept it till you study calculus). Note that we use here ln, i.e., logarithm in base "e", where e=2.7….

Finally, if there's a constant we can take it out of the integral, e.g.,

$$\int_1^2 R\,dx = R\int_1^2 dx$$

END OF DIGRESSION, BACK TO THERMODYANMICS.

The derivation so far leads to the first law, which is nothing more than a statement that energy is conserved, i.e., any energy transfer can be decomposed into a heat part and a work part:

First law:

$$\Delta U = q + w$$

Where:

- ΔU: energy change of system
- q: heat involved in process
- w: work involved in process

To conclude: change in energy is due to heat plus work.

However, we have to carefully understand what each term corrspondes to, see next page.

Note:

No matter what's the intermediate step, & whether process is reversible or not,

$$\Delta U = \Delta U(T_1, V_1, P_1 \rightarrow T_2, V_2, P_2) = U(T_2, V_2, P_2) - U(T_1, V_1, P_1)$$

is the same and depends only on initial and final states, not on process in between. (Here we assume n is fixed, this can be generalized to cases where n changes).

U is called: state function as it depends only on current state (T,V,P and n), and not on the history.

But q, w are history dependent. I.e., Diff paths will yield: same ΔU, diff. q, w

See picture—area under blue curve, i.e., -work, is different from under red curve!

$$q_A \neq q_B$$

$$\omega_A \neq \omega_B$$

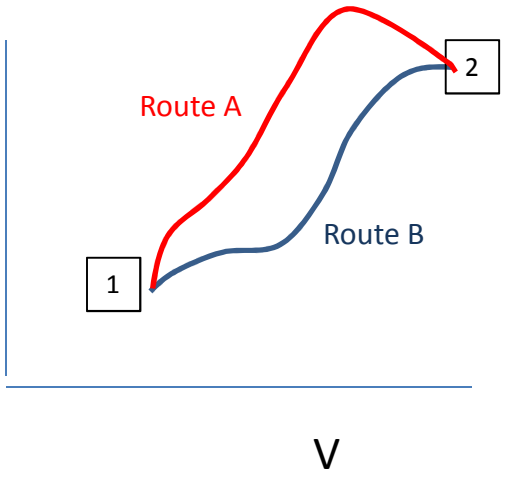
$$\Delta U = q_A + \omega_A = q_B + \omega_B$$

Note: because energy is a state function, the accumulated change dU is denoted as ΔU;

The accumulated q is denoted as q_A or q_B depending on the path taken (or q_c if another path, C, is taken, etc.); therefore, there is no such thing as

~~Δq~~ ~~Δw~~

since q,w are path dependent.



q and w in specific cases; enthalpy.

Usually it is a pain to measure w; we usually want to find out how much q is, and furthermore, we want to express q somehow as relating to state functions.

We learned now that this is not possible in the general case, as q is path dependent.

However, there are specific cases when we can do it.

Assume in the following that there is only mechanical work, i.e., no electrical current so no electrical work.

Then, the simplest case is :

Fixed Volume:

Then,

$$d\omega = -PdV = 0 \quad (\text{if V is fixed, so dV} = 0)$$

So:

$$dU = dq + d\omega = dq - PdV = dq \ (\text{for V fixed})$$

i.e., denoting q by a subscript V to emphasize that we talk about processes where the volume is fixed throughout,

$$dU = dq_V \quad (\text{if V fixed through process})$$

So we can relate the energy and the heat for a fixed volume processes, i.e., reaction in a closed rigid flask.

Two notes:

Only valid if V fixed throughout processes;
it is not enough that V(initial) and V(final) are the same.

However: Most reactions take place at fixed P, not fixed V; so need a new quantity:

Enthalpy:

For convenience (we'll see shortly why) we define a new function, which we label enthalpy:

$$H = U + PV$$

This is a general definition. It is especially useful and important however, for one type of processes, where P is fixed throughout the whole process.

Formally,

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

If the pressure if fixed, and $P=P_{ext}$ for simplicity (i.e., as in reversible processes), then

$$dH = dU + PdV$$

(This is because P is constant through the process!)

On the other hand, the 1st law gives:

$$dU = dq + d\omega = dq - PdV$$

So therefore:

$$For\ fixed\ pressure: dH = dU + PdV = dq - PdV + PdV = dq$$

i.e., for a process where the pressure is fixed throughout (so q is labeled by subscript p):

$$dH = dq_P \quad \text{(for fixed P process only!)}$$

And if we accumulate over many changes, the change in enthalpy will be related to the heat given/taken:

$$\Delta H = q_P \quad \text{(for fixed P process only!)}$$

Therefore, we don't have to worry about measuring pressures and volume if we do a process at fixed pressure; we can measure the enthalpy change directly

from the amount of heat input into/from the system, which is usually an easy task.

Conversely, enthalpy is a state function, which means it can be tabulated, so we can calculate amounts of heat given/taken from the system by using tabulated enthalpy differences; but this is only true if the pressure is fixed!

Since in real life we do experiments in labs, where usually the pressure is fixed (at 1atm or similar value), enthalpy is very useful.

Finally, some definitions for later. For a fixed P process:

$$\Delta H < 0 \rightarrow \quad q_P < 0$$

(heat released by system at fixed P process if enthalpy decreases)

Such $\Delta H < 0$ processes are called **exothermic** (since heat is released – "exo" means to output in this context).

And conversely there are **endothermic** processes where heat is absorbed:

$$\Delta H > 0 \rightarrow \quad q_P > 0$$

Heat Capacities, relations between them:

Heat capacity is amount of heat over temperature change:

$$C \equiv \frac{q}{\Delta T}$$

so

$$q = C\Delta T$$

To be more precise, we need to consider small changes, i.e.,

$$C \equiv \frac{dq}{dT}$$

C depends on:

- System (phase, identity)
- Nature of process: e.g.,

Constant P:

$$C_P \equiv \frac{q_P}{\Delta T}$$

Constant V

$$C_V \equiv \frac{q_V}{\Delta T}$$

(Other possibilities exist, but we'll usually consider only const. P or V for heat capacities.)

Note: if P is fixed and we raise T, then in 99% of the cases V expands

(an exception – water between 0 Celsius and 4 Celsius slightly shrinks)

But ignoring this exception, then, if V does expand when T rises, like in 99% of the cases, then work is done in this expansion – so more heat is needed to expand at fixed pressure than at fixed volume;

This is because in the fixed pressure case, some of the input heat goes to doing work on the environment, rather than just raising the temperature. In the fixed volume case all the heat goes into raising the temperature and none goes to work.

Therefore, q_P will be higher (for the same ΔT) than the case that no work is done (when C was fixed) and therefore:

SO: almost always, for the same ΔT, $q_P > q_V$.

I.e., almost always $C_P > C_V$

Some equations:

Molar heat capacities

$$C_{Pm} = \frac{C_P}{m}$$

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

Expressing heat capacities in terms of state-functions: C_v is related to q_v, and q_v related to U:

$$C_V = \frac{dq_V}{dT} = \frac{dU}{dT}$$

And

$$C_P = \frac{dq_P}{dT} = \frac{dH}{dT}$$

Actual relations between heat capacities

- **For solids and liquids** very little work will happen when the temperature rises (since the total volume is very small, and therefore the volume change is even smaller) so:

  There will be very little difference between q_P and q_V for solids/liquids.

  And therefore:

  C_P is almost equal to (very slightly larger usually from) C_V for solids/liquids.

- **Gases:**

  Note that for **ideal gases:**

  $$H = U + PV = U + nRT \ (ideal\ gases\ only)$$

  So (we fudge the math. a little, but that's OK):

  $$C_p - C_V = \frac{dH}{dT} - \frac{dU}{dT} = \frac{d(H-U)}{dT} = \frac{dnRT}{dT} = nR$$

  i.e., for **ideal gases only**

  $$C_p = C_V + nR \quad \text{(ideal gases only!!!!)}$$

Qualitative considerations on the heat capacities for ideal gases, and examples:

An interesting fact (no proof here:) Each degree of freedom that's "active" contributes R/2 to $\boldsymbol{C_{Vm}}$

Note on "active" degree-of-freedom: we learned when we talked about the Boltzmann factor that if there is a degree of freedom such that its excitation energy is very high compared with RT, then it will be in the ground state, i.e., will not be excited, and will therefore not contribute to heat-capactity

Examples:

Monatomic ideal gas: can move in x, y, z directions→ 3 degrees of freedom →

C_{vm} (He, etc.)= $3R/2$

Diatomic ideal gas like O_2 around T(room): in addition to center-of-mass moving in the x, y, z direction, the diatomic "rod" can rotate in 2 directions (but cannot vibrate unless T is very high) → 5 degrees of freedom

C_{vm} (O_2,etc.)= $5R/2$ 10K<T<1000K

Note:

- below ~10K rotations not excited;
- above 1000K vibrations need to be included as thy get excited; specifically, at room temperature O_2 does not vibrate, and it needs very high temperatures (higher than 1000K) to vibrate. But at high temperatures (more than say 1500K) it will vibrate freely, so its C_{Vm} will be higher than 5R/2.

Therefore:

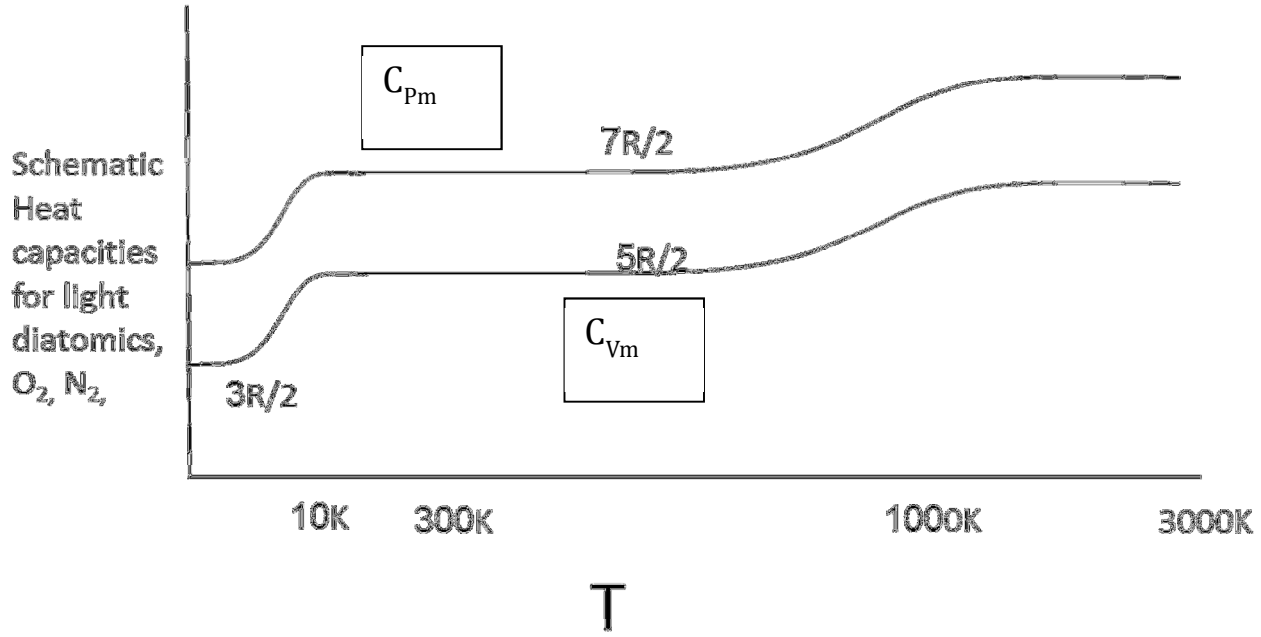
For monatomic gas (He, etc.):

$$C_{Vm} = \frac{3R}{2}, \quad C_{Pm} = \frac{5R}{2}$$

For O_2 and similar:

$$C_{Vm} = \frac{5R}{2}, \quad C_{Pm} = \frac{7R}{2}$$

Note that the heat capacity changes (increases) as we go to bigger molecule (more degrees of freedom), but the relation $C_P=C_V+nR$ is valid for any (ideal) gas (proof : 110A)



Detailed discussion of this figure.

Note that the heat capacity of oxygen is 3R/2 at very low temperatures, where the only motions are of the center of mass (rotations cannot be done since they require energy and there is not enough energy at low temperatures)

At a large range between very low temperatures and very high temperatures, 10K<T<1000K the fixed-volume heat capacity (C_{Vm}) is 5R/2, since to the 3R/2 from the center of mass motion we add 2 more degrees of freedom associated with rotations perpendicular to the diatomic axis,

I.e., if the diatom is in the z direction, there will be rotations around the x and around the y directions; rotations around the z axis do not contribute since they don't involve motion of nuclei.

Each degree of freedom gives R/2 to C_{Vm}, so altogether we have:

$$C_{VM} = \frac{3R}{2} + 2 * \frac{R}{2} = \frac{5R}{2}$$

At very high temperatures when the vibrational degrees of freedom contribute, C_{Vm} becomes even higher (7R/2, and then even higher).

At every temperature, $C_{Pm}=C_{Vm}+R$ for ideal gases, as we will not prove (but will use).

Solids and liquids heat capacity-repeat

As mentioned, for solids and liquids the $C_p=C_v + nR$ relation is **not true**; instead:

$C_P \cong C_V$ for solids, liquids.

The reason is that the volume of solids and liquids is very small, and not changeable easily, so very little work can be done on solids and liquids.

The properties of solids and liquids – including volume and entropy, as we'll see below -- are mostly determined by the temperature. Thus, we get that in some respects they are analogous to ideal-gases, their extreme opposite, since in ideal gases the energy depend solely on temperature.

However, the analogy cannot be pushed too far, since in ideal gases the volume depends on pressure, and for solids and liquids (within the same phase) it usually hardly changes with pressure.

Reversible processes in i.g. (ideal gases): isothermal expansion and adiabatic expansion

Useful to demonstrate laws and importance in thermodynamics.

Say we do a reversible isothermal expansion of ideal gases: State 1→ state 2.

(Isothermal expansion (or compression) means that T is fixed, while P and V vary.)

Then, ΔU=0 (since T is fixed and we know that for ideal gases, U is only a function of T).

Also:

$$\omega = \int_1^2 d\omega$$

$$\omega = -\int_1^2 PdV$$

where P is dependent on the volume as P=nRT/V (true only for ideal gases!)

$$\omega = -\int_1^2 \left(\frac{nRT}{V}\right) dV$$

Since nRT is fixed in isothermal expansions , take it of the integral:

$$\omega = -nRT \int_1^2 \frac{dV}{V}$$

$$\omega = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

(We used $\int \frac{dx}{x} = \ln\left(\frac{V_2}{V_1}\right)$).

What about q? well, recall thT

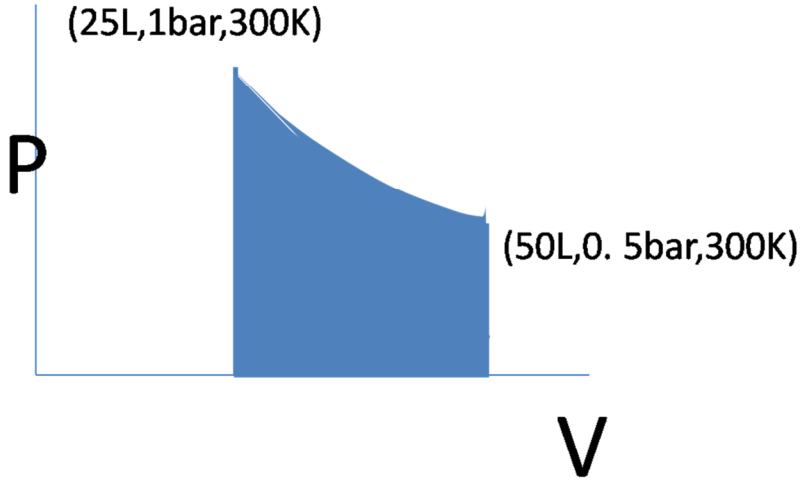
$$q = \Delta U - \omega$$

And for isothermal expansion, ΔU=0, so

$$q = 0 - \omega = -\omega$$

$$q = nRT \ln\left(\frac{V_2}{V_1}\right)$$

Example: see figure.



In this figure example: w=-nRT $ln\left(\frac{50L}{25L}\right)$

= -(1mol*8.3J/(K mol)*300K) * ln(2)

= -2500 J *0.693 = -1730J

q = ΔU -w = 0-(-1730J) = 1730J

Ostensible problem with isothermal expansion:

How come we input heat, and the temperature does not rise?

Answer:

Imagine a runner that continuously eats and drinks while she runs – she continuously converts the food and drink to energy used in running, so her body weight does not change.

Same here: the work that is done by the gas is compensated by the heat given to the gas, so the energy does not change (and therefore the temperature can stay fixed).

Adiabatic expansion

The next type of expansion is adiabatic, where, while the gas expands, work is done but it is not compensated by heat, i.e., no heat is given.

It can be proven (Chem. 110A):

$$P \propto V^{-\gamma}$$

where

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

Examples:

$$\text{He,Ne,Ar:} \qquad C_V = \frac{3}{2}R, \qquad C_P = \frac{5}{2}R \quad \rightarrow \quad \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.66$$

$$\text{O}_2\text{,N}_2\text{:} \qquad C_V = \frac{5}{2}R, \qquad C_P = \frac{7}{2}R \quad \rightarrow \quad \gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

<u>Example:</u>

- Take Air (essentially N_2), V(Initial)=6L, P(initial)=4bar, T(initial)=300K (by the way: what's n? use the gas law to calculate!)

Then either

- Expand isothermally to 12L

Or

- Expand adiabatically to 12L

<u>1st Question:</u> what's the final pressure and temperature in both cases?

Answer:

- Isothermal expansion:

T=fixed → T(final)=T(initial)=300K

P(final): since P=nRT/V, and T did not change while V doubled →

Therefore, P was halved, i.e., P(final)=4bar/2= 2bar

- Adiabatic expansion:

Fast way of getting the result: V doubled (increases by a factor of 2); so P, which is proportional to $V^{-\gamma}$, changes by a factor of $2^{-\gamma}$, i.e.,

P(final) = P(initial)* $2^{-\gamma}$ = 4bar * $2^{-1.4}$ = 1.52 bar.

What about T? Since

$$T = \frac{PV}{nR},$$

and since V doubled and P decreases from 4bar to 1.52 bar, then

$$\frac{T(final)}{T(initial)} = \frac{P(final)}{P(initial)}\frac{V(final)}{V(initial)} = \frac{1.52bar}{4bar} \bullet \frac{12L}{6L} = \frac{1.52}{4} \bullet \frac{12}{6} = 0.76$$

i.e., T(final)=T(initial)*0.76=300K*0.76=228K.

2nd question: How much work was done in the adiabatic expansion?

Answer:

The answer deserves a separate section:

Calculating work in adiabatic expansion.

We could have used

$$w = -\int P dV$$

But that will be a difficult integral. Instead, use:

$$w = \Delta U - q = \Delta U$$

where we noticed that in adiabatic expansion q=0. So all we need is the change in U, the internal energy.

Here comes a **non-trivial point:** for ideal gases (**and only for ideal gases)**, as we consider, **the energy depends only on temperature. Therefore, if we change the temperature in the adiabatic process, we can calculate the energy change by considering ANY OTHER process where the temperature changed by the same amount (even if the final volume and pressure are different).**

The simplest such 2nd process is a fixed volume process with the same temperature change; In other words, since

$dU=C_V dT$

for fixed volume process, then we know that $dU=C_V dT$ here, even though V is not fixed!

(Note that I am only talking about dU; dq and dw will be different in each of these processes -- - in one, dq=0 (adiabatic); in the other, dV=0 so dw=0 and dq=dU; but the energy change is the same in both processes, even though the final states are different – because the final temperature are the same in both!)

For the fixed volume case:

$$\Delta U = \int C_V dT = C_V \Delta T = C_{Vm} n \Delta T$$

And therefore in our case (where the volume isn't fixed, but T changes by the same amount!) we get the same energy change, i.e.,

$$\Delta U(\text{ideal gas, V not necess. fixed}) = C_{Vm} n \Delta T$$

and we know each of the terms:

$C_{Vm} = 5R/2 = 2.5*(8.3\ \text{J/(K mol)}) = 20.7\ \text{J/(K mol)}$ (for air at reasonable T's)

$\Delta T = T_f - T_i = 228K - 300K = -72K$

$n = PV/(RT) =$ (when calculated for the initial conditions, as n does not vary)

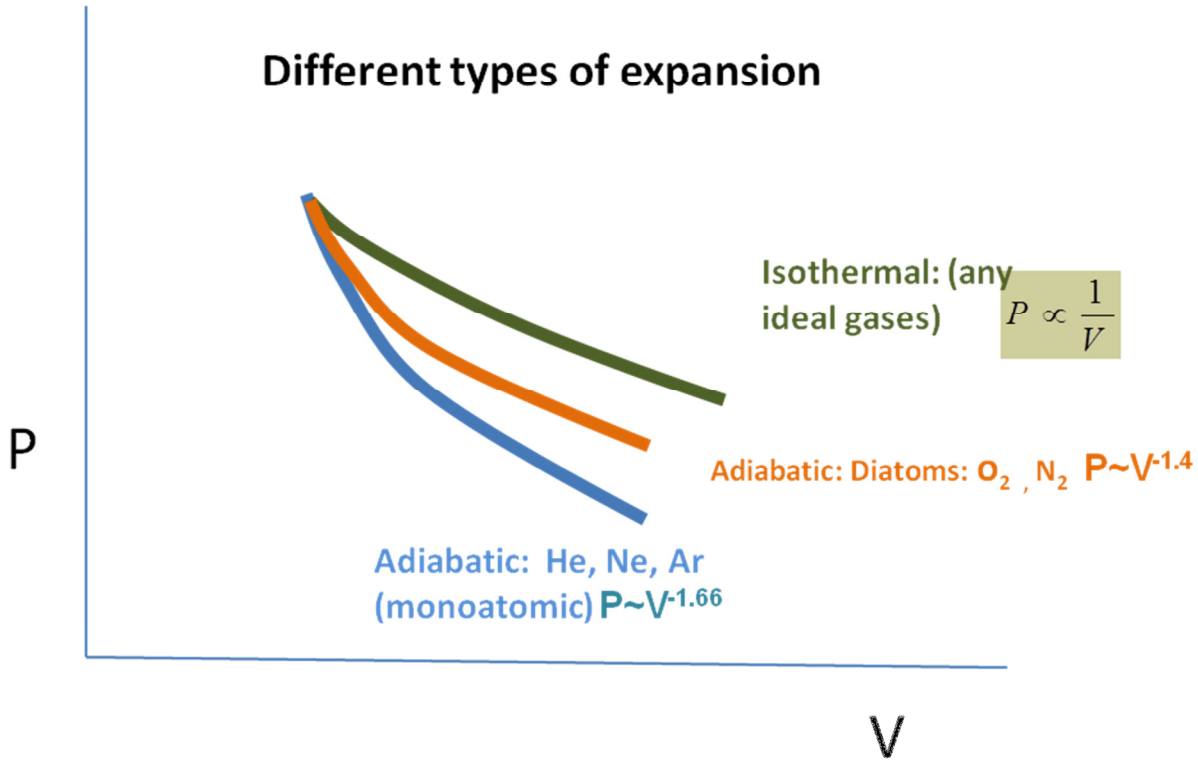
$$n = \frac{4bar \bullet 6L}{8.3\frac{J}{K\ \text{mol}}\ 300K} = \frac{2400\text{J}}{2500(J/mol)} = 0.96mol$$

We can calculate now

$$\Delta U = C_{Vm} n \Delta T = 20.7 \frac{\text{J}}{\text{K mol}} * 0.96\ \text{mol} * (-72\text{K}) = -1430\text{J}$$

So in this adiabatic expansion, 1.43kJ of work was done by the system.

Comparing adiabatic and isothermal expansion of ideal gases:



With increasing volume, P falls:

- fastest for adiabatic monatomic expansion,
- slower for adiabatic expansion of diatoms,
- even slower for adiabatic expansion of triatoms, etc.,
- and slowest for isothermal expansion.

Reason: monatomic species (He, Ne, Ar., etc.) don't have a lot of energy stored in them (only in the translational motion); so when they expand and do work, they lose, percentage wise, a lot of their energy, so their temperature falls a lot (energy is a function of T) and therefore the pressure falls a lot. (The pressure is P=nRT/V, and here both T falls a lot and 1/V decreases as V increases, so together P will fall off very quickly as a function of V; specifically, it will fall as $1/V^{1.66}$.)

Diatomics have some energy in rotations, so the loss of energy through work does not change their energy so much; they do lose energy sop their T falls, but

not as much as monatomic species. So their P will not fall as much as for monoatoms.

Similar reasoning explains that the bigger the molecules of an ideal gas, the more they have energy stored in them, and therefore the less they will be affected by the work done through the expansion, and therefore, their T will not be so affected so their P will not fall so much.

At the extreme is isothermal expansion, now of all species (whether He, O_2, or of any other ideal gas). Here, T does not fall (the energy done by work is replenished) so their P falls only because P=nRT/V and V increases.

Tabulated Enthalpy

We need to define an enthalpy or energy scale, where one of them is zero. Physicists have a general definition but it is very complicated to use in practice, so we revert to the practical definition of chemists.

In practice, of course, it rarely matters since we are generally interested in enthalpy differences (i.e., in the amount of heat spent in a reaction at constant pressure)

So, as a prelude to the practical definition of enthalpy, we need "standard states" of each species:

We define

A standard state: 1atm, specific T=298K=25 ^{o}C.:

For gases: we assume an ideal gas behavior.

For dissolved specifies: the definition used is an annoying one. We assume that the species is at a 1M (1 mol/Liter) solution, but not in its real state; instead, extrapolate from a very low concentration to what the behavior would be at 1M.

Next, we decide that the enthalpy of each element at the standard state, in its most stable form at the standard state, is assigned to be zero.

We label an enthalpy defined according to this scale as "enthalpy of formation", H_f.

For example,

$$H_f(O_2, gas, 298K, P^0)=0$$
$$H_f(C, graphite, 298K, P^0)=0$$

Note that:

$$H_f(C, diamond, 298K, P^0)>0$$

Enthalpy of formation of molecules is then defined as the enthalpy of reaction to make the molecules from their atomic ingredients in their stable form.

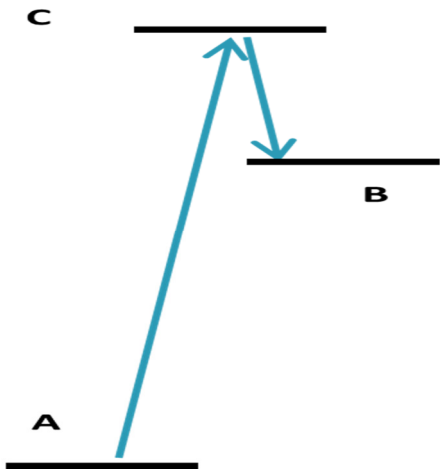
For example:

$$H_f(H_2O) \equiv \Delta H_{RXN}\left(H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O;\ \ T = 300K\right) = -2858\frac{\text{kJ}}{\text{mol}}$$

This relates to:

Hess's Law.

Graphically:



i.e.,

Hess law is general. It means that if we want an enthalpy difference, we can use an intermediate (in our case "B").

Let's apply Hess's law denoting the elements in their stable atomic state as "A"; Then the first term on the left is the formation enthalpy of C, and so is the first term on the right, i.e.,

$$H_f(C) = H_f(B) + \Delta H_{rxn}(B \rightarrow C)$$

Another example:

$$H_f(A \to B + C) = H_f(A \to B + D) + \Delta H(D \to C)$$

And in general:

$$\Delta H(B \to C) = -H_f(B) + H_f(C),$$
$$\Delta H(B \to C + D) = -H_f(B) + H_f(C) + H_f(D),$$
etc.

Realistic examples: given a table of energy of formations, then how do we calculate, for room temperature:

$$\Delta H(2NO \to NO_2 + \frac{1}{2}N_2) = ?$$

Answer

$$\Delta H(2NO \to NO_2 + \frac{1}{2}N_2) = -2H_f(NO) + H_f(NO_2) + \frac{1}{2}H_f(N_2)$$

i.e. (since $H_f(N_2) = 0$)

$$\Delta H(2NO \to NO_2 + \frac{1}{2}N_2) = -2H_f(NO) + H_f(NO_2)$$
$$= -2(90.4 \text{ kJ/mol}) + (33.1 \text{ kJ/mol}) = -147.7 \text{ (kJ/mol)}$$

Part 6: Spontaneity, entropy and 2nd law

The understanding of the 2nd law requires a lot of concepts with which you are at best barely familiar. So we will try to exemplify and relate the concepts; but beware that this is a very difficult part, because it is so qualitative and because these are new concepts.

The order of this chapter is:

- Direction of time in nature is well defined
- Entropy is a measure of disorder; 2nd law: the universe's entropy rises.
- Thermodynamics definition of entropy changes $dS = dq_{rev}/T$
- Examples:
  - ideal gas expansion (isothermal, isobaric);
  - temperature change of any substance (including solids and liquids) at fixed pressure (isobaric) or volume,
  - Phase change
- Stat. Mech. Definition of entropy: $S_{stat.mech.} = k_B \ln(\#\ of\ states)$
- Entropy tabulation; qualitative understating of how the entropy changes in chemical reactions.

Direction of time

1st law allows for processes which conserve energy but "don't make sense",

E.g., take a physical processes, like a cup falling and breaking;
The "reverse movie" of this processes, which is broken pieces of the cup coming together spontaneously and becoming one cup, isn't feasible physically.

Therefore, it isn't enough to just consider energy when we talk about processes, we need a law beyond the 1st law.

This is where the 2nd law comes.

It states, essentially, that systems evolve towards equilibrium. (More precise def.—later).

Let's first exemplify on several processes which always occur in a given direction in time (i.e., their reverse never occurs):

- Open a balloon at high P; gas always expands out and P is reduced, never back.
- Two systems initially at different temperatures, T_A and T_B, when we bring them in contact, will always reach a temperature T_f which equals in both
- A little of NaCl (table salt, Sodium chloride) in water will always dissociate.

So: nature is directional in time.

Entropy: measure of disorder; and 2nd law.

So the **2nd law of thermodynamics** is:

The Entropy of the world (i.e., the disorder in the world**), never decreases;** more precisely: **entropy increases if there are irreversible processes and stays constant for reversible processes.**

This is a "law" i.e., something we stipulate and don't prove, but we can justify it using some examples based on statistics. If you take a course in statistical mechanics, you will be able to prove and expand much on the concepts we introduce.

Thermodynamic entropy

It turns out (no proof) that we can write the change of entropy of a given system as

$$dS = \frac{dq}{T} \qquad \text{thermodynamics definition}$$

where dq is the amount of heat if the process is reversible (we'll review this and define more precisely later).

Clarification on entropy:

- First, the 2nd law talks about the entropy of the universe (that never decreases). The entropy of a system can decrease, if the entropy of the surroundings increases. For example, we can cool water (and thereby decrease their entropy), but when we do it, the entropy of the surroundings must increase correspondingly, so that the change of entropy of everything together (the universe) will not decrease.

So: dS can be >0 or <0 or =0, as long as:

$$dS + dS_{\text{SURROUNDING}} = dS_{\text{WORLD}} \geq 0$$

- Next, consider qualitatively the 1/T in the relation between entropy and heat, dS=dq/T.

Think of dq as "applied mess", and of dS as "resulting disorder"

Then we learn that if the temperature is high, the effect of the mess on the disorder is small (since it is divided by 1/T, and T is high);

But when T is low, a small dq will affect the entropy strongly, as 1/T is large

You know this from daily life: if your dorm room is clean (equivalent to low T), then a little mess (dq) will make it look quite messy (increase S significantly);

But if your dorm room is already messy (high T), then making it a little messier (dq) won't have much of an effect (since dq/T will be small, as 1/T is small).

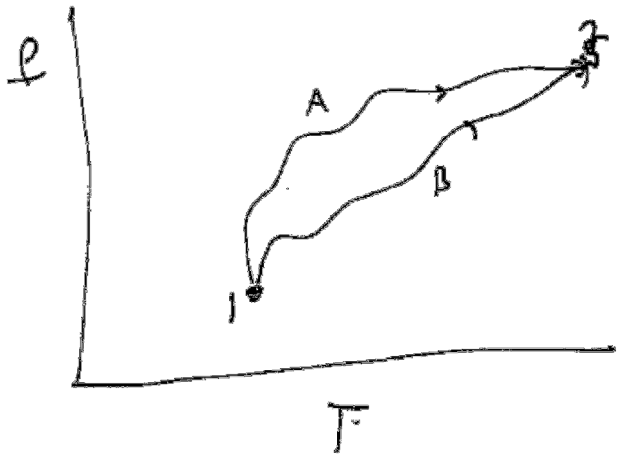
- Finally, the entropy change is strictly not dq/T, but

$$dS=dq_{rev}/T$$

This means that to calculate an entropy change we must take a reversible path connecting the initial and final states.

And another thing it tells us: it won't matter which path we actually take for entropy changes!

Graphically:.



$q_A \neq q_B$..

but ΔS(route A)= ΔS(route B)

You'll see an example in a H.W. problem later.

Examples for entropy changes, and entropy tabulation.

- Expansion of an ideal gas at constant temperature:

$$dS = \frac{dq}{T}$$

Isothermal expansion is a very simple case, since 1/T is fixed during the expansion. If we start at a volume V_0 and end at volume V then (recalling that q(isothermal expansion)=nRTln(V/V_0), as proved):

$$\Delta S(\text{isothermal}) = \int_{V_0}^{V} \frac{dq}{T} = \frac{1}{T}\int dq = \frac{q_T}{T} = \frac{nRT}{T}\ln\left(\frac{V}{V_0}\right)$$

$$= nR\ln\left(\frac{V}{V_0}\right)$$

So as V increases, the entropy increases; when the volume doubles, the entropy increase by nRln[2]. The reason is that as we increase the volume, each particle has more space to roam through.

For future reference, let's write isothermal expansion in terms of pressures, and not volumes (they carry the same info for ideal gas). We know that P=nRT/V, so

$$PV = P_0V_0 \rightarrow \frac{V}{V_0} = \frac{P_0}{P}\text{ , so}$$

$$\Delta S = nR\ln\left(\frac{P_0}{P}\right) = -nR\ln\left(\frac{P}{P_0}\right)$$

Where we're using

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b) = -(\ln(b) - \ln(a)) = -\ln\left(\frac{b}{a}\right)$$

So to conclude:

$$S(T,P) = S(T,P_0) + \Delta S = S(T,P_0) - nR\ln\left(\frac{P}{P_0}\right)$$

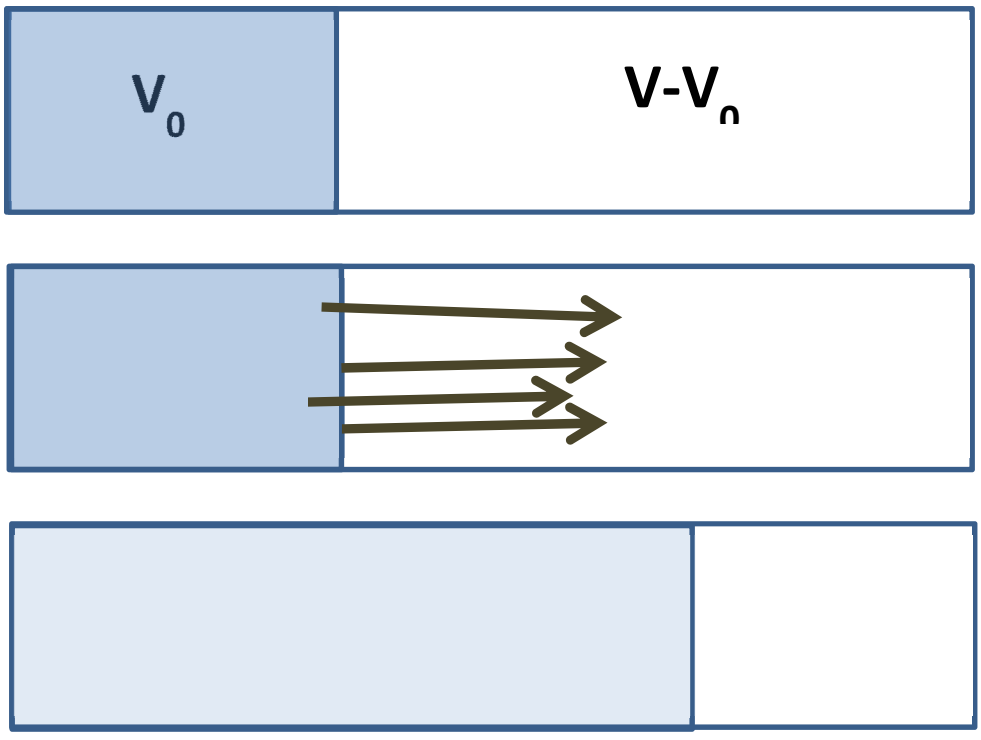
Important note: this formula is valid regardless of how the actual expansion went;

For example, say we consider the expaple we considered earlier, of a gas expanding into vacuum (e.g., b puncturing a hole in an initially full container where the gas can expand into an empty container, see picture

,

Even then the entropy will increase in the same way sicne we cant use the actual path in this stage (with its dq=0)

Instead we'll have to use a reserible path, and the simplest in this case is reversible isothermal path (see 3rd frame in picture)



Example: entropy calculation for a gas expanding into an empty container will not be calculated through actual path (where dq=0, 2nd frame) but by following a reversible path, e.g., the isothermal one for this case. (3rd frame)

- Expansion at fixed volume: analogous to the fixed P case; same derivation, replace the P subscript by V, get:

$$\Delta S_V = \int_1^2 \frac{dq_V}{T} = C_V \int_1^2 \frac{dT}{T} = C_V \ln\left(\frac{T_2}{T_1}\right)$$

- Similarly Expansion of any substance (solid, liquid, gas) **at fixed pressure**:

$$\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right)$$

- **<u>INSERT: Reading Example: (not lectured on) for the 2nd law:</u>** We bring together in a room two identical pieces of iron, the first (left one) initially at 300K and the second (right one) at 310K.

Once they reach equilibrium, then from conservation of energy the T(final)=305K = average of two initial temperature. (We can show this rigorously, but we don't have time; but this makes sense)

We can prove that the entropy increases!

$$\Delta S_1 = C_P \ln\left(\frac{T_f}{T_1}\right) = C_P \ln\left(\frac{305}{310}\right) < 0$$

$$\Delta S_2 = C_P \ln\left(\frac{T_f}{T_2}\right) = C_P \ln\left(\frac{305}{300}\right) > 0$$

$$\Delta S_1 + \Delta S_2 = C_P \left(\ln\left(\frac{305}{300}\right) + \ln\left(\frac{305}{310}\right)\right) = 0.00027\,C_P > 0$$

This goes in line with what we know -- the final process has more entropy than the initial, just like the 2nd law says! (the final-initial entropy difference is tiny, but that's enough to ensure that the system will settle there).

END OF INSERT

- Phase change:

  We learned that, since a phase change takes place at a constant P:

$$q(\text{phase change})=\Delta H$$

  Further, dS=dq/T, and since T is also fixed in a phase change,

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

  Example.

  Freezing (called "fusion" by chemists/physicists):

  Ice->water:

$$\Delta H_{fusion}=6.0\frac{\text{kJ}}{\text{mol}},\quad \text{T}_{fusion}=273\text{K}$$

$$\rightarrow \Delta S_{fusion}=\frac{\Delta H_{fusion}}{T_{fusion}}\sim\frac{\frac{6000\text{J}}{\text{mol}}}{273\text{K}}\sim 22\frac{\text{J}}{\text{K mol}}$$

H.W. problem exemplifying that two different paths give the same entropy:

We have a piston of 2 mol, containing He.

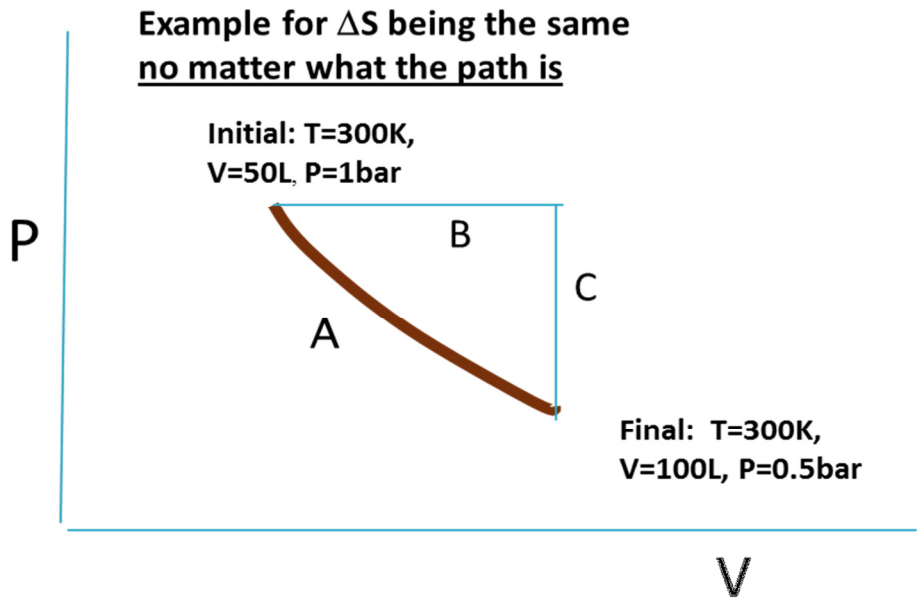
The initial point is "1" : T=300K, V=50L, P=1bar. (Verify that PV=nRT!)
The final point is "2": T=300K, V=100L, P=0.5bar.
Consider then the following two paths (see figure).

Path "A" is isothermal --- i.e., we keep T fixed and just increase the volume from 50L to 100L and the pressure decreases from 1bar to 0.5bar.

Path "B+C" is a two-stage path:

In part (B) of this path, P is fixed at 1bar, V increases from 50L to 100L (and therefore T rises, to 600K).;

In part (C) of this path V is fixed at 100L and P decreases from 1bar to 0.5bar (so T decreases from 600K to 300K).



QUESTION: Calculate ΔS(part A), and ΔS for part B+C, and prove that they are the same.

Note: Remember that we calculated ΔS for each of the processes you encounter here: isothermal expansion, expansion at const. pressure and expansion at const.

volume. All you have to do is add up these contributions we previously discussed, and prove that the entropy change in stage A equals the sum of the two changes in step B.

Interpreting entropy from a statistical-mechanics (stat. mech.) perspective.

Here we'll introduce a whole different definition of entropy, coming from stat. mech., whereby the entropy has the following meaning, which ostensibly has nothing to do with thermodynamics:

$$S(\text{stat.mech.}) = k_B \ln(D)$$

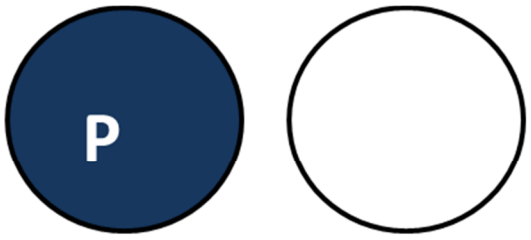
where we introduced "Boltzmann's constant",

$$k_B \equiv \frac{R}{N_{Avogadro}}$$

and where "D" is the **number of states the system can go through.** (Everybody else uses W and not D as the symbol for the number of states, but I am worried that you'll think it is related to work – it does not – so I use D instead)

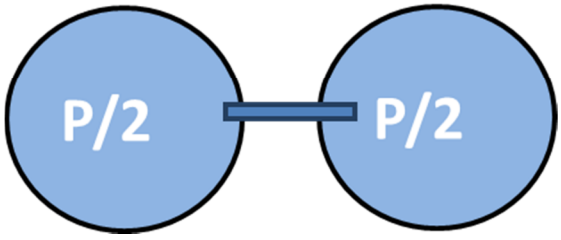
This definition of S(stat.mech.) may sound incomprehensible, but let's exemplify. Our example will give us a numerical result, which will be shown to match the thermodynamic entropy.

Let's take a gas of temperature T and volume V, and Pressure P, on a left container; and an empty container (of equal volume) on the right;



Now open the valve so molecules can also go to an initially-empty container on the right.

The pressure halved, but the temperature is unchanged (if this is an ideal gas), and the **only thing each molecule feels differently is, essentially, that it can now be in twice as big a volume.**



Let's now calculate what will be the

increase in the stat. mech. entropy, and verify that it will be exactly what thermodynamics predicts – so thermodynamics and stat. mech. match (at least for this case – for a general proof see 110B).

Take a single molecule; its velocity, position within the sphere, internal vibration, etc. are all things that do not change when the molecule can share its time between the spheres. So we won't considered them (we are interested in changes in the number of states, which will lead to entropy difference, much more than we care about the total number of states, so we'll only consider the new feature, being on the left or right).

So: the new "state" (really "label") each molecule can be in is only whether it is left (L) or right (R).

So we can label this "extra" molecular label or state as L or R, and the number of states for a single molecule is 2.

Now consider 2 molecules; we have LL (two molecules on left), LR, RL, and RR. Overall 4 states ($4=2^2$)

Now 3 molecules: there are $2^3=8$ possibilities: LLL, LLR, LRL, LRR, RLL, RLR, RRL, RRR

And in general for N molecules, $D=2^N$ possibilities.

So if we have "n" moles, they contain $N=n*N_{Avog}$ molecules; so the change in entropy will be:

$$S(\text{stat.mech}))=k_B \ln(2^N),$$

and using

$$\ln(x^y)=y\ln(x)$$

we get

$$S(\text{stat.mech.})= k_B N \ln(2),$$

and since

$$k_B *N= (R/N_{Avog})*(n\, N_{Avog})=n\, R$$

we get

S(stat.mech.)= nR ln(2).

Now this is really not the total stat. mech. entropy, just the change when we expanded the gas, so we should add a "Delta", i.e.,

ΔS(stat.mech.)= nR ln(2).

Next let's compare it to the thermodynamics prediction; in thermodynamics, when a gas is isothermally expanded:

ΔS(thermodynamics)= nR ln($V_{final}/V_{initial}$) **(**look at the formulae we derived earlier) i.e., here, when the volume is doubled (and the temperature unchanged):

ΔS(thermodynamics)= nR ln(2V/V)= **nR ln(2)** = **ΔS(stat.mech.) !!**

So the two formulations agree, at least for this case.

END OF STAT. MECH., BACK TO THERMODYNAMICS

Entropy tabulation and qualitative consideration:

From tables we can determine ΔS^0, change in entropy upon reaction.

Example:

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$

Each species contributes to the entropy, with a coefficient that's the same as in the reaction, but reactants get a minus
(as ΔS is figuratively products-reactants)

$$\Delta S^0 = -S_m{}^0(N_2) - 2S_m{}^0(O_2) + 2S_m{}^0(NO_2)$$

Where the ^{0} superscript indicates we calculate at 1 bar.

From tables we find that:

$$\Delta S^0 = -191\frac{\text{J}}{\text{K mol}} - 2 \bullet 205\frac{\text{J}}{\text{K mol}} + 2 \bullet 240\frac{\text{J}}{\text{K mol}} = -121\frac{\text{J}}{\text{K mol}}$$

SIDE NOTE: Note that the entropy is reduced in this reaction

Figuratively, we can understand the entropy reduction, since this reaction reduces the number of molecules (3 molecules become 2) so there is less disorder as there are less molecules to roam around.

There are of course complications in reality, but this is a reasonable qualitative explanation for the entropy reduction.

END OF SIDE NOTE

Part 7: Gibbs Free Energy

Summary:

i. Clausius relation: fixed T $\Delta S_{environment} = -\frac{q}{T}$ and q≤q(rev.)=TΔS.

ii. Gibbs free energy G=H-TS;
Proof that at fixed P and T, and no electrical work $\Delta G \leq 0$, and implications

iii. Predicting transition temperatures $T^* = \frac{\Delta H^o}{\Delta S^o}$

iv. $(dG/dT)_{P\ fixed} = -S$

v. G vs. T diagram at fixed P, stable phase at T,P: lowest G.

vi. Incorporating electrical work $\Delta G \leq \omega_{el}$ at fixed, T, P

Overview:

We learned that we can see if a process is spontaneous or is reversible according to the change of entropy in the world:

$$\Delta S(\text{world}) > 0 \rightarrow \text{spontaneous (irreversible)}$$
$$\Delta S(\text{world}) = 0 \rightarrow \text{reversible}$$
$$\Delta S(\text{world}) < 0 \rightarrow \text{forbidden}$$

But it is inconvenient to talk about the change of entropy of the whole world. Luckily, we can define a new quantity, the Gibbs free energy:

$$G = H - TS$$

Such that in the crucial case of reactions at fixed T and P (e.g., bench experiments in a lab), G will give us the same information as S(world) will (although with a reverse of signs), i.e.,

FOR FIXED P, T (and an assumption we'll relax later: no electrical work):

$\Delta G < 0 \rightarrow$ spontaneous (irreversible)

$\Delta G = 0 \rightarrow$ reversible

$\Delta G > 0 \rightarrow$ forbidden

Let's prove.

7.i) Reversible and irreversible for the environment, Clausius relation

For simplicity, in all the discussion below, the pressure is fixed and the temperature is fixed.

First, let's refine our understating of what reversible and irreversible mean as far as system and as far as surroundings;.

Imagine, e.g., a little balloon containing hydrogen and oxygen and placed in a pool of fixed temperature

Then, have the hydrogen react with the oxygen to produce water (e.g., maybe put there a metal that will help catalyze the reaction). As far as the system is concerned, this is definitely an irreversible process – we cannot do a small change to make from water back again H and O. (We could put a lot of electricity to do that, but that's not a small change).

However, since this is all done in a balloon "immersed" in a pool of fixed temperature, then, as far as the surroundings are concerned, all that happened was that the materials in the balloon gave away to the surroundings some heat, which barely affected the surroundings (maybe very slightly raised the temperature of the surrounding water).

So: while in the system the process is irreversible, **as far as the surrounding all processes look reversible!**

So, if we label the heat given in a process as q, this heat is taken from the surrounding, so we can say that –q was given to the surrounding

(e.g., 10J given to the system is -10J given to the surroundings).
Then:

$$\Delta S(surr.) = -\frac{q}{T} = -\frac{\Delta H}{T}$$

where the 2nd equality is since we consider fixed pressures.

(Note that we don't have this rule for the system: if the process is irreversible,

$$\Delta S(sys.) \neq \frac{q}{T} \quad \text{for irreversible processes)}$$

Possible values of the heat.

There is a very interesting point "buried" in the derivation above.

This point is called the "**Clausius rule".**

The point is that

$$0 \leq \Delta S(world) = \Delta S + \Delta S(surr) = \Delta S - \frac{q}{T} = \frac{q(rev.)}{T} - \frac{q}{T}$$

where the last equality is since we consider a fixed T processes.

So we get:

$$0 \leq q(rev.) - q$$

i.e.,

$$q \leq q(rev.) \qquad \text{(Clausius rule)}$$

or equivalently, since ΔS=q(rev.)/T,

$$q \leq T\,\Delta S$$

I.e., for any process, reversible or not, the amount of heat input to the system is limited to be less than the amount of heat which will be input in a reversible process.

INSERT Example for Clausius rule (required, not covered in class):

Say we're at 300K and we start at state I (e.g., a liquid phase of a compound, or a gas at a given volume, or anything else); and we do a process (expansion, melting, reaction, or something else) that changes the system to a different state, II, with S higher by 4J/K, i.e., $\Delta S=4J/K$.

Assume the process is such that the surroundings are at constant temperature; for example, they could be a very large water container into which we "drop" the system.

Question: Now let's pose the hypothetical question: is it possible to do that same process with (a) q=0; or (b) q=900J; or (c) q=1200J; or (d) q=1500J; and in every case, will the process be reversible, irreversible, or impossible, and why.

Answer:

(a) q=0 : that means the process was adiabatic. It was irreversible, since the entropy of the surroundings did not change (they did not give heat), while the systems' entropy increases, so the world entropy increases, i.e., the process is irreversible. An example we discussed is a rapid adiabatic expansion of a gas without doing work, e.g., when we rupture the separation between a container full of gas and an initially empty ("vacuum") 2nd container, so the gas expands irreversibly from the initial container to the total final volume (encompassing both containers).

(b) q=900J. In that case, the surroundings gave away q, (i.e., "got –q" heat) and since as far as the surroundings this looks reversible, the surr. entropy change is –q/T, i.e.,

$$\Delta S(surr.)= -q/T=-900J/300K = -3J/K$$

So

$$\Delta S(world)= \Delta S+\Delta S(surr.)= 4J/K + (-3J/K) = 1\ J/K > 0$$

So the process is possible but again irreversible, since the entropy of the world increases.

(c) $q=1200J \rightarrow \Delta S(surr.)= -q/T=-1200J/300K = -4J/K$

So

$$\Delta S(world)= 4\ J/K\ - 4J/K = 0$$

So the process is <u>reversible</u> (as it does not change the entropy of the world, so in principle we could reverse it)

(d) Finally, the most interesting part:

$$q=1500J \rightarrow \Delta S(surr.)= -q/T=-1500J/300K = -5J/K$$

So

$$\Delta S(world)= 4\ J/K\ - 5\ J/K = -J/K$$

So the process is <u>impossible</u>.

The reason is it impossible is that when we inject heat into the system we reduce the entropy of the surroundings, and we cannot reduce it by more than 4 J/K, i.e., q needs to be smaller than q(rev.)

END OF INSERT EXAMPLE ON CLAUSIUS RULE

7.ii) NOW BACK TO DERIVING THE FREE ENERGY AND IMPLICATIONS

Using the equations above, we get (because we assume that the initial and final state are at the same temperature and pressure – which is always fixed here, and the surroundings are at the fixed T and P):

First, assume that there is no electrical work (we'll relax this later). Since the pressure is fixed,

$$\Delta S(world) = \Delta S + \Delta S(surr.) = \Delta S - \frac{\Delta H}{T}$$

Rearrange to give:

$$\Delta S(world) = -\frac{(\Delta H - T\Delta S)}{T}$$

Now at fixed temperature, a change in G is

$$\Delta G = \Delta(H - TS) = \Delta H - \Delta(TS) = \Delta H - T\Delta S$$

(where the 2nd equality is since T is fixed), so that (only at fixed T and P):

$$\Delta S(world) = -\frac{\Delta G}{T} \qquad \text{(if T,P are fixed)}$$

Note: on the left we have a "world" quantity, hard to find;
on the right a system quantity, ΔG, much easier to find.

Since the entropy of the world never decreases, -ΔG never becomes negative, i.e.:

$$\Delta G \le 0 \quad \text{(if T,P are fixed G never decreases!)}$$

Very convenient way to know if a process is spontaneous, reversible or forbidden – since G is a system's quantity! We don't have to worry anymore (as long as we consider processes at fixed T and P) about "world" quantities, only system quantities!

Example

$C_6H_6(l) \rightarrow C_6H_6(g)$, 1atm, 298K.

At 298K, 1atm (we'll use a ^{0} superscript, i.e., an **umlaut**, to denote a quantity calculated for 1 bar), you can calculate from the information at the appendix of the book that the reaction enthalpy and entropy is:

$$\Delta H^0 = \Delta H\left(C_6H_6(l) \rightarrow C_6H_6(g)\right) = 33.9\frac{kJ}{\text{mol}}$$

$$\Delta S^0 = 96.4\frac{\text{J}}{\text{K mol}} = 0.0964\frac{\text{kJ}}{\text{K mol}}$$

Therefore:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 33.9\frac{\text{kJ}}{\text{mol}} - 298\text{K} \bullet 0.0964\frac{\text{kJ}}{\text{K mol}} = 5.17\frac{\text{kJ}}{\text{mol}} > 0$$

Therefore, at room temperature and pressure, $\Delta G^o > 0$, so the reactant side is favored, i.e., benzene is a liquid at room temperature and pressure (as we know!)

7.iii) Predicting transition temperature

Let's say we know at a given temperature what $\Delta H^0, \Delta S^0$ are. We can approximate that they usually don't change much with temperature (we could find their exact temperature dependence, from what we know already, based on the heat capacities, but usually this change with T is relatively small so it can be ignored in many cases).

Then, we can predict the transition temperature, T*, where the reactants and products are both allowed, since then $\Delta G(T^*) = 0$:

$$0 = \Delta G(T^*) = \Delta H^o - T^* \Delta S^o$$

So:

$$T^* = \frac{\Delta H^o}{\Delta S^o}$$

(Of course, this expression predicts that transition never happens if $\Delta H^o, \Delta S^o$ don't have the same sign).

In the Benzene example: $T^* = \frac{\Delta H^o}{\Delta S^o} = \frac{33.9 \text{ kJ/mol}}{0.0964 \text{ kJ/mol}} = 353\text{K} = 80\ ^\circ C$.

True value: $80.1\ ^\circ C$ – excellent agreement! (actually, that's a little of a coincidence, usually the agreement is not as good as in this case).

7.iv) Derivative of G

Recall that we define G=H-TS. We see that if H and S are constant as a function of T, then

$$\left(\frac{dG}{dT}\right)_{P\ fixed} = -S.$$

(we inserted the "P fixed", since this equation needs to be evaluated for fixed pressure.). This equaiotn was calculated fr H and S which don't change with T (and P fixed); however, it turns out **it is a general relation, valid even if we don't approximate H and T as constant.** (Proof: 110A).

Therefore, this gives a very nice graphic interpretation of G: its slope w.r.t. T at any T (at fixed pressure of course) is the negative of the entropy.

Example:

For example consider a "reaction" A(liq)→A(gas). Consider it at 1 bar:

$\Delta G^0 = G_f{}^0(\text{A gas},T) - G_f{}^0(\text{A liq},T)$

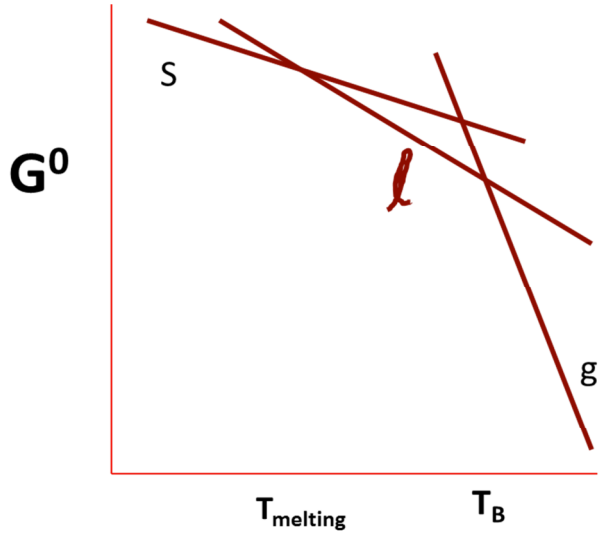
And recall

$\Delta S^0 = S_m{}^0(\text{A gas},T) - S_m{}^0(\text{A liq},T)$

$-\Delta S^0$ will be the slope of ΔG^0 w.r.t. temperature!

G vs. T diagram

At the region of T where $G_l{}^0$ is lower than $G_s{}^0$ and $G_g{}^0$, the system is liquid, and analogously for gas and solid.



7.v) G AND BATTERIES:

ΔG also tells you something very important: how much electrical energy you can get out of a reaction (or needs to make a reaction happen). Recall that without electrical work, we derived that

$$dG \leq 0 \ (T, P \ const., no \ electrical \ work)$$

It turns out (a few lines derivation, see 110A if you take that course), that when we allow electrical work input or output, then

$$dG \leq dw(elec.) \quad (T, P \ const.)$$

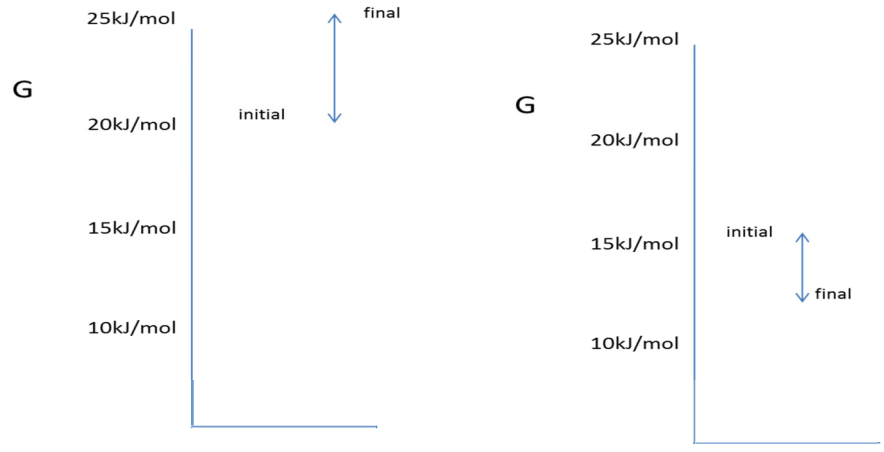
Integrate, get

$$\boldsymbol{\Delta G \leq} \textbf{ w(elec.) (const. T and P only)}$$

EXAMPLES:

Left: G(final) is higher than G(initial) by 5kJ/mol; this means that ΔG = 5 kJ/mol, we need to inject at least 5kJ of electrical energy to enable one mole to react. Without electrical energy, this reaction won't happen.

Right: G(final) lower than G(initial) by 3kJ/mol – we could use this G difference to get 3kJ of electrical work from this reaction (for one mole). If reaction is allowed to happen without extracting the electrical energy, this 3kJ/mol will be "wasted", i.e., turn to extra heat.



Part 8: Chemical Equilibrium and law of mass action.

Summary: Getting reactions from $\boldsymbol{\Delta G = 0}$ ***in equilibrium*** using a proof that

$$\boldsymbol{\Delta G = \Delta G^o + RTlnQ},$$

$$\boldsymbol{0 = \Delta G^o + RTlnK}$$

i. Deriving G for an ideal gas:

$$G_m(T,P) = G_m^0(T) + RT\left(\frac{P}{P^0}\right)$$

and mentioning the analogy for solutions:

$$G_{m,A}([A],T) = G_{m,A}^0 + RTln\left(\frac{[A]}{1M}\right)$$

i. Reactions and deriving Q
ii. Evolution of Q to $K=Q_{eq}$
iii. The mass reaction law K and K_c
iv. Properties of K – derived from K_c

Law of mass action and Q.

We will derive two major relations in this chapter, which are essentially (once we understand the meaning of the symbols Q and K) the law of mass action:

$$\Delta G = \Delta G^0 + RT \ln(Q)$$

$$0 = \Delta G^0 + RT \ln(K)$$

The book starts from law of mass action; instead, we will derive it. The approach we'll take is to **derive a relation between P_j's in a reaction and ΔG and use it to get relations about what happens on the way to and in equilibrium.**

The key will be to realize that $\Delta G=0$ in equilibrium, and use it, as well as the relations between G of a substance and that same substance in a "standard state", to get the densities in equilibrium.

(8.ii) G for ideal gas: pressure dependence

We first need the **dependence of the molar Gibbs free energy, G_m on pressure or density, at a fixed temperature.**

Three possibilities:

- Solids and liquids: G essentially independent of pressure (at least for our purposes here), so $G_{m,A} \cong G^0_{m,A}(T)$, where ^{0} refers to calculation at 1bar, m denotes molar, and A is a superscript
- Vapors (gases): at a fixed T, G depends on pressure since the entropy depends on the pressure. Recall that for an isothermal expansion of an ideal gas, we proved that (see middle of Part 6):

$$S_m(T,P) = S^0_m(T) - R \ln\left(\frac{P}{P^0}\right)$$

- Further, the energy of an ideal gas is independent of pressure at fixed T , and since H=U(T)+PV= U(T)+nRT the enthalpy is also independent of pressure, i.e., H=H(T) for an ideal gas (and we often label it with a 1bar superscript, as $H=H^0(T)$, even though it is the same at other pressures).

  Taken together we get for G of an ideal gas

  $$G_m(T,P) = \left(H^0(T) - TS_m(T,P)\right) = \left(H^0(T) - T\left(S_m^0(T) - R\ln\left(\frac{P}{P^0}\right)\right)\right)$$

  i.e.,

  $$G_m(T,P) = G_m^0(T) + RT\left(\frac{P}{P^0}\right) \qquad \text{(ideal gas only!)}$$

  where:

  $$G_m^0(T) \equiv G_m(T,P^0) = (H^0(T) - TS_m^0)$$

- **Solutions:** Finally, consider solutions, i.e., a species "A" in a solution, with a concentration [A] (for me concentration means molar density, and will be measured usually in mol/Liter). The Gibbs free energy is dependent on the concentration, and can be related to a reference concentration (1 M = 1mol/L) as:

  $$G_{m,A}([A],T) = G_{m,A}^0 + RTln\left(\frac{[A]}{1M}\right) \quad \text{(solutions, approximate)}$$

  where the zeroth-order Gibbs free energy is now defined NOT with respect to pressure (the solution's internal properties do not depend much on external pressure) but with respect to the reference density,
  $G_{m,A}^0 = G_{m,A}(1M,T)$.

  Note that the dependence on concentration looks almost the same as the dependence on pressure of a gas (here the concentration of the solute is analogous to the pressure of the gas, and the reference concentration, 1M = 1mol/Liter, is analogous to the reference pressure 1bar. This relation is no coincidence, as we will see later in Section 12 on Raul's law.

(8.iii) Reactions and deriving Q

Now that we have the dependence of G, let's put it together.

For simplicity, consider a "generic" reaction (actual examples follow later):

$$3A(g) + 2B(s) \rightarrow AB(g) + A_2B(aq.)$$

And consider a fixed T (all quantities depend on T, we'll often hide this dependence in the derivation to avoid excessive writing).

We know that

$$\Delta G = G_m(AB(g)) + G_m\big(A_2B(aq.)\big) - 3G_m\big(A(g)\big) - 2G_m(B(s))$$

Of these terms:

- the G of the gases (A, AB) depend on ln of the pressure, e.g.,

$$G_m(AB) = G_m^o(AB) + RT \ln\left(\frac{P_{AB}}{P^o}\right)$$

- and for the solution (A_2B) G depends on ln of the density,

$$G_m\big(A_2B(sol.)\big) = G_m^o(A_2B) + RT \ln\left(\frac{[A_2B(aq.)]}{1\text{M}}\right)$$

- While the G_m of the solid is independent of pressure

$$G_m\big(B(s)\big) = G_m^o(B(s))$$

so we get

$$\Delta G = G_m^o(AB) + RT \ln\left(\frac{P_{AB}}{P^o}\right) + G_m^o(A_2B) + RT \ln\left(\frac{[A_2B(aq.)]}{1\text{M}}\right)$$
$$- 3\left(G_m^0(A) + RT \ln\left(\frac{P_A}{P^0}\right)\right) - 2G_m^o(B)$$

So collecting the G^0 terms, we get (very important for the rest of the course!)

$$\Delta G = \Delta G^0 + RT \ln Q$$

Where

$$\Delta G^0 = G_m^o(AB) + G_m^o(A_2B) - 3G_m^0(A) - 2G_m^o(B)$$

and we defined the **reaction quotient**, which is here defined as

$$\ln Q = \ln\left(\frac{P_{AB}}{P^o}\right) + \ln\left(\frac{[A_2B(aq.)]}{1\text{M}}\right) - 3\ln\left(\frac{P_A}{P^0}\right)$$

To develop the ln terms further, recall that

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$$

$$a\ln(b) = \ln(b^a)$$

$$-a\ln(b) = \ln\left(\frac{1}{b^a}\right)$$

So

$$\ln Q = \ln\left(\frac{\left(\frac{[A_2B]}{1M}\right)\left(\frac{P_{AB}}{P^0}\right)}{\left(\frac{P_A}{P^0}\right)^3}\right)$$

i.e., here

$$Q = \frac{\left(\frac{[A_2B]}{1M}\right)\left(\frac{P_{AB}}{P^0}\right)}{\left(\frac{P_A}{P^0}\right)^3}$$

Note: the solid does not enter into Q, since its density does not change (and therefore its Gibbs free energy does not change.

The same considerations apply to any other reaction; for example, in the reaction $3NO(g) \rightarrow NO_2(g)+N_2O(g)$, then the same relation ($\Delta G = \Delta G^0 + RT\ln Q$) applies, where now

$$Q = \frac{\left(\frac{P_{NO_2}}{P^o}\right)\left(\frac{P_{N_2O}}{P^o}\right)}{\left(\frac{P_{NO}}{P^o}\right)^3}$$

Another important thing to note about Q is that it is defined always, even if the reaction did not reach equilibrium; i.e., if we inject NO to a container which is initially empty, then initially Q will be zero (as N_2O and NO_2 are initially zero) but as time passes some NO_2 and some NO_2 will be made, so Q will grow, until there is equilibrium, and then Q does not change anymore (since the pressures of NO, NO_2 and N_2O will not change anymore). More on this later (we first need to understand the equilibrium case)

(8.iv) Evolution of Q to K=$Q_{eq.}$

At the end of the reaction $\Delta G = 0$, i.e., we reach equilibrium.

The value of Q at equilibrium, is a very special quantity, which we call

$$K \equiv Q(eq.)$$

K has no relation to K used for Kelvin! Just an unfortunate coincidence of using the same symbol to denote several different things! (Just like we use P for probability and pressure…)

Since $\Delta G = 0$ at equilibrium,

$$0 = \Delta G(eq.) = \Delta G^0 + RT\ln(Q(eq.)$$

i.e.,

$$0 = \Delta G^o + RT\ \ln K$$

So

$$K = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

We'll spend the next few lessons discussing K; but before we do that, let's conclude with the more general quantity, Q (recall: K is the equilibrium value of Q).

Q yields ΔG and therefore the **electric work** needed or extractable from the reaction.

For a general reaction,

Reactants ←→ products

Depending on the initial condition, if we have too much products or too much reactants, Q will be larger or smaller than its final value, K (i.e., the equilibrium value):

If Q is too small initially, then the reaction will shift to the right, i.e., products will be made;

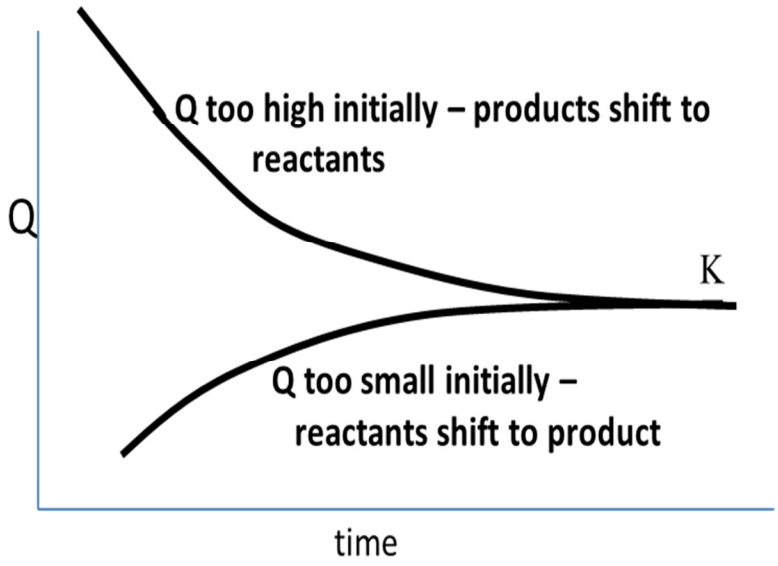
Q(t)<K → products rise.

If Q is too large initially, then the reaction will shift to the left, reactants will be made at the expense of the products.

Q(t)>K → reactants rise, products lost.

Q can have any value from 0 to infinity. As the graph shows, Q will evolve in time until it reaches the equilibrium. value, K (which is Temperature-dependent).

We reemphasize that **Q is related to the amount of electric work, $-\Delta G$, that can be extracted from the reaction:**



$$\Delta G = \Delta G^0 + RT \ln Q$$

From def. of K, get:

$$\Delta G = -RT \ln K + RT \ln Q$$

So:

$$\Delta G = RT \ln(Q / K)$$

Divide by RT and expontentiate:

$$\frac{Q}{K} = e^{\Delta G / RT}$$

Note that at late times, when equilibrium is established so Q=K, the overall difference in Gibbs free energy, ΔG, vanishes, so no more electrical work can be extracted.

Of course, the change of Q in time does not affect the value of ΔG^0 which refers to what happens when products and reactants are at 1 bar, so it (ΔG^0) does not change in time.

From now one we'll mostly concentrate on equilibrium (i.e., on K(T)) , mention Q sporadically, until we get to electrochemistry (batteries) where Q determines the potential in the battery.

(8.v) The mass reaction law, K and K_C

In the remainder of the chapter we will relate K to the mass reaction law as presented in the book. Further, we will get some properties of K. The next section, LeChatelier's principle, will allow us to learn how to use K in specific examples to predict the equilibrium, changes in it, and the reason for the direction of the change.

Relating to the mass action law.

Take for concreteness the reaction we considered earlier,

$$3A(g) + 2B(s) \rightarrow AB(g) + A_2B(sol.)$$

and assume it is in equilibrium. **Further, we will not write the "eq" subscript, but you need to remember that all quantities (pressures, densities) that we consider in this example are only predicted at equilibrium.**

We have

$$\exp\left(-\frac{\Delta G^0}{RT}\right) = K(T) = \frac{\left(\frac{[A_2B]}{1M}\right)\left(\frac{P_{AB}}{P^0}\right)}{\left(\frac{P_A}{P^0}\right)^3} \quad (now\ all\ refer\ to\ equilibrium!)$$

Now, we could write this in in a form that involves all the densities, and only the dentists (not pressures), or all products and reactants. That will be called the mass reaction law; however, it is really not as useful as the equation above, but since the book covers it we will do that to.

Specifically, first convert the pressures of the gases to densities (since $[A] = \frac{n_A}{V}, etc.$)

$$P_A = RT[A], \quad P_{AB} = RT[AB]$$

$$K(T) = \frac{\left(\frac{[A_2B]}{1M}\right)\left(\frac{P_{AB}}{P^0}\right)}{\left(\frac{P_A}{P^0}\right)^3} = \frac{1}{1M}\left(\frac{P^o}{RT}\right)^2 \frac{[A_2B][AB]}{[A]^3}$$

i.e.,

$$\frac{[A_2B][AB]}{[A]^3} = K(T) * 1M * \left(\frac{RT}{P^o}\right)^2$$

Further, [B(s)] is independent of pressure and only depends on temperature, so we can multiply the eq. above for K by its density (with the appropriate power), i.e., multiply by $\frac{1}{[B(s)]^2}$, yielding

$$\frac{[A_2B][AB]}{[A]^3[B]^2} = K_C(T)$$

where we called the right-hand side the concentration (c) form of the equilibrium constant, $K_C(T)$:

$$K_C(T) = \frac{1}{[B(s)]^2} * 1M * \left(\frac{RT}{P^o}\right)^2 * K(T)$$

The nice thing about $K_C(T)$ in the emphasized equation (in blue) is that it is looks very symmetrical; it has all the densities, and each density is multiplied or divided and is to the power of its stoichiometric coefficient.

Obviously, we can have such an equation for any reaction, i.e., for a general reaction

$$aA + bB + cC \leftrightarrow xX + yY + zZ$$

We can write

$$K_C(T) = \frac{[X]^x[Y]^y[Z]^z}{[A]^a[B]^b[C]^c}$$

regardless if the compounds are gases, liquids, etc., and can relate K_c to K and therefore to ΔG. This also makes it easier to derive some properties. However, you should remember that ΔG is related to K , not to K_c

(8.vi) Properties of K – derived from K_c

We will use K_c here, but these properties also apply to K

Consider the reaction

$$aA+bB \Leftrightarrow xX$$

With

$$K_c(T) = \frac{[X]^x}{[A]^a[B]^b}$$

- Reverse reaction – invert K

Now consider the reverse reaction

$$xX \Leftrightarrow aA+bB$$

By construction (since the meaning of reactants and products was reversed):

$$K_{c,reverse}(T) = \frac{[A]^a[B]^b}{[X]^x}$$

So: $$K_{c,reverse}(T) = \frac{1}{K_c(T)}$$

And similarly if we use K, and not K_c

$$K_{reverse}(T) = \frac{1}{K(T)}$$

- When we add 2 reactions, the K's multiply:

This is obvious from $K = \exp\left(-\frac{\Delta G^o}{RT}\right)$: The ΔG^o add, so their exponentials multiply.

Example:

$$A + B \rightarrow 2C \quad (1)$$

$$C \rightarrow 3D \quad (2)$$

We can add the 2nd reaction (once we multiply it by 2 in this case!) to the first; symbolically, in this example:

$$(1) + 2 * (2) = (3).$$

and specifically

$$A + B + 2C \rightarrow 6D + 2C \quad (3)$$

i.e.,

$$A + B \rightarrow 6D \quad (3)$$

But when we add reactions, the ΔG^o add (with the correct coefficients), i.e.,

$$\Delta G_3^0 = \Delta G_1^o + 2\Delta G_2^0$$

So

$$K_3 = \exp\left(-\frac{\Delta G_3^0}{RT}\right) = \exp\left(-\frac{\Delta G_1^o + 2\Delta G_2^0}{RT}\right) = \exp\left(-\frac{\Delta G_1^o}{RT}\right)\exp\left(2 * \left(-\frac{\Delta G_2^0}{RT}\right)\right)$$

i.e.,

$$\boldsymbol{K_3 = K_1(K_2)^2}$$

Part 9: Solving for reactions and LeChatelier's principle

Summary

i. LeChatelier's principle: system rearranges to mitigate change

ii. Example: $3NO \leftarrow \rightarrow NO_2+N_2O$ reactions, given initial pressures:

   a. Determine K (at desired T), Pick any v, Determine initial n's R

Relate n for each species with "x", amount of reaction

For each "x", from the n's get the P; find the "x" such that the combination on P gives "Q" that fits K.

iii. Then, shrink V →
All P's rise, Q bigger, system away from equilibrium; trace system till it re-equilibrates →
As we'll see P_{tot} slightly reduced, in accordance with LeChatelier's principle.

iv. T-dependence of chemical reactions: K decreases when T rises for exothermic reaction, explaining how it comes from:

$$K = \exp\left(-\frac{\Delta H^0}{RT}\right)\exp\left(\frac{\Delta S^0}{R}\right)$$

LeChatelier's principle: a general principle, mostly (but not always!) obeyed:

Says:

When a system is in equilibrium, and we change some condition, then the system "fights back" a little, i.e., rearranges itself to somewhat mitigate the effect of the change of external conditions;

In short:

Systems act to <u>mitigate change.</u>

<u>Simple example:</u>

Consider a reaction room temperature,

$$A \rightarrow 2B$$

With K=1 at this temperature. Say we reach equilibrium with $P_{TOT}=0.75*P^0$;

(a) What's P_A, P_B

(b) Now we change the external conditions, i.e., reduce the total volume. The system rearranges, as we'll see. At the new equilibrium the total pressure is doubled $P_{TOT} = 1.5P^0$; <u>what's $P_{A\ final}$, $P_{B\ final}$</u>, and what's the relation to LeChatelier's principle

Answer (we'll use units where $P^0=1$ and therefore drop the P^0 symbol):

(a)

$$\frac{P_B^2}{P_A} = K = 1 \quad \text{so:}$$

$$0.75 = P_{tot} = P_A + P_B = \frac{P_B^2}{K} + P_B = P_B^2 + P_B$$

The solution to this 2nd order equation is $P_B = 0.5, P_A = 0.25, i.e.$, twice as much B as A.

(b) Now P_{tot} is higher, so

$1.5 = P_{B_{final}}^2 + P_{B_{final}}$. A simple 2nd order equation, with solution:

$$P_{B_{final}} = \frac{-1 + \sqrt{1 + 4 * 1.5}}{2} = 0.82$$

$$P_{A_{final}} = 1.5 - P_B = 0.68$$

Note that now the ratio of B to A is much less than 2 (0.82/0.68=1.2!). The reason is LeChatelier's principle: the system tries to act to mitigate the pressure increase; it can do so by converting some of the B into A, as each time 2B converts to become a single A, the number of molecules is reduced by 1, therefore relieving some of the increased pressure.

<u>Details of the pressure mitigation</u>

You may ask: where is the pressure mitigation? We started with 0.75 bar, and ended with 1.5 bar? What was mitigated?

To answer, realize that we only considered what happened **at the end, i.e., at the initial equilibrium and the final equilibrium.**

Let me give you the details on what happened, without showing you how I got this numbers (you'll see how to do it in a realistic example, in an insert that follows). **See also figure in the next page or two!**

Imagine that we reduced the volume extremely fast, before the system had time to "act", i.e., so fast that no reactions happen while we reduced.

Turns out that for our problem, the volume was reduced by a factor of 2.18, i.e., the final volume is about 46% of the initial volume.

Then, the individual pressures jump.

We know that P=nRT/V, and, since n_A, n_B had no time to change, PV is fixed, the volume reduction by a factor of 2.18 caused a pressure increase of 2.18, so:

$$P_A(\text{just after push }) = 2.18 * P_A(\text{before push}) = 2.18 * 0.25bar = 0.545$$

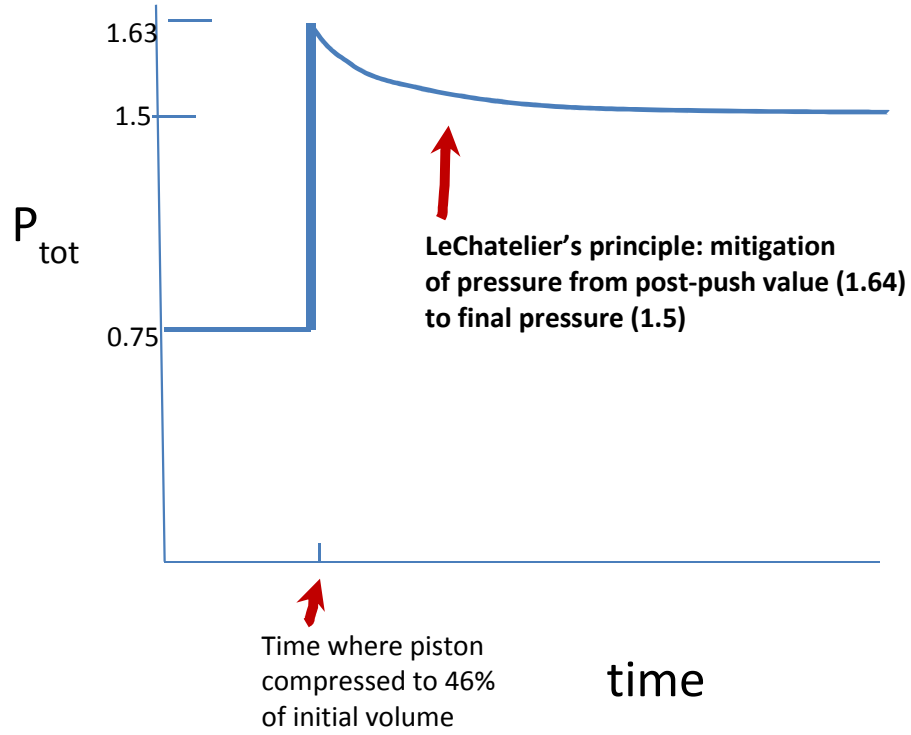
$P_B(\text{just after push }) = 2.18 * P_B(\text{before push}) = 2.18 * 0.5bar = 1.09$ So

$$\boldsymbol{P_{tot}(\text{just after push}) = 0.545 + 1.09 = 1.635}$$

However, when that happens, A and B are no more in equoilibreium, since

$$Q = \frac{P_B^2}{P_A} = \frac{1.09^2}{0.545} > 1$$

i.e., Q will not equal K (which is 1).



Then, what the system, needs to do to rereacxh equilibrium is to **shift some products towards reactants; that will cause of course a net reduction in the number of moles here, since 2 moles of B make, when they are consumed, only one mole of A!**

Let's then denote the eventual increase in P_A -(from its after-push value, 0.545) as "y"; i.e.,

$$P_{A\ final} = 0.545 + y$$

then, the pressure decrease in B from the aft-erpush value will be twice as much (with the opposite sign):

$$P_{B_{final}} = 1.09 - 2y$$

So then we need to solve:

$$1 = K = \frac{P_{B}{}^{2}_{final}}{P_{A_{final}}} = \frac{(1.09 - 2y)^2}{0.545 + y}.$$

The solution is, as you can verify

$$y \sim 0.135,$$

so

$$P_{A_{final}} \sim 0.68, \quad P_{B_{final}} \sim 0.82,$$

as we derivd in the beginning.

<u>So to conclude:</u>

- We started with P_{tot} =0.75, with the system at equilibrium.

- Compressed very quickly reducing the volume by a factor of 2.18 (i.e., reducing the total volume to about 46% of its initial value), yileding P_{tot}=1.635; that took the system away from equilibrium.

- Then the system rearranges, 2B converts back to A, causing reduction in the pressure, so P_{tot} is reduced back to 1.5; this last part is the LeChateliere's principle regime – the system fought back a little, and, within the new total volume (46% of the initial volume), it reached a new equilibrium where the rise in pressure (from P_{tot}=0.75 to 1.635) is somewhat mitigated, so the final total pressure is P_{tot}=1.5
  I.e.,

P: 0.75→1.64→ (LeChatelier's) 1.5.

INSERT: Comprehensive reliastic example (will teach us about reactions in general). **VERY LONG! NOT COVERED IN CLASS, BUT YOU NEED TO KNOW IT**

Take the reaction (all gases)

$$3NO \leftrightarrow N_2O + NO_2$$

at room temperature.

Assume that we do the experiment at 800K, and inject NO and NO_2 so that

- the initial pressure of NO is 0.4 bar;
- and the initial pressure of NO_2 is 1.6 bar;
- and there's no N_2O initially

Then:

a) Calculate K(T=800K) (don't get confused between K used for reactions and K as Kelvin).

b) Calculate the pressures of NO, NO_2, N_2O in equilibrium, if the total pressure is kept constant at the same value as it is initially (i.e., P_{tot} = 2 bar)

c) The next stage will be to increase SUDDENLY the total pressure from 2bar to 4bar and then keep the volume fixed (i.e., shrink the total volume by a factor of 2) calculate the pressures at the new equilibrium (i.e., the equilibrium at the reduced volume). **You'll see that the new equilibrium is shifted toward s the products, and this will help to somewhat mitigate the pressure increase (i.e., the total pressure increased from 2bar to 4bar and is then slightly reduced).**

Answer:

The solution is quite lengthy; we'll skip over some details.

Schematically:

First determine K;
Then initial pressures (P's) → initial density (n's) → vary the density → determine the pressures and Q → till Q =K.

In detail:

(i) First: determining K

$$K=\exp(-\Delta G^o/RT);$$

The initial temperature is not room temperature; we don't have ΔG^o at that temperature tabulated.

So to calculate, we'll have to use

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

We'll approximate (good enough):

$$\Delta H^o(T) \cong \Delta H^0(T_{room})$$
$$\Delta S^o(T) \cong \Delta S^0(T_{room})$$

so In our case: at room temp., from the table at the end of the book (rounding to 1 significant digit after the period):

$$H^o(T_{room}) = H_{f,NO_2} + H_{f,N_2O} - 3H_{f,NO} = -155.4\frac{\text{kJ}}{\text{mol}}$$
$$S^o(T_{room}) = S_{m,NO_2} + S_{m,N_2O} - 3S_{m,NO} = -172.1\frac{\text{J}}{\text{K mol}} = -0.1721\frac{\text{kJ}}{\text{K mol}}$$

Where in the last part we converted the entropy so it is in kJ/ (mol K), making it easier to add –TS to H (i.e., ensuring that energy is always in the same unit, kJ).

Next:

$$\Delta G^o(800K) \cong \Delta H^o(T_{room}) - 800K \bullet \Delta S^0(T_{room}) \quad \cong -17.7\frac{\text{kJ}}{\text{mol}}$$

so

Also, a useful fact for below is that $R * 800K = 6.64$ kJ/mol (verify!), so

$$K(T = 800K) = \exp\left(-\frac{\Delta G^o}{R * 800K}\right) = \exp\left(\frac{17.7\frac{\text{kJ}}{\text{mol}}}{6.64\frac{\text{kJ}}{\text{mol}}}\right) = e^{2.67} = 14.4$$

(ii) SECOND PART: Determining the pressures, assuming P(total)=2bar

The initial pressures are: (**for simplicity we often don't include the "i" or "initial;" subscript, but all our results in this subsection are for the initial pressures and densities).**

We need P→n, i.e., the discussion and intermediate formulas should really be in terms of mole numbers, not pressure.

We know P V= nRT, so, initially:

$$n_{NO} = \frac{V_i}{RT} P_{NO}$$

$$n_{NO_2} = \frac{V_i}{RT} P_{NO_2}$$

The problem is that we don't know the initial volume; in essence, we can take any value of the initial volume, and that will give us a corresponding number of moles.

Let's take, e.g., V_i=20.75 L (we could have taken any other value, this turns out to be convenient in the manipulations below). Then:

Using, 1P^0*L=100J=0.1kJ, we get

$$n_{NO} = \frac{V_i}{RT} P_{NO} = \frac{20.75\text{L} * 1.6\ \text{P}^o}{6.64\ \text{kJ/mol}} = 5\frac{\text{P}^o\text{L}}{\text{kJ}}\text{mol} = 0.5\text{mol}$$

As $P_{NO_2} = 0.25 * P_{NO}$, we get $n_{NO_2} = 0.25 * n_{NO} = 0.125$ mol

(iii) Next, what will happen after the compounds react?

Well, we know the reaction is

$$3\text{NO(g)} \leftarrow\rightarrow \text{N}_2\text{O}+\text{NO}_2$$

That means that when 1 mol of NO_2 is made, then 1 mol of N_2O will be made, and 3 moles of NO will be consumed; so if an "x" amount of moles is made in the reaction, then the number of moles of each species will be (we don't write it explicitly, but all the densities are in "mol")

$$n_{NO} = n_{NO}(i) - 3x = 0.5 - 3x$$

$$n_{NO_2} = n_{NO_2}(i) + x = 0.125 + x$$

$$n_{N_2O} = n_{N_2O}(i) + x = x$$

And, as useful for the future:

$$n_{tot} = n_{NO} + n_{NO_2} + n_{N_2O} = 0.625 - x$$

The allowed values of x are those that lead to non-negative number of moles for each of the species, i.e., in this case

$$0 \leq x \leq \frac{0.5}{3} = 0.1666$$

(Note that if initially we had all product species, i.e., if N_2O was also present, then "x" could have also been negative).

What's the value of x?

For this we need to go back from densities to pressures.

We are told what's the final pressure, P_{tot}=2bar, not the final volume; so we use:

$$P_{NO} = \frac{n_{NO}}{n_{tot}} P_{tot} = \frac{0.5 - 3x}{0.625 - x} * 2$$

Note we calculate all pressures henceforth in units of P^0, so we omit the P^0 symbol, i.e., P_{tot}=2, and

$$P_{NO_2} = \frac{0.125 + x}{0.625 - x} * 2 \qquad P_{N_2O} = \frac{x}{0.625 - x} * 2$$

Now that we have the pressures, we can write Q:

$$Q = \frac{P_{NO_2} P_{N_2O}}{P_{NO}{}^3}$$

We could have copied the values of the P's in terms of x and inserted them into Q, to get a monstrous looking expression that depends only on x, but instead it is much better to prepare a table that will give us, for progressively better guesses for x, the values of the pressures and Q. Here's the table (using excel or your calculator):

x (between 0 and 0.1666)	$\frac{P_{NO}}{P^o} = 2\frac{0.5-3x}{0.625-x}$	$\frac{P_{NO_2}}{P^o} = 2\frac{0.125+x}{0.625-x}$	$\frac{P_{N_2O}}{P^o} = 2\frac{x}{0.625-x}$	$Q = \frac{\frac{P_{NO_2}}{P^o}\frac{P_{N_2O}}{P^o}}{\left(\frac{P_{NO}}{P^o}\right)^3}$	K
0.0	**1.60**	**0.40**	**0.00**	**0.00**	**14.40**
0.08	0.95	0.75	0.29	0.25	14.40
0.12	0.55	0.97	0.48	2.71	14.40
0.14	0.33	1.09	0.58	17.57	14.40
0.13	0.44	1.03	0.53	6.16	14.40
0.135	0.39	1.06	0.55	10.03	14.40
0.138	0.35	1.08	0.57	13.89	14.40
0.139	0.34	1.09	0.57	15.60	14.40
0.1385	0.35	1.08	0.57	14.71	14.40
0.1383	**0.35**	**1.08**	**0.57**	**14.38**	**14.40**

Note what we have done: we started with a random value of x (0.08, midway within the allowed range), then adjusted it up or down till Q essentially equals K. So the final prediction is that when Ptot=2bar, then at equilibrium the pressures of NO, NO_2 and N_2O are, are, respectively,, 0.35 bar, 1.08 bar and 0.57 bar.

By the way, what's the final volume at this stage? Can use any of the species to calculate, e.g., NO;

$$n_{NO} = 0.5 - 3 * x_{final} = 0.5 - 3 * 0.1383 = 0.0851$$

$$V_{endstage\ ii} = RT\frac{n_{NO}}{P_{NO}} = 6640\frac{\text{J}}{\text{mol}} * \frac{0.0851\ \text{mol}}{0.35\ \text{P}^{\text{o}}} = 1615\frac{\text{J}}{\text{P}^{\text{o}}} = 16.15\ \text{L}$$

Of course, we'll get the same answer if we were to put in the pressure and number of moles of the other species. Note by way how the final volume in stage (ii) is smaller than the initial volume we started with (20.75 L); this is because the reactions reduces here the number of moles, so the same total pressure is obtained with a smaller volume to accommodate the smaller total number of moles.

Next part:

(iv) Recall Question (c) from a few pages ago: what happens when we shrink the resulting system in part ii so that the pressure suddenly rises from 2bar to 4bar, and then keep the volume fixed.

When we quickly double the pressure, before any reactions happened *(it may be very difficult in practice to do it so quickly, but let's assume we can shrink it very fast),* then V is shrank by a factor of 2, from $V_{\text{endof ii}} = 16.14\text{L}$ to $V_{iii} = 8.08\text{L}$

Then, we need to do a similar table to the one we had before, except that now we know the volume, not the total pressure. So therefore we use:

$$\frac{RT}{V_{iii}} = \frac{6640\frac{J}{mol}}{8.08L} = 8.21\frac{P^0}{mol}$$

So:

$$P_{NO} = \frac{RT}{V_{iii}}n_{NO} = 8.21 \cdot (0.5 - 3x) \cdot P^0$$

And similarly:

$$P_{NO_2} = \frac{RT}{V_{iii}}n_{NO_2} = 8.21 \cdot (0.125 + x) \cdot P^o,$$

$$P_{N_2O} = \frac{RT}{V_{iii}}n_{N_2O} = 8.21 \cdot x \cdot P^o$$

$$P_{tot} = \frac{RT}{V_{iii}} n_{tot} = 8.21 \cdot (0.625 - x) \cdot P^o,$$

Let's insert into a table (that now includes the number of moles for each species). Each line is associated with a different value of x; we iterate till convergence, as before.

An important point: notice that initially, even though the number of moles did not change, Q will be different from K (i.e., its value will be 7.20 while before it was close to 14.4), since the volume changed after we reached equilibrium, and therefore the pressure changed.

	mole numbers (in mols)			Pressures (all in bars)					
x (between 0 and 0.1666)	n(NO) = 0.5-3*x	n(NO2) =0.125+x	n(N2O)=x	p(NO) = 8.21 n(NO)	p(NO2) = 8.21 n(NO2)	p(N2O) = 8.21 n(N2O)	Ptot	Q	K
0.1383	0.0851	0.2633	0.1383	0.70	2.16	1.14	4.00	7.20	14.40
0.1500	0.0500	0.2750	0.1500	0.41	2.26	1.23	3.90	40.19	14.40
0.1450	0.0650	0.2700	0.1450	0.53	2.22	1.19	3.94	17.36	14.40
0.1420	0.0740	0.2670	0.1420	0.61	2.19	1.17	3.97	11.40	14.40
0.1430	0.0710	0.2680	0.1430	0.58	2.20	1.17	3.96	13.04	14.40
0.1437	0.0689	0.2687	0.1437	0.57	2.21	1.18	3.95	14.38	14.40

Note an important point: we get that **now that the volume is halved, than in order to reach equilibrium x needs to be increased, i.e., some more NO needs to be consumed. This results in a reduction of the total number of moles, s**

n_{tot} =0.625-x (see before) changed from

n_{tot} = 0.625-0.1383=0.487 mol initially (at the beginning of stage iii)

to

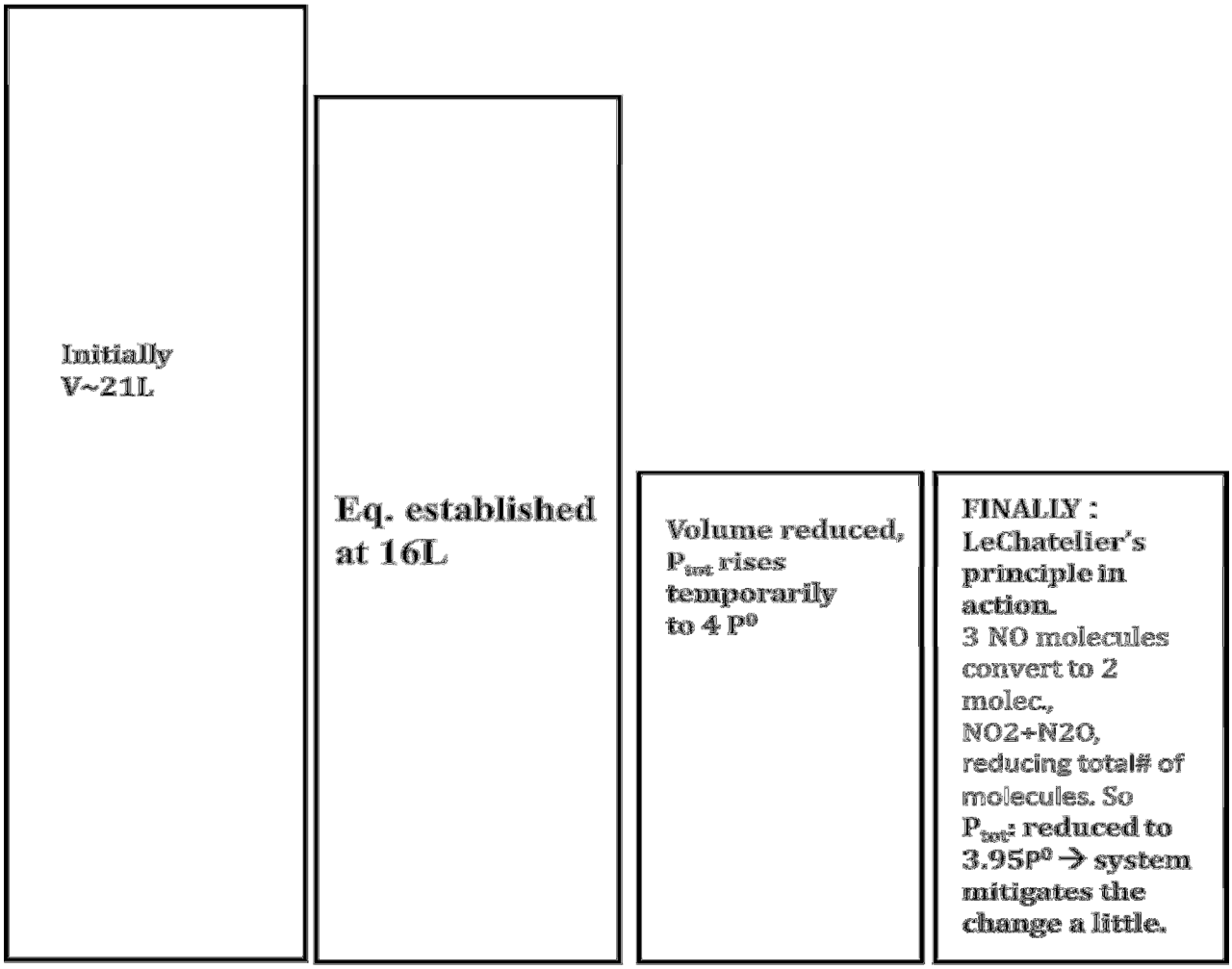
n_{tot} = 0.625-0.1437=0.481 mol finally (at the end of stage iii),

i.e., a 0.0054 mol decrease (about 1.1% decrease).

Put differently: **LeChatelier's principle worked:**

- After stage (ii) the total pressure was 2bar
- Then, at the beginning of stage (iii), volume reduction temporarily increased the total pressure to 4bar
- The gases then rearranged by <u>removing reactants and making products</u>, ($3NO \rightarrow NO_2+N_2O$) since that reduces the total number of moles, thereby slightly relieving the pressure, i.e., reducing P_{tot} to 3.95bar.

Graphical summary:



END OF COMPREHENSIVE EXAMPLE INSERT!

LeChatelier's principle for the T-dependence of K(T).

Prologue: for pressure LeChatelier's principle implied that a reacting system fights back a pressure increase by rearranging products or reactants to decrease the change,

Similarly, for a raise of Temperature a similar phenomenon occurs, as we will show now – the system rearranges (shifts towards products or reactants) in a way that will "absorb" some of the extra energies.

In detail: First, recall some definitions.

Reactions with **$\Delta H^0<0$ are called exothermic; the reaction releases heat.** (H of reactants higher than that of product).

$\Delta H^0>0$ are called **endothermic;** the reaction absorb heat from surrounding.

Let's see the temperature dependence of K and how it relates to LeChatelier's principle.

$$K=\exp\left(-\frac{\Delta G^0}{RT}\right)=\exp\left(-\frac{\Delta H^0-RT\Delta S^0}{RT}\right)=\exp\left(-\frac{\Delta H^0}{RT}+\frac{\Delta S^0}{R}\right)$$

Which we'll write as

$$K=\exp\left(-\frac{\Delta H^0}{RT}\right)\exp\left(\frac{\Delta S^0}{R}\right)$$

Now usually, as mentioned, ΔH^0 and ΔS^0 don't change much with temperature, so **the T-dependence of K is due to the 1/T term in** $\exp\left(-\frac{\Delta H^0}{RT}\right)$**.**

For an exothermic reaction, $\Delta H^0<0$ – Thus, at low temperatures (where 1/T is very large) $-\frac{\Delta H^0}{RT}$ is very positive,

but when T is larger, 1/T is smaller, so $-\frac{\Delta H^0}{RT}$ is less positive;

In short, **for exothermic reactions lnK (and therefore K) decreases with T.**

Let's understand it in terms of LeChatelier's principle.

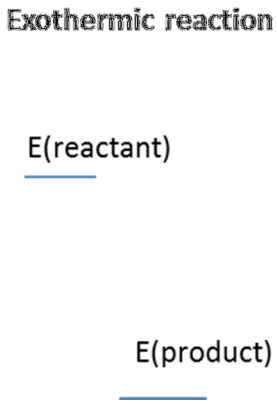
For an exothermic reaction, when we raise the temperature, the system wants to fight this change;

The way to do it is to move products back into reactants, since reactants store energy in them, i.e.,

By moving products back to reactant the system :

- reduces the kinetic energy (and therefore reduce the temperature) and
- convert it to the potential energy stored by the reactant.

Qualitatively, imagine that we consider some exothermic reaction, which is at equilibrium at room temperature; raise the temperature VERY QUICKLY (before the system has time to react and change the number of products and reactant) In); and then let it evolve;



What LeChatelier's principle tells you is that the system will then shift so more products to reactants (reduce # of products, raise # of reactant' moles), as this will cause the "absorption" of kinetic energy.

Practical calculation of K at different temperatures:

From:

$$K = \exp\left(-\frac{\Delta H^0}{RT}\right)\exp\left(\frac{\Delta S^0}{R}\right)$$

we get:

$$\ln K(T) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Again, approximate that ΔH^o and ΔS^o are both T-independent.

We apply this equation at two different temperatures we get

$$\ln K(T_2) = -\frac{\Delta H^o}{RT_2} + \frac{\Delta S^o}{R}$$

$$\ln K(T_1) = -\frac{\Delta H^o}{RT_1} + \frac{\Delta S^o}{R}$$

Subtracting gives

$$\ln K(T_2) - lnK(T_1) = -\frac{\Delta H^o}{RT_2} - \left(\frac{\Delta H^o}{RT_1}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Therefore, from the rate at one temp. and from ΔH^o, the amount of heat given or taken in the reaction, we can find the rate at other temperature.

Part 10: Acids and Bases

Contents:

NOTE: THROUGOUT THIS CHAPTER WE'LL ALWAYS REFER TO MOLAR DENSITIES [A] IN MOLES PER LITER, M, AND WE OFTEN WON'T DESIGNATE THE UNIT M.

i) Definitions – acids and bases.

Define:

Acid: (Bronsted-Lowry) – Proton Donor

Base (Bronsted-Lowry) – Proton Acceptor

Dissolution in Water:

$$HA(aq.) + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq.)$$

(acid) (base) (conjugate acid) (conjugate base)

Equivalently we write: $HA(aq.) \Leftrightarrow H^+(aq.) + A^-(aq.)$

Similarly, we write a generic base equation:

$$B(aq.) + H_2O(l) \Leftrightarrow BH^+(aq.) + OH^-(aq.)$$

base acid conj. acid conj. base

More generally:

HA	+	B	$\Leftrightarrow$	A^-	+	BH^+
acid		base		base conj.toA		acid conj. to B

Note that we don't need to have a water solution at all, as in the reaction

$$HCl(g) + NH_3(g) \Leftrightarrow NH_4Cl(s)$$

Since the latter is essentially a $NH_4^+ + Cl^-$ solid; i.e., this reaction shifts H^+ from HCl to $NH_4{}^+$

Protons and protonated water:

Note that a proton in water will always get water around it.

Notation equivalence:

$HA + H_2O \Leftrightarrow H_3O^+ + A^-$

means the same as:

$HA \Leftrightarrow H^+ + A^-$

H_3O^+(aq.) or H^+ (aq.) are equivalent ways of denoting proton solvated in water, so we can use $[H_3O^+] = [H^+]$ interchangeably.

Lewis acids and Bases

The Bronsted-Lowrey definition (acid is proton donor, base acceptor) is pretty broad;

but the Lewis def. is even more inclusive:

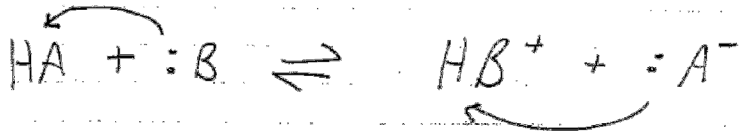
> Acid: an electron pair acceptor
>
> Base: an electron pair donor

We can see how the Lewis definition includes the Bronsted-Lowrey definition i.e., a proton donor (HA) can be viewed as accepting an electron pair (when it becomes A^-);

i.e., before dissociation(when the acid was in the form of HA, or formally H:A), A was attached to a proton and had no free electron pair; now, after releasing the H+, the remaining A^- is in the form

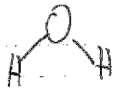
:A,

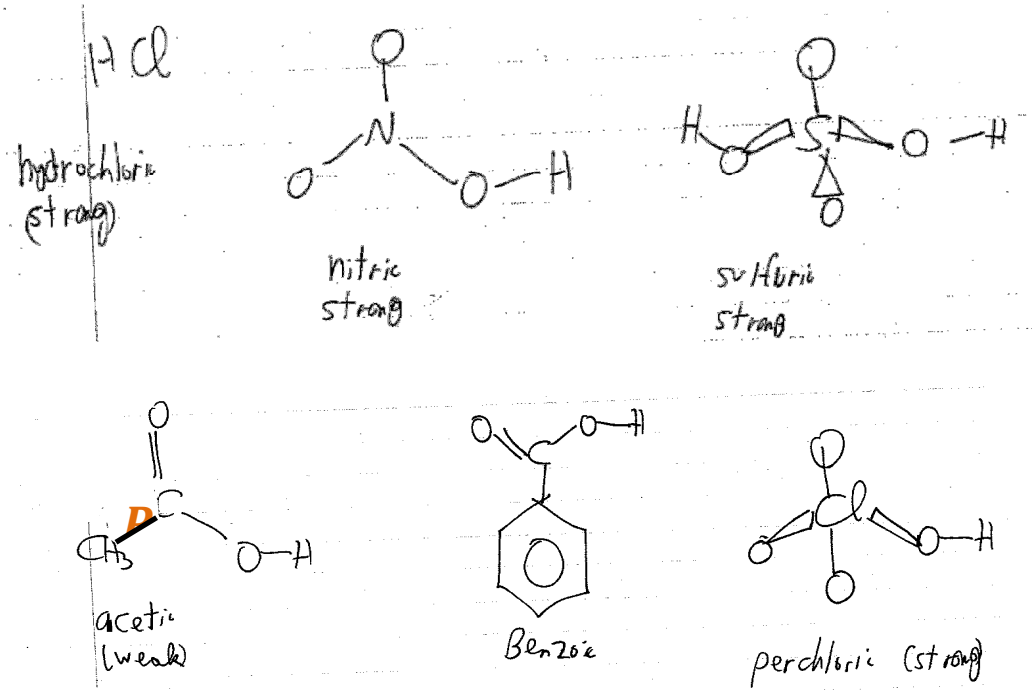
i.e., it has a free electron pair)



(The arrows mean movement of an electron).

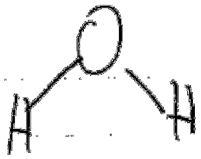
Acid examples:

Water: 

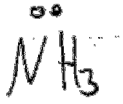


Note: most are oxyacids (release H bonded to O).

Base examples:

- Water :  (i.e., water is <u>amphoteric</u> – both base and acid).
- Sodium and potassium hydroxides, etc. NaOH (OH^-), KOH

Note:

- In NaOH we release OH^- which in water combines with H^+ to produce H_2O → End result is: release of OH^- is equivalent to being an acceptor of H^+ i.e., a base.
- Ammonia:  , other amines:  :
  Lone pair facilitates proton acceptance

Acid anhydrides and Base anhydrides.

Note: some substances do not appear to be acids or bases by themselves, but when dissolved in water form acidic or basic solutions because of subsequent reactions. These are called anhydrides. Example:

$$\text{acid (accepts } OH^-\text{):} \quad CO_2(g) + 2H_2O(l) \Leftrightarrow HCO_3^-(aq.) + H_3O^+(aq.)$$

$$\text{base (causes release of } OH^-\text{)} \quad CaO(s) + H_2O(l) \Leftrightarrow Ca^{2+}(aq.) + 2OH^-(aq.)$$

Acid strength: refers to species ability to donate proton to water:

$$HA(aq.) + H_2O(l) \Leftrightarrow H_3O^+(aq.) + A^-(aq.)$$

And since it is impossible to designate whether a proton is free (H^+) or bound to water molecule (H_3O^+), we can rewrite the equation above simply as

$$HA(aq.) \Leftrightarrow H^+(aq.) + A^-(aq.)$$

Def.:

$$K \equiv K_A(\text{acid dissoc. const.}) = \frac{[H^+][A^-]}{[HA]}$$

$K_A >> 1$ → HA is a strong acid.

$K_A << 1$ → HA is a weak acid.

Strong acids: equilibrium in highlighted equation lies to the right →When an acid HA (initially of concentration $[HA]_0$) is poured into water almost all of it dissociates, i.e., $[\boldsymbol{A^-}] \cong [\boldsymbol{HA}]_\mathbf{0}$.

Weak acids: equi. is often (some exceptions) far left, $[\boldsymbol{A^-}] \ll [\boldsymbol{HA}]_\mathbf{0}$ but this depends on $[HA]_0$

Convenient characterization of strength of acid is pK_a,

$$pK_a = -\log_{10}(K_a)$$

(Note: acids and bases are the only time in this course where we refer to $\log_{10}$, as in other places we use ln, i.e., log in base e).

Examples:

$$K_a = 10^7 \rightarrow pK_a = -7 \quad \text{(strong acid)}$$
$$K_a = 10^{-5} \rightarrow pK_a = 5 \quad \text{(weak acid)}$$

Clearly a species with a more positive pKa will be a weaker acid as its K_a is lower.

Base Strength

Species ability to snatch proton from water to form OH^-(aq.)

$$H_2O(l) + B(aq.) \Leftrightarrow OH^-(aq.) + BH^+(aq.)$$

$$K \equiv K_b = \frac{[OH^-][BH^+]}{[B]}$$

And of course:

$$pK_b = -\log_{10}(K_b)$$

Note:

$K_b >> 1$: strong base, many OH^- produced, little [B] left.

$K_b << 1$: weak base, most [B] remains.

Acid Strength: factors that influence

Acid strength of [HA] is determined by

- Strength of covalent bond if there is one

HF HCl HBr HI

$\longrightarrow$

(Acid strength grows down the halogens column -- weaker bond)

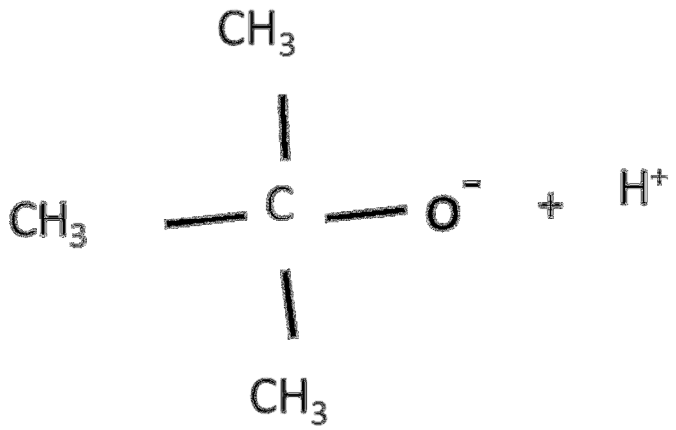
- Solution stabilization of A^-

$$CH_3OH \rightarrow CH_3O^- + H^+$$

vs.

$$(CH_3)_3COH \rightarrow (CH_3)_3CO^- + H^+$$

The latter ion is harder to stabilize in H_2O due to bulky CH_3 groups, so $(CH_3)_3COH$ is a weaker acid.



K_W

Water: acts as acid and base, i.e.,

$$H_2O(l) \Leftrightarrow H^+(aq.) + OH^-(aq.)$$

($sometimes$ written as $H_2O(l) + H_2O(l) \Leftrightarrow H_3O^+(aq.) + OH^-(aq.)$)

$$K_W = [H^+][OH^-]$$

K_w(T) *:* water dissociation constant.

In any aq. solution at equi., $K_W(T) = [H^+][OH^-]$ is constant, i.e., independent of everything else except T.

[word of caution – if the solution stops being aqueous solution, i.e., if it is, say, less than ~ 70% water, the product can change; but we won't discuss such situations]

The most important K_W is for T=25^{0}C: $K_w(298K) = 10^{-14}$

(not exactly, but very close to this round number; also, K_W has units of M=mol/Liter, so it is really $10^{-14}M^2$, but we often don't carry the M units around).

Since in pure water the positive and negative ions have the same conc., than in pure water: $[H^+] = [OH^-] = 10^{-7}$ M

An aq. solution with $[H^+] = [OH^-]$ is called <u>neutral solution</u>.

<u>Acidic aq. solution has</u> $[H^+] > [OH^-]$

<u>Basic aq. solution has:</u> $[H^+] < [OH^-]$

Note that the fact that $K_W = [H^+][OH^-]$ allows to connect:

- K_A for acid HA and
- K_B for the conj. base, A^-

Method: Since

$$HA(aq.) \Leftrightarrow H^+(aq.) + A^-(aq.)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

and

$$A^-(aq.) + H_2O(l) \Leftrightarrow HA(aq.) + OH^-(aq.)$$

$$(i.e., \quad B(aq.) + H_2O(l) \Leftrightarrow HB^+(aq.) + OH^-(aq.), \qquad \text{where } B = A^-)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

It follows that:

$$K_a K_b = \frac{[H^+][A^-][HA][OH^-]}{[HA][A^-]} = [H^+][OH^-] = K_W$$

The product on the right is just our good old K_W! I.e.,

$$K_b = \frac{K_W}{K_a}$$

I.e., if K_a is known → find K_b for conj. basis.

PH scale:

Acidity quantified by def. of "pH" or "power of hydrogen ion":

$$pH \equiv -\log_{10}[H^+]$$

At 25 Celsius:

$$\text{Neutral:} \quad [\mathrm{H}^+] = 10^{-7} M \rightarrow pH = 7$$

$$\text{acidic:} \quad [\mathrm{H}^+] > 10^{-7} M \rightarrow pH < 7$$

$$\text{basic:} \quad [\mathrm{H}^+] < 10^{-7} M \rightarrow pH > 7$$

(10.ii) The relation between pH and pK_a and acid ionic/neutral densities, and LeChatelier's principle.

Much of what we discuss below relies on the simple reaction equilibrium equation:

$$HA \Leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

So:

$$\frac{[H^+]}{K_a} = \frac{[HA]}{[A^-]}$$

I.e., the ratio of neutral to ionic form of any acid equals to the ratio of the proton concentration and K_a.

We can convert it to an equation in terms of pH by taking the logarithm of each side in the equation:

$$\log_{10} \frac{[HA]}{[A^-]} = \log_{10} \frac{[H^+]}{K_a}$$

$$\log_{10} \frac{[HA]}{[A^-]} = \log_{10}[H^+] - \log_{10} K_a$$

i.e., we get the **Henderson-Hasselbalch equation**

$$\log_{10}\left(\frac{[HA]}{[A^-]}\right) = -\mathrm{pH} + \mathrm{pK_a}$$

APPLYING THESE RELATIONS: Mathematically, these equations can give the concentration as a function of pH as following. When we throw a fixed amount, $[HA]_0$, into water, it breaks as follows:

$$[HA]+[A^-]=[HA]_0$$

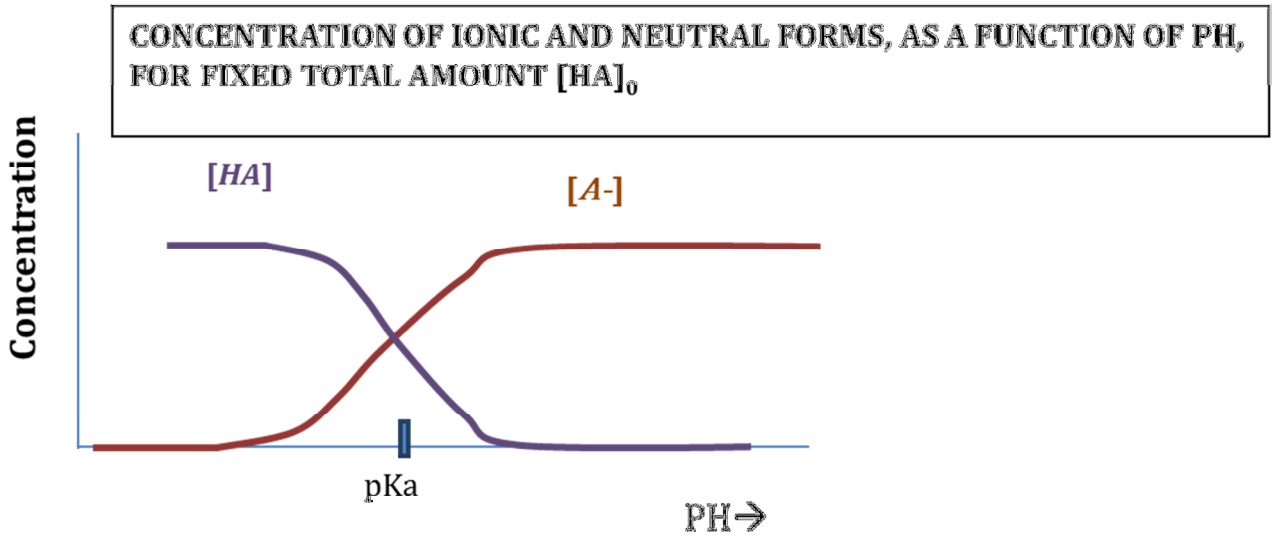
Therefore, combine with the eqs. above to get:

$$\frac{[H^+]}{K_a} = \frac{[HA]}{[A^-]} = \frac{[HA]_0 - [A^-]}{[A^-]} = \frac{[HA]_0}{[A^-]} - 1$$

And therefore:

$$[A^-] = \frac{[HA]_0}{1 + [H^+]/K_a} = \frac{[HA]_0}{1 + 10^{pK_a - pH}}$$

The solution is presented, as a function of pH, in the figure below.



Note that when pH is less than, say, pKa-1 the acid is has mostly [HA] with very little $[A^-]$; the opposite for a more basic solution with pH being pKa+1 or higher, where the solution is mostly ioni;

This is in line with $\log_{10}\left(\frac{[HA]}{[A^-]}\right) = -\text{pH} + \text{pK}_\text{a}$, as we derived in the previous page; if the LHS is small then -1 (i.e., pK_a less then pH-1) then there's very little [HA], etc.

Side note: LeChatelier's principle

Note that the $\log_{10}\frac{[HA]}{[A^-]} = pK_a - pH$ equation is according to LeChatelier's principle: if the equilibrium is shifted so that the solution is more acidic (H+ increases e.g., if another acid is poured in), then the solution will "fight" this change by decreasing $[A^-]$, i.e., shifting some of the protons so that they react with $[A^-]$ and make HA. So the more acidic the environment (the lower the pH), the more neutral the acid; and if the environment is less acidic, than the acid will ionize.

- **Indicators:**

  From the graph above we see how to determine pH:
  Throw in an acid a known pK_a that absorbs in different colors in the neutral [HA] and ionic $[A^-]$ forms; if the color is mostly of [HA], then $pH > pK_a$, and vice versa. If we throw several indicators, each with a different pH, we can nail the pH fairly accurately – this is how litmus paper works.

(10.iii) Finding proton densities in acidic or basic solutions

In the previous section we found out the acidic densities when the proton densities are known. Here we go one step further and discuss cases when we don't know the final proton densities, but wish to calculate them from known initial conditions.

A complication in acids/basis is that even for a single acid, [HA], 2 things are unknown:

x = amt. of [HA] that dissociates.

y = degree of water dissociation into H^+ and $[OH^-]$.

E.g., put an acid [HA] into water. [HA] dissociates; the amount of [A-], which we label as "x", is exactly the same as the amount by which [HA] is reduced from its initial value:

$[HA] = [HA]_0 - x \qquad [A^-]=x$

and the amount of protons is the sum of the protons from the dissociation of the acid (x) and the amount from the dissociation of the water (y):

$[H^+] = x + y \qquad [OH^-]=y$

Note again: the source for the H^+ is both the acid and the water!

The equilibrium constant eq. is:

$$\frac{[H^+][A^-]}{[HA]} = \frac{(x+y)x}{[HA]_0 - x} = K_A$$

And:

$$[H^+][OH^-] = (x+y)y = K_W$$

These equations (2 equations for two unknowns, x and y) need to be solved in practice.

Simplification: Strong acids:

Simplification: in strong acids, since there's "a lot" of $[H^+]$, then $[OH^-]$ is almost zero (since the product of these two ions is fixed, i.e., is K_w).

Therefore, y (i.e., $[OH^-]$) is almost zero, so we can neglect it relative to x, (i.e., we can't assume that y is zero, but we can assume that x+y equals x) . So we'll find x first, then y later.

Example: HCl at room temp. where $K_{cl}=10^7$; let's say that the initial conc. of [HCl] is 2 (i.e., 2M, i.e., 2mol/L, the unit we are always using)

So:

$$K_W = 10^{-14} = y(x+y) \sim yx \quad \text{i.e.,}$$
$$K_W \sim xy$$

And similarly:

$$K_{Cl} = \frac{[H^+][Cl^-]}{[HCl]} = \frac{x(x+y)}{2-x} \sim \frac{x^2}{2-x}$$

Since $K_{Cl} = \text{large } (\sim 10^7)$,

and the numerator above (x^2) cannot be too large,

Then 1/(2-x) must be large, i.e., 2-x is small

so x~2 (not exactly, but close to it),

and $y \cong \frac{10^{-14}}{x} \cong \frac{10^{-14}}{2} = 5 \square 10^{-15}.$

So to conclude:

$$[H^+] = 2M, \quad [Cl^-] = 2M, \quad [\mathrm{OH}^-] = 5 \bullet 10^{-15} M$$
$$[HCl] = \frac{[H^+][Cl^-]}{K_{Cl}} = \frac{(2M)(2M)}{10^7 M} = 4 \bullet 10^{-7} M$$

Key point: for all practical purposes, strong acids dissociate completely.

Strong bases: completely analogous.

Neutralization:

Say we have solution of strong acid + strong base.

Assume strong acid dissociates completely to $H^+ + A^-$

And B similarly dissociates: $H_2O + B \Leftrightarrow HB^+ + OH^-$

Physically we know what will happen: the OH^- and H^+ will neutralize each other, and the one which has a higher conc. will prevail.

I.e., let's denote by $[H^+]_0 = [HA]_0$ the max. conc. of protons (or $[H_3O^+]$) just due to dissociations of the acid and similarly define $[OH^-]_0 = [B]_0$; this is before neutralization of the $[OH^-]$ and $[H^+]$.

Then, if $[H^+]_0 > [OH^-]_0$, then almost all the $[OH^-]$ is neutralized by reactions with protons, so we can:

* find the remaining $[H^+]$,
* and from that we find the small number of $[OH^-]$ remaining:

$$[H^+] \cong [H^+]_0 - [OH^-]_0$$

$$[OH^-] = \frac{K_W}{[H^+]} \qquad (\text{so } [H^+][OH^-] = 10^{-14})$$

and opposite to this if $[H^+]_0 < [OH^-]_0$.

EXAMPLE:

1M HCl + 0.4 M NaOH

$[H^+]_0$ = 1M, $[OH^-]_0$=0.4M →

$[H^+]$ = 1M-0.4M=0.6M,

$[OH^-]=(10^{-14}\ M^2 / 0.6M) = 1.6*10^{-14}$ M

Weak acids:

Mathematical solution has to be done explicitly then.

But if pH<5, $[H^+] >> [OH^-]$, so we can apply similar techniques, i.e., we can assume that the water isn't ionized (i.e., in our language, y<<x). (I.e., since the [OH-] concentration is small, it means that very little [OH-] was produced from water, i.e., the water was not ionized, the H^+ concentration is almost all due to the acid.)

Polyprotic acids: (poly- a lot; protic – proton):

Acids which can lose more than one proton

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad K_1 = 1.2*10^{-4}$$
$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad K_2 = 4*10^{-11}$$

Note that in the first reaction, HCO_3^- has the role of a base (conjugate base), and in the 2nd reaction it is an acid.

Question:

Say that we pour into water 0.034M H_2CO_3, which then reacts via the reactions above;

what's the concentration of the resulting HCO_3^- and CO_3^{2-} as a function of PH?

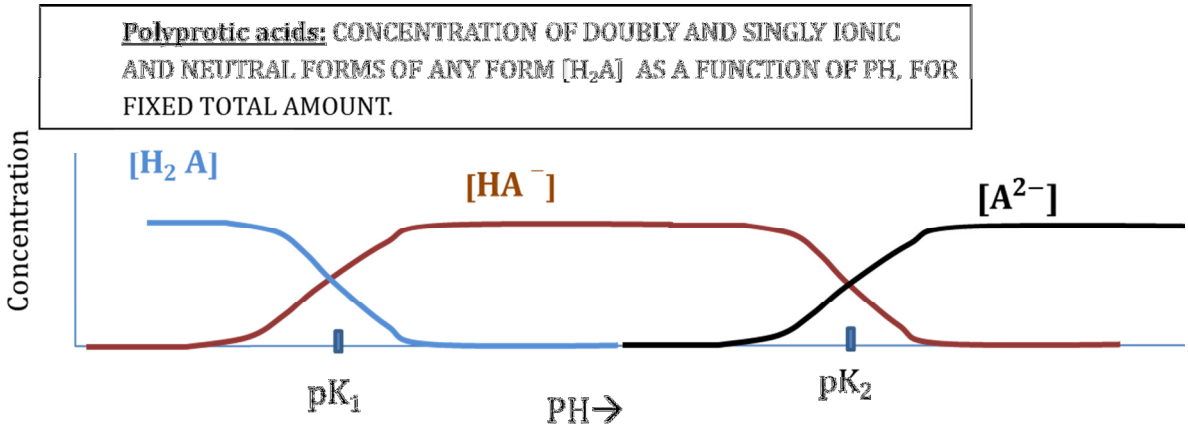
Answer:

There are 2 ways to answer this.

First, almost blindly following the mathematics. This is done in the book.

Second, a graphical solution.

We know that compound will shed its H when pH starts very low and then increases past pK_1. At a much higher pH, around pK_2 the singly ionized form sheds the 2nd hydrogen. Since pK_2 and pK_1 are far away, pK_2 (here $pK_1 \sim 3.8$; $pK_2 \sim 10.5$) the polyprotic acids change of distribution as a function of proton concentration can be viewed as two separate processes.



From this diagram we can "read off" the concentrations as a function of PH. Clearly, from the figure we can ignore the fact that this is a polyprotic acid; i.e., what happens near PH~PK_1 is not influenced by the second reaction, and vice versa.

EXAMPLE

We are given that pH=pK_2-0.5. What's the concentration of the 3 form of A?

Answer.

First:

$$pK_2 = -\log_{10}(4 * 10^{-11}) = 10.4$$

So:

$$pH = 10.397 - 0.5 = 9.9$$

We can find the concentration by assuming that only $[HA^-]$ and $[A_2^-]$ have appreciable densities (as pH is far from pK_1), i.e., that the original acid is in the form of the ionized species.

I.e., just like we derived from the Henderson Hasselach equation before the blue-highshed equations for the density which were derived about 8 pages ago, we get here similarly (with HA- replacing A, and A_2^- replacing A-), that

$$[HA^-] = \frac{[H_2A]_0}{1 + 10^{pK_2 - pH}} = \frac{[H_2A]_0}{1 + 10^{0.5}} \sim 0.24\,[H_2A]_0$$

(You can just read this, approximately, from the graph above).

What about the concentrations of the other species then? Well, the fully-ionized form is

$$[A_2^-] \sim [\mathrm{H_2A}]_0 - [HA^-] \sim 0.76[H_2A]_0$$

Finally, the neutral form, which we know will be present only in very small quantities, can be obtained from pK1, i.e., we apply a Henderson-Hasselblach equation:

$$\log_{10}\frac{[H_2A]}{[HA^-]} = pK_1 - pH$$

but

$$pK_1 = -\log_{10}(1.2 * 10^{-4}) = 3.9$$

So

$$\log_{10}\left(\frac{[H_2A]}{[HA^-]}\right) = pK_1 - pH = 3.9 - 9.9 = -6$$

and therefore

$$[H_2A] = 10^{-6}[HA^-] = 2.4 * 10^{-7}\,[H_2A]_0$$

And it is indeed very small as we knew!

Buffers: Best understood by example:

Without buffers, a little bit of acid can change the acidity wildly.

For example, take 1L of water, neutral – so pH=7. Then, take a small amount, 0.01 mole, of a strong acid added to the water→ density is 0.01 m/L = 0.01 M, pH=-$\log_{10}(0.01)$= 2 → Very acidic (high proton concentration).

Can we find a way to have a weaker acidity, which will be less dependent on what else happens?

The first key is to invoke the equation as we had before, that says that for any acid:

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

So if we can find an acid HA such that $[HA]$, $[A^-]$ can be made to be <u>both</u> appreciable, then $[H^+]$ won't change much, and will be very close to Ka (i.e., pH will be close to pKa).

Another way to see it is to remember that:

$$\log_{10} \frac{[HA]}{[A^-]} = pK_a - pH$$

So if $\frac{[HA]}{[A^-]}$ is not large nor small (say is between 0.1 and 10), its logarithm will not be a very big number, and therefore pH will be close to pK_a.

The way to assure that $\frac{[HA]}{[A^-]}$ is not too large or small is:

- Put in a specific amount of weak acid, HA with weak base $[A^-]$ as conjugate., and:
- At the same time add a source of the conjugate.

Let's exemplify (most likely will only be briefly covered in class, but as you know by now, you need to know this for the exam!): add a weak acid HCOOH, and also add a source, NaCOOH, for its conjugate basis, $COOH^-$.

E.g., add to 1 Liter of water, 0.2 mol of HCOOH, and 0.1 mol of NaCOOH.

We know that NaCOOH easily dissociates:

$$NaHCOO \rightarrow Na^+ + HCOO^-$$

So there's an appreciable amount of the weak acid (because it does not dissociate much), and the conjugate is also appreciable (because it came from a source that easily dissociates.).

Let's put numbers in a table (all in M), ignoring the dissociation of water

	[HCOOH]	**[H^+] (i.e.,[$H3O^+$])**	**[$HCOO^-$]**
Before dissoc. of acid	**0.2**	**0**	**0.1 (from Na^+ + $HCOO^-$)**
Due to acid dissoc.	**-y**	**y**	**y**
Total	**0.2-y**	**y**	**0.1+y**

The table above is known as "Initial, Change, Equilibrium" – i.e., "ICE" table.

Now we know that

$$\frac{[H^+][HCOO^-]}{[HCOOH]} = K_a = 1.77 \bullet 10^{-4}$$

So:

$$\frac{y(0.1+y)}{0.2-y} = K_a = 1.77 \bullet 10^{-4}$$

We can solve this eq. exactly; more simply, we guess that y will be small compared with 0.1 or 0.2, so the previous eq. becomes approximately

$$\frac{y(0.1)}{0.2} \sim K_a = 1.77 \bullet 10^{-4}$$

So

$$y \sim 2 \bullet K_a = 2 \bullet 1.77 \bullet 10^{-4} = 3.54 \bullet 10^{-4}$$

Note that our assumption on y being small relative to 0.1 or 0.2 is consistent (y is small indeed!).

Since y is small, essentially 0.2 moles of HCOOH and 0.1 moles of its conjugate remain (see the table), and the PH is $-\log_{10}(y) = -\log_{10}(3.54*10^{-4}) = 3.45$

Now let's see the power of this "buffer".

Add: 0.01 mole HCl, which essentially completely dissociates to 0.01 mole of H^+ +0.01 mole Cl^- .

Most of this extra H^+ will combine with the $HCOO^-$; so the acidic ion/neutral concentration will be

$$[HCOO^-] \sim 0.1\text{-}0.01 = 0.09$$

$$[HCOOH] \sim 0.2 + 0.01 \sim 0.21$$

So we replace in the peach-color equation above, 0.2 by 0.21 and 0.1 by 0.09

I.e.,

$$[H^+] = \frac{0.21}{0.09} \bullet 1.77 \bullet 10^{-4} = 4.15 \bullet 10^{-4}$$

And when we take -$\log_{10}$ of both sides, we get:

$$pH = -\log_{10}[H^+] = -\log_{10}(4.15 \bullet 10^{-4}) = 3.38$$

I.e., the acidity barely changes! (changed from pH=3.45 to 3.38 only!)

10.iv) Final acids/bases subpart: TITRATIONS

The goal in titrations is: **find the unknown concentration of an acid or base** (called "analyte") in a solution with a known volume.

The idea is simple: add the opposite (i.e., base to acid or vice versa); what we add is called a "titrant".

Titrations involve the addition of a titrant to a solution of analyte containing an unknown amount of acid or base (i.e., the concentration of the acid is unknown).

The volume of the analyte (the acid or base in the solution) is known, but its concentration is not known. In titration we find this unknown analyte concentration by adding to it a known volume of a different solution (the titrant) with a known concentration; essentially, if the analyte is acidic we add to it a base titrant and vice versa (not exactly accurate, since a given compound can be viewed as both acidic and basic, but it is good enough for our purposes).

The **key is that there will be a concentration (the equivalence point) where the actual amounts (moles) of the analyte and titrant will match; at that point, the ions (H+ and OH-) from the analyte and titrant will almost exactly match, so the pH of the solution will change to be close to neutral. The pH change will signify that the amount of moles of the titrant added will be the same (or close to) the amount of initial analyte.**

The amounts of H^+ initially present (or added) is often called "acid equivalent"; a base equivalent is the amount of OH^- in moles for a basic solution.

This **stoichiometric point**, to be discussed later in this section, is the point at which the number of moles of titrant added is equal to the # of moles of analyte in the solution, i.e., the acid and base equivalents will match (for polyprotic acids see below);

Strong Acid-Strong Base Titrations

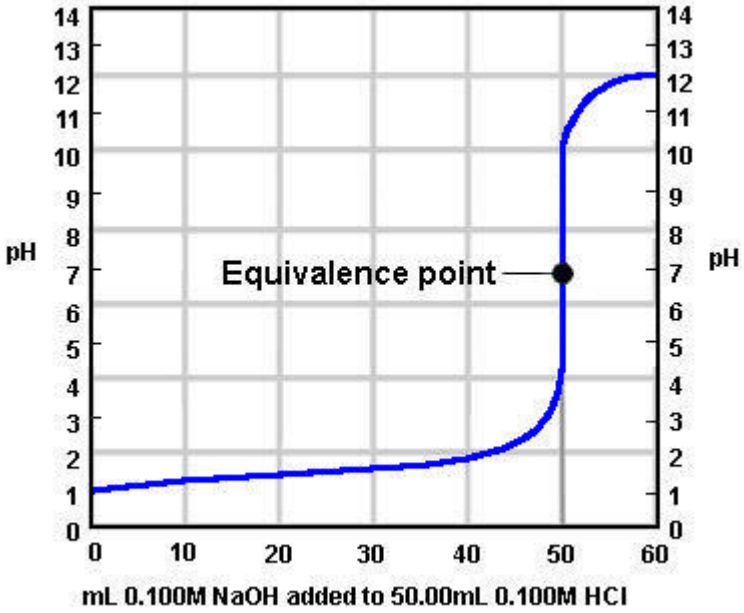
Mixing acids with bases, or bases with acids, the ions react thusly:

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$

Example: add increasing amounts of 0.1M NaOH to a 50.0mL solution of 0.1M HCl:

$HCl (aq) + NaOH (aq) \rightarrow NaCl (aq) + H_2O (l)$

The "titrant" is the NaOH, with known concentration.
The initial solution (which we want to study) is the HCl. This reaction will result in the following pH curve:



The reason for this curve is simple: initially the strong acid leads to a very acidic pH (low pH).

When we add the strong base, then the OH^- "cancels" some of the H^+, (i.e., reacts with it to form water) but as long as the amount of the OH^- added is not too big, the solution will be very acidic.

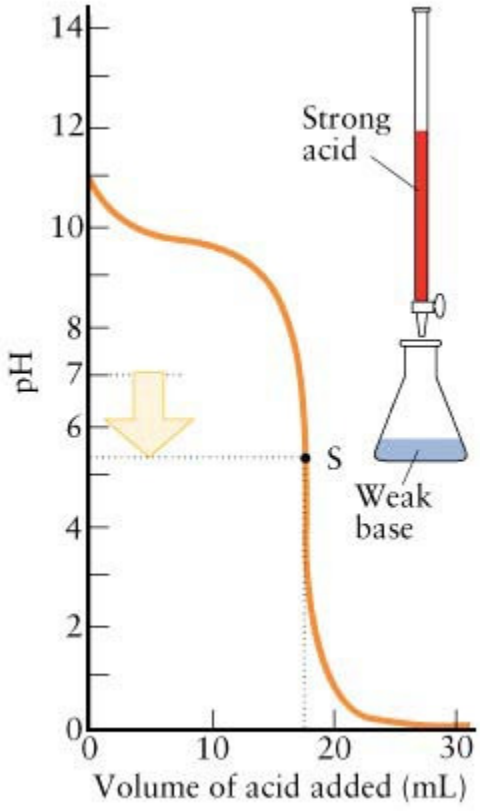
But once we add enough titrant (close to 50ml or above in this example) then very little H^+ remains.

Note that with the addition of strong acids to strong bases and vice versa, the equivalence point occurs at pH=7. I.e., when the amount of the strong base and acid match, the solution will be neutral so pH=7.

Based on the pH of the titrant, the volume of the titrant added, and the volume of the analyte, one can determine the desired unknown, i.e., the concentration of the analyte. See HW for examples

Strong Acid-Weak Base and Weak Acid-Strong Base Titrations

We can also apply the concept of titrations to determine the pH of solutions of weak bases by titrating with a strong acid and the pH of solutions of weak acid using a strong base. The titration curve for the titration of a weak base with a strong acid is shown below.



Note that the stoichiometric point does not occur at pH=7, but the pH still changes most sharply near it (though not as sharply as with a strong acid and strong base).
The reason is clear:

When we throw in, say, 0.05 moles of a strong base HA to an analyte contains 0.05 moles of a weak base HA, then first, before the ions combine, essentially all the strong acid will be ionized, i.e., we will produce initially 0.05 moles of H+;

But NOT all the weak base will dissociate, so we will have less than 0.05 moles of OH^- say only 0.04999 moles of the weak base dissociated.

The resulting 0.04999 moles OH- and 0.050 moles of H+ will combine and as a result we will have a non-zero amount (0.00001 moles) of H+ and a much smaller amount of OH- (determined from K_w/(concentration of H+)).

So therefore, at the equilibrium point for a strong base and a weak acid, where the same number of moles of acids and basis were thrown in, the solution will have a non-neutral pH (in our case 10^{-5} moles).

We won't review the opposite (strong base with weak acid), but it is obviously analogous.

INSERT (NOT COVERED IN CLASS, BUT IS REQUIRED KNOWELDGE)
Polyprotic Acid Titrations

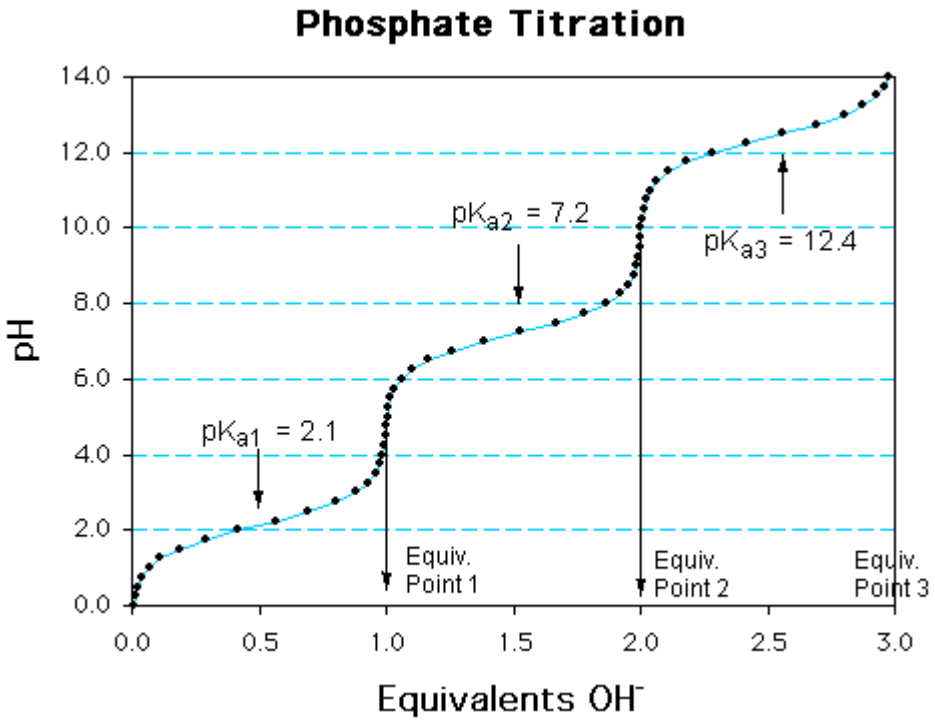
Polyprotic acid titrations are those that involve acids with several hydrogen atoms, e.g. H_3PO_4. They proceed the same way as monoprotic acid titrations, but there is a stoichiometric point for each proton. Consider the titration of H_3PO_4. The titration of this substance consists of three subsequent reactions, occurring in the order listed:

$H_3PO_4\ (aq) + OH^-\ (aq) \rightarrow H_2PO_4^-\ (aq) + H_2O\ (l)$ [1]

$H_2PO_4^-\ (aq) + OH^-\ (aq) \rightarrow HPO_4^{2-}\ (aq) + H_2O\ (l)$ [2]

$HPO_4^{2-}\ (aq) + OH^-\ (aq) \rightarrow PO_4^{3-}\ (aq) + H_2O\ (l)$ [3]

The titration curve is below (the OH- equivalents are here the amount of base added relative to the number of moles of the initial acid):



Reaction [1] corresponds to the first region in the titration above (from 0 to 1 equivalents). Notice that this region has a well-defined buffer region as well as an equivalence point. The pK_a of this region corresponds to the pK_a of reaction [1].

When we add enough base (more than the amount of acid originally present) then the polyprotic acid will turn from neutral to the first ionic form (in this case, $H_2PO_4^-$); that's the region beyond Equiv. point 1.

When we add even more base (beyond twice the initial amount of acid present, i.e., Equiv. point 2), then the polyprotic acid will shed an additional hydrogen';

Also, note that reactions [2] and [3] also have buffer regions and equivalence points. The equivalence point of reaction [3] is less well defined because the pK_a is so close to that of water.

END OF INSERT

PRECIPITATION

(i) **Solid/pure liqu. Reactants: possibility of consuming all reactants**

So far we only discussed acid/base reactions where reactants (at least some) are dissolved.

These are equivalents of reactions with gases where there are gases on both side.

Now we'll tackle cases where the reactants are all solid (liquid too if the liquid is not part of the aqueous solution, but that's a rarity).

Example: Calcium hydroxide, a base.

$$Ca(OH)_2\ (s) \rightarrow Ca^{2+} + 2(OH^-)$$

$K = [Ca^{2+}][OH^-]^2$ (if there's equilibrium with $Ca(OH)_2\ (s)$ existing!)

Note that we did not divide by 1M=1 mol/L, for simplicity; and, more importantly the **concentration of the solid does not appear in the equation for K** (since the Gibbs free energy does not depend on concentration for the solid). **So unlike the previous discussions in this section, where the equality means equality, here, it just means IF THERE'S EQUILIBRIUM BETWEEN REACTANTS and products, such that the REACTANTNS EXIST AT EQUILBRIUM the LHS and RHS will equal**

Turns out that at room temperature, for this reaction,

$$K_{Ca} = 5.5 * 10^{-6}$$

(practice question: what's ΔG^0 then?)

Now, take a specific case – throw in 0.01M amount of $[Ca(OH)_2]$ – e.g., throw in 10 moles to 1000 liter, etc.

Even if all the reactants are consumed, i.e., from 0.01 Moles $CaOH_2$ we make

$$0.01\text{M } Ca^{2+},\ 0.02\text{M } OH^-$$

(Two hydroxide ions for each calcium ion), then still the RHS of the highlighted eq. will be

$$[\text{Ca}^{2+}][\text{OH}^-]^2 = 0.01 * (0.02)^2 = 4 * 10^{-6} < K_{Ca}!$$

So since the density product is lower than K, we won't have an equilibrium where reactants coexist – so all the $Ca(OH)_2$ will be consumed.

In our earlier language, we'll say that the G_m for the product side is lowered than the G_m for the reactant side (solid calcium hydroxide), so $Ca(OH)_2$ will be consumed; but since this reactant is not in solution, as we consume the reactant its G_m will not change.

Contrast this with HCl → H_+ + Cl-, for example – as we consume HCl its concentration changes so its (the HCl's) G_m chances (is lowered), so eventually we'll reach equilibrium ($\Delta G = 0$) where all reactants and products coexist.

(ii) **Precipitating the solid compounds**

If we increase the concentration of one of the products (in our case say OH^- by changing pH), then eventually the density product ($[\text{Ca}^{2+}][\text{OH}^-]^2$) can reach K_{Ca}. Let's calculate the threshold concentration of OH- required in this case to make the first little piece of solid.

$$[Ca^{2+}][OH^-]^2 = K_{Ca} \rightarrow$$

$$[OH^-] = \sqrt{\frac{K_{Ca}}{[Ca^{2+}]}} = \sqrt{5.5 * \frac{10^{-6}}{0.01}} = 0.023$$

Note several things:

- This threshold conc. is HIGHER than 0.02, the conc. of OH^- obtained when all the 0.01 M $Ca(OH_2)$ is released to the solution – so without another

source of hydroxide (another base) the calcium will not precipitate and remain wholly in the ionic form.

- I used 0.01 for the concentration of Ca^{2+} in the eq. above The reason is that we consider the case that almost all the calcium hydroxide is dissolved, and ask what will be the concentration where just a tiny bit is calcium is precipitated , so the ionic liquid form will still have almost the same concentration as if none precipitated. Of course, if the conc. of OH^- was raised even further, then the conc. of the calcium ion will decrease, and more solid calcium hydroxide will precipitate.

- We are treating things like precipitation as if they will immediately occur when they are thermodynamically favored. In reality we can have supersaturated solutions – we'll discuss these later

Let's relate the threshold conc. of OH^- for precipitation to pH:

$$[OH^-] = 0.023 \rightarrow pOH = -\log_{10} 0.023 = 1.64 \rightarrow$$

$$pH = Kw - pOH = 14 - 1.64 = 12.36$$

So for pH above 12.36 the calcium hydroxide will precipitate. (Just like Lechatelier's principle says, think about it!)

(iii) Selective precipitation.

We throw in 0.05 Mole of $Mg(OH)_2$, which is less soluble

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$$

$$\mathrm{K}_{Mg} = 1.1 * 10^{-11},$$

i.e., if there's equilibrium (i.e., if there's solid $Mg(OH)_2$) then

$$1.1 * 10^{-11} = K_{Mg} = [Mg^{2+}][OH^-]^2$$

Repeating the steps in the $Ca(OH)_2$ example, we see that selective precipitation will occur when

$$[OH^-] = \sqrt{\frac{K_{Mg}}{[Mg^{2+}]}} = \sqrt{1.1 * \frac{10^{-11}}{0.05}} = 1.5 * 10^{-5}$$

So

$$\text{pOH} = \log_{10}(1.5 * 10^{-5}) = 4.82 \rightarrow \text{pH} = 9.18$$

We therefore see that selective precipitation, i.e., precipitation of $Mg(OH)_2$ but not of $Ca(OH)_2$,occurs between pH of 9.18 and 12.36.

So:

- below pH of 9.18 – both metal ions (Mg^{2+} , Ca^{2+}) are in the solution;
- between 9.18 and 12.36, Mg^{2+} precipitatres, i.e., is in equilibrium with the solid $Mg(OH)_2$; as pOH is raised from 9.18 gradually, the concentration of the Mg^{2+} is decreased. For example, just before the point where the Calcium hydroxide starts precipitating, at pH-12.36, the concentration of the Mg^{2+} ion will be tiny:

$$[\text{Mg}^{2+}] = \frac{\text{K}_{\text{Mg}}}{[\text{OH}^-]^2} = \frac{1.1 * 10^{-11}}{(0.023)^2} \quad (at\ pH = 12.36, where\ [OH^-] = 0.023)$$

$$[\text{Mg}^{2+}] = 2.08 * 10^{-8}\text{M} = 21\text{nM}$$

- for pH>12.36, even the calcium will precipitate.

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Part 11: Electrochemistry

Overview:

11.i Oxidation-Reduction (redox) reactions: Reactions that involve the exchange of electrons between atoms, compounds, and molecules.

11.ii Half reactions.

Appendix (required) Balancing half-reactions

11.iii Galvanic cells and batteries

11.iv Half-cell potentials; the Faraday equation

11.v Potentials; relation between free energies and potentials.

(11.i) Oxidation and reactions

- **Oxidation:** the loss of electrons in a redox reaction. (Think of H_2O – the hydrogens lose "part" of their electrons to the oxygen – so the hyrodgens are oxidized) . **Oxidizing agent:** species in a redox reaction that is **reduced.**
- **Reduction:** the gain of electrons (or reduction of charge) in a redox reaction (so in H_2O the oxygen is reduced). **Reducing agent:** species in a redox reaction that is **oxidized.**

Oxidation and reduction always occur together, as electrons cannot be created nor destroyed.

To monitor redox reactions, we can use **the oxidation number: the effective charge on a compound or atom.**

- Oxidation results in an increase in oxidation number (i.e., making it more positive); e.g., in Na_2O the oxidation number of Na will be +1.
- Reduction results in a decrease in oxidation number. (E.g., in Na_2O it will be -2, i.e., decrease from 0).

(11.ii) Half Reactions

To properly describe a redox reaction, one must balance both the atoms and the charge, i.e. the charge on both side of the equation must be equal. For example, consider the net ionic equation for the oxidation of copper metal to copper(II) ions by silver ions:

$Cu(s)\ ,\ Ag^{+}(aq) \rightarrow Cu^{2+}(aq)\ ,\ Ag(s)$ (CHARGE STILL UNBALANCED!)

While the atoms are balanced, notice that the left side of the equation has a charge of +1, and the right side has a charge of +2. To balance the charges, write:

$Cu(s) + 2\ Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$

To make balancing redox reactions easier, we can write **half reactions:** the oxidation or reduction part alone. For the above reaction:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^{-}$

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Now, balance the electrons by multiplying the reduction half reaction by 2 and removing electrons.

Note that the half reactions are not just a mathematical trick; in batteries, as we'll show later, they actually occur separately (one part of the battery has one half-reaction, the other part has the other half reaction).

For more complicated reactions involving H's and O's, use the following insert.

INSERT: Rules to balance Redox equation: (not covered in lecture but I'll expect you to know them for the exam!)

1. **Identify the species** being oxidized and the species being reduced from the changes in their oxidation numbers. **Write the skeletal (unbalanced) equations** for the oxidation and reduction half reactions.

2. **Balance all elements** in the half reactions **except O and H.**

3. Find the **change in the Oxidation numbers** of the species, and account for it by adding electrons to the reactant or product side as the case may be.

4. **Balance charge**

- In acidic solution, balance charge by using H^+
- In basic solution, balance charge by using OH^-

5. Then **balance the amount of hydrogens** on both side of each half reaction by using H_2O

6. **Multiply** all species in either one or both of half reactions by factors that result in equal numbers of electrons in the two half reactions, and then add the two equations and include physical states.

7. Finally, simplify the appearance of the equation by **cancelling species** that appear on both sides of the arrow and check to make sure the charges as well as the numbers of atoms balance.

Example:

$$\boldsymbol{MnO_4^- + H_2S \rightarrow Mn^{2+} + SO_4^{2-}}$$

1) First break the reaction to two reactions that take place in 2 half-cells

$$\boldsymbol{MnO_4^- \rightarrow Mn^{2+}}$$

$$\boldsymbol{H_2S \rightarrow SO_4^{2-}}$$

2) Balance the element that undergoes the change in oxidation state on either side of the equation: In this reaction, there is no need to do so, as

the number of species are already equal. But it may not be the case always, as we saw in the Ag Cu example above.

3) Find the change in the Oxidation Number of the species, and account for it by adding electrons to the reactant or product side as the case may be.

$$\overset{+7}{MnO_4^-} + 5e^- \rightarrow \overset{+2}{Mn^{2+}}$$

(each oxygen's formal charge is -2, so the initial manganese must be formally, at +7 so that together we have +7+4*(-2)=-1, as the overall charge of the manganese oxide is -1). Similarly:

$$\overset{-2}{H_2S} \rightarrow \overset{+6}{SO_4^{2-}} + 8e^-$$

4) Now comes the charge balancing step. Find the total charge on each side of the equation and account for it using:
H+ in **acidic** condition and
OH- in **basic** condition

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+}$$

(before the $8H^+$ were added to the eq. above, the left hand side had charge -6, the right +2)

And similarly: $H_2S \rightarrow SO_4^{2-} + 8e^- + 10H^+$

5) Add H_2O to balance the # of hydrogens on either side:

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$
$$H_2S + 4H_2O \rightarrow SO_4^{2-} + 8e^- + 10H^+$$

If you've done parts 1 to 5 correctly, all oxygens should balance out.

6) Now just multiply by factors to make the # of electrons in the two half cells equal, add the two half-=reactions up, write the final equation…and you're done!

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \qquad \text{X8}$$

$$H_2S + 4H_2O \rightarrow SO_4^{2-} + 8e^- + 10H^+ \qquad \text{X5}$$

i.e.,

$$8MnO_4^- + 40e^- + 64H^+ \rightarrow 8Mn^{2+} + 32H_2O$$
$$5H_2S + 20H_2O \rightarrow 5SO_4^{2-} + 40e^- + 50H^+$$

So finally add them up to get (after cancelling $40e^-$, $50H^+$, and $20H_2O$ on both sides) :

$$\mathbf{8MnO_4^- + 5H_2S + 14H^+ \rightarrow 8Mn^{2+} + 5SO_4^{2-} + 12H_2O}$$

The manipulations done here are important later for the discussions of batteries (actually, steps 1-3 are the crucial ones for batteries, the next steps are less crucial).

END OF INSERT: RULES OT BALANCE REDOX REACTIONS

(11.iii) Galvanic Cells and Batteries

Electrochemical cell: device in which **an electric current is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction.**

Galvanic cell: electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current

We use special type of Galvanic cells every day. For example, **batteries are one type of Galvanic cells,** in which the materials are sealed within the battery in individual cells, and the cells are linked directly so that the voltage generated in each can be added to give a higher total voltage. Also, **fuel cells** are a type of Galvanic cell, but in these, the materials that participate in the redox reaction are constantly added and the products are taken away.

Structure of Galvanic Cells

If we simply mix two species that undergo a redox reaction, energy is released as heat, but no electricity is generated. However, if we separate the reactants and provide a pathway for the electrons to travel, the electrons can do work, generating an electric current.

A galvanic cell consists of **two electrodes, or metallic conductors,** which make electrical contact with the contents of the cell but not with each other, and an **electrolyte,** an ionically conducting medium, inside the cell.

The two electrodes are called the:

Anode, at which oxidation takes place, and

Cathode, **at which reduction takes place**

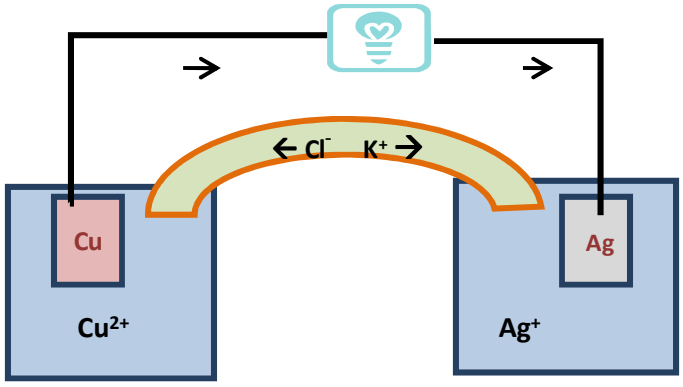
Electrons are released by the oxidation half reaction at the anode, travel through the external circuit, and reenter the cell at the cathode, where they are used in the reduction half reaction.

Acronym: AOL – Anode: Oxidation, Loss of electrons

Example: (see the attached figure)

Take our favorite reaction,

$Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$



Batteries are made essentially out of the two half reactions.

<u>Intuitively,</u> we know which direction is preferred (we'll quantify that later):

- Ag hates to lose electrons (so it rusts very slowly, i.e., it is hard to oxidize it, as rusting is simply due to reactions with oxygen in which the metal is oxidized).
- Cu loses electrons more easily.

So it is preferential to have the reaction as we wrote it above, in which copper is oxidized and silver reduced.

<u>In detail:</u>
Let's write the half-reactions such that a **single electron is given or taken**, i.e.,

$$\frac{1}{2}Cu(s) \rightarrow \frac{1}{2}Cu^{2+}(aq) + e^-$$

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

so the total reaction is now written, for 1 mole of transferred electrons, as:

$$\frac{1}{2}Cu(s) + Ag^+(aq) \rightarrow \frac{1}{2}Cu^{2+}(aq) + Ag(s)$$

Similarly, for n moles of transferred electrons, the reaction will be

$$\frac{n}{2}Cu(s) + nAg^{+}(aq) \rightarrow \frac{n}{2}Cu^{2+}(aq) + nAg(s)$$

We'll see shortly why it is important to write it in such a form.

In the anode, the copper electrode is oxidized, so copper ions join the solution.

The electrons **leave the anode and will like to reach the cathode**, where they combine with the silver-ions (Ag+) to form a solid silver, i.e., silver is deposited on the cathode.

The salt bridge is needed, since without it there will be an accumulation of electrons in the cathode.

But with the salt bridge, there will be charge balancing;

E.g., for a KCl salt-bridge:

- In the anode, as electrons leave the anode, and positively-charge copper is released to the solution, negative Cl^- ions come from the salt bridge and balance the charge.
- And analogously for the cathode, where K^+ ions come from the salt bridge to the solution to replace Ag^+ ions which are deposited on the curve.

To quantify the battery, we need to consider the next section:

(11.iv) Potentials; relation between free energies and potentials, and Faraday equation

We know that the amount of useful electric work remaining is essentially related to the free energy difference in the reaction.

So the Gibbs free energy difference **for n moles of transferred electrons is then**

$$\Delta G_{tot} = G_{\text{products}} - G_{\text{reactants}}$$

$$\Delta G_{tot} = n\left(\frac{1}{2}G_m\left(Cu^{2+}\right) + G_m\left(Ag\right) - \frac{1}{2}G_m\left(Cu\right) - G_m\left(Ag^{+}\right)\right)$$

i.e.,

$$\frac{\Delta G_{tot}}{n} = \frac{1}{2}\left(G_m\left(Cu^{2+}\right) - G_m\left(Cu\right)\right) - \left(G_m\left(Ag^{+}\right) - G_m\left(Ag\right)\right)$$

Therefore:

$$\frac{\Delta G_{tot}}{n} = \underbrace{\Delta G\left(\frac{1}{2}Cu \rightarrow \frac{1}{2}Cu^{2+} + e^{-}\right)}_{ANODE} - \underbrace{\Delta G\left(Ag \rightarrow Ag^{+} + e^{-}\right)}_{CATHODE}$$

We did not include, for brevity, the phases; i.e., Cu and Ag are solids, and the ions are in aqueous solutions, e.g., $Cu^{2+}(aq.)$.

This is a very interesting form, since it allows to break the free energy difference in the battery, to **a difference between half-cell potentials, i.e., the difference between the free energy of reactions per electron in** the cathode and anode.

In principle, the highlighted expression is all that should have been needed for us to determine the electric properties of the battery.

For **historical reasons, however, two changes in the expression** are done; **(1) we subtract a reference quantity and (2) divide by a negative constant**.

THE REFERENCE REACTION

The reference, ΔG_{ref} **,** is defined customarily, at any temperature, as the ΔG (i.e., free energy difference) for a half-cell made of H^+ ions in solution converting to (or "reduced to") H_2 gas:

$$\Delta G_{ref} \equiv \Delta G^0\left(H^+ + e^- \rightarrow \frac{1}{2}H_2\right)$$

The "umlaut " (^{o} superscript) refers to **standard conditions, i.e.,** the proton concentration is 1M=1m/L, and the gas is at 1 bar.

The only difference of the H+ to H_2 cell and the Ag^+ to Ag half-cell is that the reduced hydrogen will be gas rather than solid as in the case of silver. Also, in practice such a half cell will involve a catalyst, such as platinum, that will "lower the barrier" to reaction and therefore speed it up (see later); the catalyst, however, does not change the potential, just speeds up the reaction.

ENERGY TO VOLTAGE:

Specifically from the expression Charge*Voltage=Energy that you learn in physics, it follows that

Voltage=Energy/Charge,

i.e., we can get a **voltage** from the free energy change by dividing it by F, the **charge of one mole**

$F=eN_{Avogardo}$~96,500 Coulomb/mol

where e is the absolute value of the charge of the electron, and to remind you – a Columb is the amount of charge that a current of 1 Ampere carries in 1 second.

Further, we divide by minus, so a negative free energy difference, which means that the system really likes to react, will translate to a very positive potential.

So the **cell potential (voltage) is**;

$$\mathrm{E}^0\left(\mathrm{Cu}^{2+}|\mathrm{Cu}\right)=-\frac{1}{F}\left(\Delta G_m\left(\frac{1}{2}\mathrm{Cu}^{2+}+\mathrm{e}^-\rightarrow\frac{1}{2}\mathrm{Cu}\right)-\Delta G_{ref}\right)$$

Where we subtracted a constant which does not change the total battery voltage. Specifically, defining the battery voltage as the difference between the two cells, i.e., here as:

$$\mathrm{E}^0(\mathrm{cell})\equiv\mathrm{E}^0\left(\mathrm{Cu}^{2+}|\mathrm{Cu}\right)-\mathrm{E}^0\left(\mathrm{Ag}^{+}|\mathrm{Ag}\right)$$

we see that the half-cell is related to the free energy difference

$$\Delta\mathrm{E}^0(\mathrm{cell})=$$

$$\mathrm{E}^0\left(\mathrm{Cu}^{2+}|\mathrm{Cu}\right)-\mathrm{E}^0\left(\mathrm{Ag}^{+}|\mathrm{Ag}\right)=$$

$$-\frac{\Delta G_m\left(\frac{1}{2}\mathrm{Cu}^{2+}+\mathrm{e}^-\rightarrow\frac{1}{2}\mathrm{Cu}\right)-\cancel{\Delta G_{ref}}-\left(\Delta G_m\left(\mathrm{Ag}^{+}+\mathrm{e}^-\rightarrow\mathrm{Ag}\right)-\cancel{\Delta G_{ref}}\right)}{F}$$

$$=-\frac{\Delta G_m\left(\frac{1}{2}\mathrm{Cu}^{2+}+\mathrm{e}^-\rightarrow\frac{1}{2}\mathrm{Cu}\right)-\Delta G_m\left(\mathrm{Ag}^{+}+\mathrm{e}^-\rightarrow\mathrm{Ag}\right)}{F}=-\frac{\Delta G_{tot}}{nF}$$

1.

i.e. we get the:

Faraday equation

$$\Delta E^0(cell)=-\frac{\Delta G_{tot}}{nF}$$

i.e.,

$$\Delta G_{tot}=-nF\Delta E^0$$

(Most books will not use the "tot" subscript).

Faraday equation and the current that passes through:

n, the number of models of electrons transferred, can be related to the total charge transferred. Specifically: Current is : charge/time.

(Note units: Charge has units of Coulomb, current has units of Amperes=Coulomb/sec)

Therefore,

If a current "*I*" is acting over time: *t* then: Total charge transferred= *I*t*

The charge is made of *n* moles of electrons; to get *n,* divide the total charge transferred (*I*t*) by the charge of one mole, i.e., $eN_{Avogadro}$ Therefore:

$$n=I*t/(e\ N_{avogardo}) = I*t/F$$

Therefore: The Faraday equation

$$\Delta G_{tot} = -nF\Delta E$$

can be written as:

$$\Delta G_{tot} = -nF\Delta E = -\frac{F}{eN_{avogadro}}\Delta E\ I\ t$$

i.e.,

$$\Delta G_{tot} = \Delta E\ I\ t$$

The units all work out (by construction).

Faraday equation and typical voltages:

The Faraday constant can be rewritten by multiplying numerator and denominator by 1 Volt, which is defined as 1Volt=Joule/Coulomb

$$\mathbf{F=96{,}500\ \frac{Coulomb}{mol}=96{,}500\ \frac{Volt\ Coulomb}{Volt\ mol}=96{,}500\ \frac{Joule}{Volt\ mol}}$$

i.e.,

$$\mathbf{F=96.5\ \frac{\frac{kJ}{mol}}{Volt}}\sim 100\frac{\frac{kJ}{mol}}{Volt}$$

So batteries with potential of 1.5 Volt correspond to reactions with a difference in the free energies (per mole of transferred electrons) of about 150 kJ/mol – that's indeed a typical range for free energies of reactions, as we have seen before and as the appendix in the book shows.

EXAMPLE: SMALL FLASHLIGHTS AND BATTERIES: Let's use the Faraday relation this to **estimate how much energy can be stored in a battery.** Assume a small battery, say, AA or AAA, has 0.01 moles of reactants (the reason for adopting this number is the following guess: say each is having a molecular weight of, very roughly, about 100 g/mol; i.e., each of the reactants weights 1g, and for 2 reactants (one in the cathode and one in the anode) we'll have therefore a weight of 2gram – that's typical for small batteries)

The Faraday equation, $\Delta G_{tot} = -nFE^0$ then tells us that if the battery potential is 1.5 Volt (like your typical AAA battery), then from 0.01 mol of reactants we should be able to get

$$|\Delta G_{tot}| = nF\Delta E \sim 0.01\text{mol}*100\frac{\text{kJ/mol}}{\text{V}}*1.5\text{V} \sim 1\text{kJ} \sim 1000\text{J}$$

(We use V for volt, named after the Italian scientist Volta; don't confuse with volume or potential-energy).

A typical light bulb in a very small flashlight consumes ~0.5Watt, and 1Watt= 1Joule/sec, so a light bulb should be able to run on a small battery for about

2000secounds, i.e., about half-an-hour (till it consumes $|\Delta G_{tot}|$=1000 Joule). This is a surprisingly accurate estimate.

Some standard half-cell potentials:

Half reaction	E^0(=E^0 for reduction, (i.e., electron(s) addition), in volts
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Ag^+ + e^- \rightarrow Ag$	0.80
$Cu^{2+} + e^- \rightarrow Cu$	0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00 (by definition)
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.77
$K^+ + e^- \rightarrow K$	-2.93

Note:

- From these tables we get the battery potential,

  e.g., for our $Cu^{2+} + 2e^- \leftrightarrow$ Cu anode and $Ag^+ + e^- \leftrightarrow$Ag cathode, we get:

$$\Delta E^0 = E^0(cathode) - E^0(anode) = 0.80 - 0.34 = 0.46\ \text{V}$$

- These umlaut (^{o}) in these cell potentials refers to **standard conditions,** i.e., all reactants and products species in solution at 1M=1mol/Liter, and all gases at 1bar. We'll talk later about what happens to these voltages when the reactants get consumed as the battery is working – in short, not much until the end of the life of the battery,

- The table follows the trend for electron affinity/ionization expected; i.e.,

  O_2 likes to add an electron, so the potential for reduction is high (i.e., the free energy for the reaction where oxygen adds an electron is very

negative).
Conversely, K^+ doesn't like to add an electron so much, so the potential is negative.

- **By construction, the half-cell potentials for Hydrogen (i.e., proton converting to hydrogen) are zero**. (Since in the definition of the potential, we subtract the reference Gibbs free energy, which is exactly the free energy of proton to add H!)

- The potentials refer to the free energy per transferred electron, so they are **invariant to multiplying the reaction by an integer multiple; i.e.,**

The potential for $Zn^{2+} + 2e^- \rightarrow Zn$ is the same as for $\frac{1}{2}Zn^{2+} + e^- \rightarrow \frac{1}{2}Zn$

(in the first case we calculate the free energy for $Zn^{2+} + 2e^- \rightarrow Zn$ and divide by 2, in the second case we divide by 1)

As a corollary, the potentials for a combined reaction are averaged (rather than summed), e.g.,

$$E^0(Cu^{2+} + 2e^- \rightarrow Cu) = \frac{1}{2}\left(E^0(Cu^+ + e^- \rightarrow Cu^+) + E^0(Cu^+ + e^- \rightarrow Cu)\right)$$

i.e., in the left reaction 2 electrons are transferred, so we divide by 2.

(from tables: Left side = 0.34V

*Right side= 1/2 * (0.16 V + 0.52 V)=0.34V*

So both sides agree , as expected)

(11.v) Nernst Equation

The Nernst equation allows us to calculate the electric potential of a cell in non-standard conditions. This is important as cells in real life are almost never in standard conditions. The Nernst equation follows from the relation we learned

$$\Delta G = \Delta G^0 + RT \ln Q$$

When combined with the Faraday relation (now we remove the subscript "tot", as we know it refers to the full battery; since we don't refer to standard condition we drop the umlaut (°) in the Faraday equation)

$$\Delta G = -nF\Delta E$$

we get

$$\Delta E \equiv -\frac{\Delta G}{nF} = -\frac{\Delta G^o + RT \ln Q}{nF} = -\frac{\Delta G^o}{nF} - \frac{RT}{nF} \ln Q$$

i.e.,

$$\Delta E = \Delta E^0 - \frac{RT}{nF} \ln Q$$

Note: RT/nF is **a very small factor:**

$$\frac{RT_{room}}{nF} = \frac{8.3 \frac{\text{J}}{\text{K mol}} 300\text{K}}{n \bullet 96500 \frac{\text{J/mol}}{\text{V}}} = 0.026 \frac{\text{V}}{n}$$

Therefore, for a reaction with n=1, a change of Q of a factor of 2 will only change the potential by 0.026V *ln(2) ~ 0.02 V. **This is the reason that batteries are so stable.**

INSERT: NOT Covered IN CLASS, BUT REQUIRED: NERNST EQ. EXAMPLE

An example will show how to use the Nernst equation in practice, and will also show in more detail how the Nernst equation predicts that batteries will be very stable throughout their lifetime.

Take a Zn Ag battery (of course, it will be usually too expensive to make a battery with silver, but it serves our purpose).

Write the two half-cell reaction for simplicity with n=2 transferred electrons

$$Zn \rightarrow Zn^{2+}+2e^-$$

(Anode, oxidation; written as reverse of reduction; E^0(reduction)=-0.77)

Also

$$2Ag^+ + 2e^- \rightarrow 2Ag \text{ (Cathode, } E^0\text{(reduction)=0.80)}$$

So:

$$\Delta E_0 = 0.80 - (-0.77) = 1.57\ V$$

Further, add the half-cell reactions to get:

$$Zn+2Ag^+ + 2e^- \rightarrow Zn^{2+}+2e^-+2Ag$$

$$\mathbf{Zn(s)+2Ag^+(aq.) \rightarrow Zn^{2+}(aq.)+2Ag(s)}$$

Where we added the relevant phases. Further, since only the ions are in aqueous solution (the neutrals are solids), then

$$Q = \frac{[Zn^{2+}(aq.)]}{[Ag^+(aq.)]^2}$$

Assume that we start with

$$[Zn^{2+}]_{start}=0.01\text{ M}, \quad [Ag^+]_{start}=0.03\text{ M},$$

then, after an amount "x" of change of concentration of zinc has happened, the concentrations are (all in mol):

$$[Zn^{2+}]=0.01+x, \quad [Ag^{+}]=0.03-2x,$$

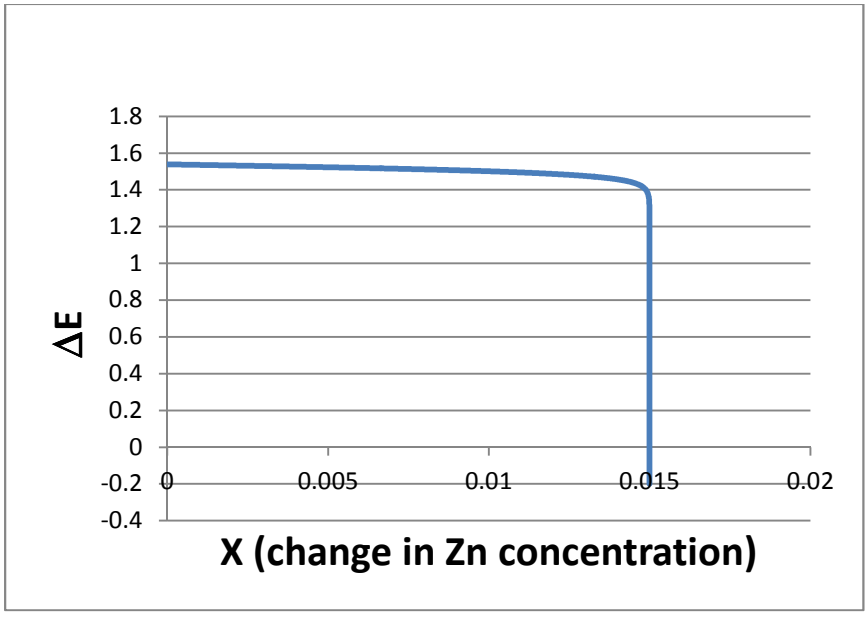
so

$$Q=\frac{0.01+x}{(0.03-2x)^2}$$

Let's put this to the Faraday equation (remember n=2):

$$\Delta E = \Delta E^\circ - (RT/nF) * \ln(Q) = \Delta E^\circ - 0.026/2 * \ln(Q) = \Delta E^\circ - 0.013 * \ln(Q)$$

See the dramatic plot showing the essentially until x=0.15, i.e., until almost all the silver is consumed , the potential of the battery is almost unchanged – this is because the log function (in ln(Q)) is very slowly changing until the argument (Q) is extremely large or small.



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Part 12: Kinetics

Big field; here we'll cover:

(I) Rates;

(II) Unimolecular and bimolecular elementary steps, and half-lives

(III) Including back reactions to give rates of complicated reactions

(IV) Steady state and local equi. Approximations

(V) Equilibrium

(VI) The dependence of the rate constants on T

(VII) Enzymes (if time permits).

There is a whole course (110B, highly recommended) devoted to kinetics as well as stat. mech.; we won't have too much time so we'll omit many topics (polymerization, combustion, rate-constants details, etc.)

(I) RATES:

All rxn, with time, reach equi.

Some go all the way "to the right"

$$H_2 + \tfrac{1}{2}\, O_2 \rightarrow H_2O$$

(At Eq., virtually no H_2, O_2 left.)

Some "never happen", i.e., only reactants remain, e.g.,

$$NaCl(s) \rightarrow Na(s) + 1/2\ Cl_2(g)$$

Many are in between with both reactants and products coexisting in significant amounts:

$$NH_3(aq) + H_2O(s) \rightarrow NH_4^+(aq) + OH^-(aq)$$

For this reaction, at Eq. all reactants and products exist in appreciable amounts.

REACTION RATES:

When reactions occur, e.g.,

$$aA+bB \rightarrow xX+yY+zZ$$

(and we can also have that the reaction proceeds in the opposite direction, products to reactants), then we can relate the change in the moles, i.e.,

$$rate \equiv -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{x}\frac{d[X]}{dt} = \frac{1}{y}\frac{d[Y]}{dt} = \frac{1}{z}\frac{d[Z]}{dt}$$

For example, in $3NO \rightarrow N_2O+NO_2$, for every three moles of NO consumed, 1 mol of N_2O and 1 mol of NO_2 will be made, so

$$rate = -\frac{1}{3}\frac{d[NO]}{dt} = \frac{d[NO_2]}{dt} = \frac{d[N_2O]}{dt}$$

The question then what is this rate, (which we can write as rate=(1/x)d[X]/dt ?)

In some cases the rate is very simple (I.e., depends in a simple way on the concentrations of the products and reactants) , in others very complicated.

There are three prevalent questions in kinetics:

1) From the rates, what happens in equilibrium;
2) How do the rate change in time (i.e., and from that how the concentrations change in time).
3) Can we represent the rates in terms of simpler ingredients (like "Lego blocks")

Let's start with the 3rd point:

A huge simplification, which is NOT ALWAYS VALID is to assume that the rate is made from two components, a "forward" rate which depends on the reactants concentration, and a "backward" rate which depends on the products concentration. For the "general" reaction above this will amount to writing:

$$rate = rate_{forward}([A],[B]) - rate_{backward}([X],[Y],[Z])$$

If:

Forward rate > backward : then more products are made in time.

Forward rate < backward : then more reactants are made.

= : equilibrium, conc. unchanged in time.

In general : rate depends on concentration.

Forward rate: usually (not always!) depends mostly on reactant's concentration (zero if no reactants);
Backward rate depends usually mostly on products conc.

Example:

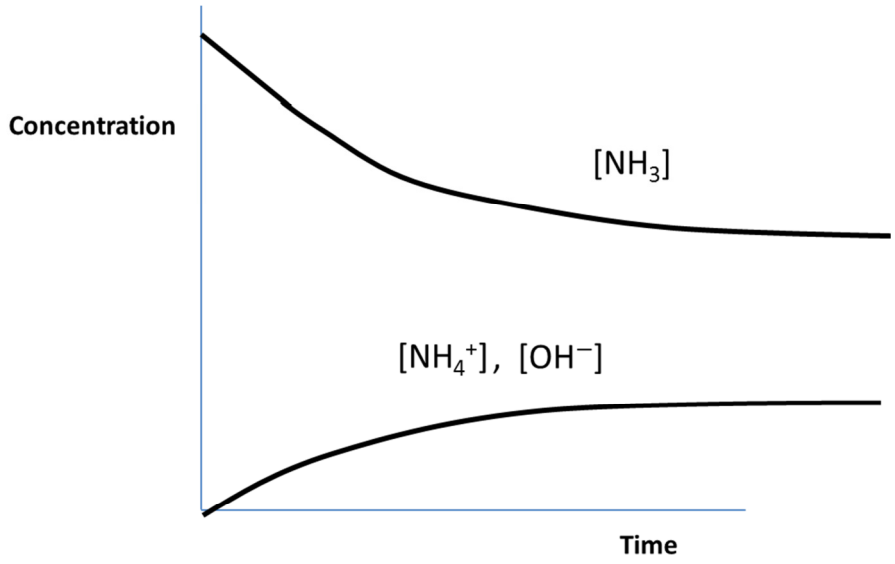
Say initially we throw NH_3 into water.

Initially only reactants. Forward rate appreciable; backward rate small since there are no products.

As more products made, backward rate starts to be appreciable, until forward and backward rate balance each other.

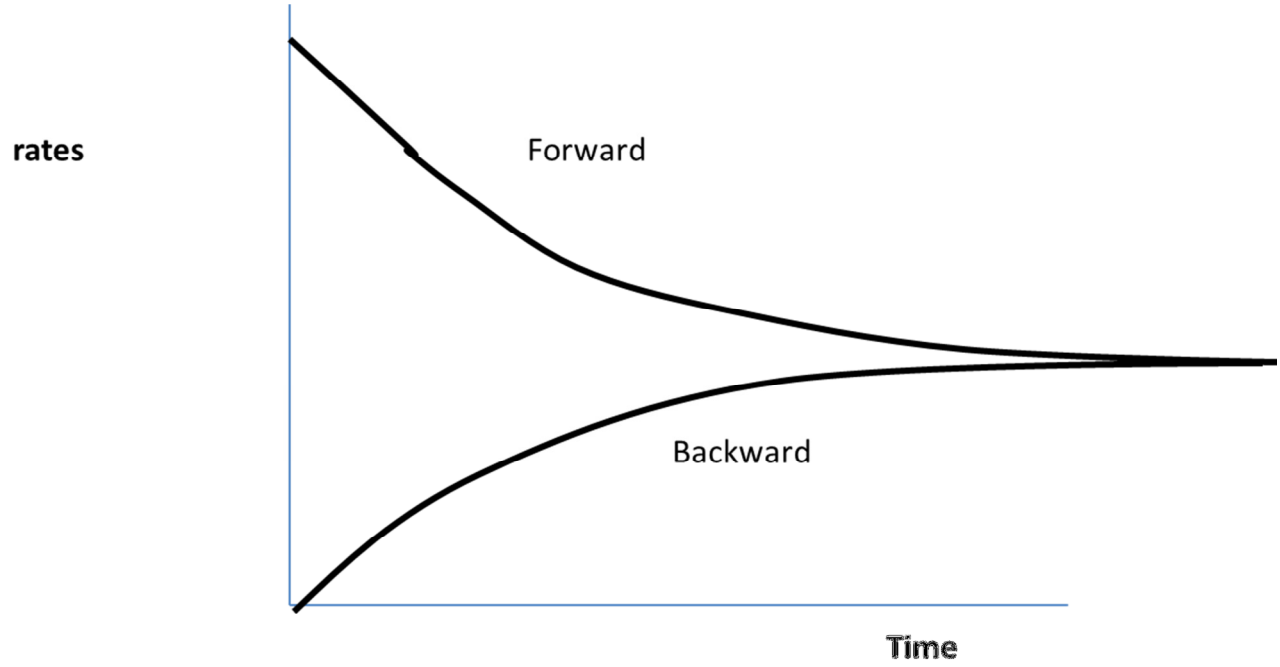
See figure:

Concentration vs. time: levels off



Rate vs. time: rates

level off and match eventually.



(II) ELEMENTARY REACTIONS

Luckily in many cases we can understand complicated rates as the "result of one or several elementary reactions."

The 2 basic ingredients are :

- Unimolecular reactions , A→ products
- Bimolecular reactions, A+B→ products

We first write these reactions as if the backward rate is zero; later, we will see how these basic ingredients (forward uni- and bi-molecular reactions) can be used to understand reactions which go both backward and forward.

But for right now, it will be forward only; so let's tackle each case.

<u>Elementary Unimolecular reactions</u>:

$$A \xrightarrow{k_1} products$$

Examples of unimolecular decays:

- **Radioactive decay** – the half-lives of radioactive elements ranges between billions of years and tiny fractions of seconds.
- **Transition state** – when molecules collide (typically in bimolecular reactions, see below), the transition state (see later) usually decays by itself.
- **Excited molecules** – more generally, molecules can be excited not just by collisions but e.g., by radiation, and then the excited state decays.

Many unimolecular reactions are not really unimolecular, but are "disguised" bimolecular, as we'll see

Mathematically, we write:

$$\frac{d[A]}{dt} = -k_1[A]$$

(**Note:** as mentioned above, our analysis below assumes we <u>can ignore the back reactions;</u> that's OK for radioactive decay but in many other cases we do have to include the back reactions (products → A), as we'll do later)

Here, k_1 is a constant, which has units of 1/time (d[A]/dt has units of concentration/time, [A] has units of concentration, so k_1 has to have units of 1/time so the units match).

(Note: k has nothing to do with Boltzmann's constant which you may encounter in the class).

Even without doing any math we can guesstimate how long it takes for the reaction to proceed "significantly", i.e., for the concentration to fall by a factor of, say, 2:

T(half-life) = Time for concentration to fall by 2 ~ $1/k_1$

This is because the only quantity with units of time we have in this problem is $1/k_1$!

INSERT: (not covered in class , but is expected knowledge):
MATHEMATICAL SOLUTION OF FIRST-ORDER EQUATIONS.

Mathematically, we can write

$$\frac{d[A]}{dt} = -k_1[A]$$

Multiply by dt and divide by k_1 :

$$\frac{d[A]}{A} = -k_1 dt$$

Integrate:

$$\int \frac{d[A]}{[A]} = -k_1 \int dt$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k_1 t \qquad \text{(where } [A]_0 = [A(t=0)]\text{).}$$

Exponentiate:

$$\frac{[A]}{[A]_0} = \exp(-k_1 t)$$

So

$$[A] = [A]_0 \exp(-k_1 t)$$

And indeed, if the time=$1/k_1$, then the concentration will be about ½ what it was initially (or more precisely 37% of its initial value).

$$\left[A\left(t = \frac{1}{k_1}\right)\right] = [A_0]\exp\left(-\frac{k_1}{k_1}\right) = [A_0]\exp(-1) \sim 0.37[A_0]$$

Mathematically, the "half-life" (time for the concentration to fall off by a factor of 2) is more precisely $\ln(2)/k_1 = 0.7/k_1$, as you can readily prove from the highlighted eq.

END OF INSERT

Next:

Elementary bimolecular reactions: the most important type of elementary reactions.

$$A + B \xrightarrow{k} AB$$

$$\frac{d[AB]}{dt} = k[A][B],$$
$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B],$$

Note units, k has units now of **1/ ((molar-density) time)** (it multiplies molar density squared to give molar density over time, so it needs to have units of inverse(time*molar-density).

Physically, the reason for this rate law can be understood by realizing what happens when the concentration is, e.g., made to be 10 times higher (e.g., for gases, reduce the volume by a factor of 10); then, in a given volume there will be 10 times as many molecules (say "A"), and each of them will have 10 times as many chances to interact with a "B" (since the conc. of B was also increasing), so the rate is becoming 100 times as big – and that's what k[A][B] will indeed give.

More precisely, the reaction above is a **"heterogeneous bimolecular reaction";** we'll deal mathematically below with: **"homogenous bimolecular reaction",** $A+A \rightarrow A_2$;

(Note stoichiometry; if we only have A, i.e., homogenous reaction,

then $d[A]/dt = -\mathbf{2}k[A]^2$, i.e., $d[A_2]/dt = -1/2\ d[A]/dt$).

We'll consider first the $A+A \rightarrow A_2$ homogenous case

Physical considerations: If there are no back reactions we can also integrate these reactions; before the math. note that physically we expect that as the product dwindle with time, their decay will be much slower. To see this, let's look at the **instantenous decay rate,**

$$(1/[A])\ d[A]/dt$$

A quantity which has the units of 1/time, so it is a measure of how fast the reaction goes.

In unimolecular decay (1/[A]) d[A]/dt is fixed, i.e., it is k_1. For bimolecular reactions this relative decay becomes smaller in time; e.g., for the A+A→A_2 reaction, as [A] is, say, ten times smaller , d[A]/dt becomes 100 times smaller, so the relative decay becomes $(1/(0.1)) * (0.1)^2 = 0.1$ of what it was. So: the smaller the density the slower the decay.

A little more quantitatively, we can estimate the time it takes to reduce the concentration significantly (say by 50%, i.e., the "half-life" time); if we start at $[A_0]$, then the only two quantities with units will be $[A_0]$ and k, and the only possible combination of units of time is $\frac{1}{k[A_0]}$ so we predict that the half-life will now be proportional to the density squared.).

INSERT: MATHEMATCIAL SOLUTION OF BIMOLECULAR REACTIONS:

The math in that case also verifies this rate, as the book shows:

$$\frac{d[A]}{dt} = -2k[A]^2$$

$$\frac{d[A]}{[A]^2} = -2kdt$$

$$\int \frac{d[A]}{[A]^2} = -2k\int dt =$$

$$-\frac{1}{[A]}\Big|_0^t = -2kt;$$

mutlply by -1,to take away the - in front, and get

$$\frac{1}{[A(t)]} - \frac{1}{[A_0]} = 2kt$$

So, e.g., at $t_{1/2}$, when the concentration is halved, i.e., $\left[A\left(t_{\frac{1}{2}}\right)\right] = \frac{[A_0]}{2}$,then

$$\frac{1}{[A(t_{1/2})]} - \frac{1}{[A_0]} = 2kt_{1/2}$$

$$\frac{2}{[A_0]} - \frac{1}{[A_0]} = 2kt_{1/2}$$

$$\frac{1}{[A_0]} = 2kt_{1/2}$$

$$t_{1/2} = \frac{1}{2k[A_0]}$$

Similar to the rate we predicted on physical grounds.

END OF INSERT.

The solution to the heterogeneous case is mathematically analogous but could be physically different; there could be **"limiting reagent",** e.g., if we have initially 6moles of A and 2 of B, then after a while we'll almost have 0 moles

of B and close to 4 moles of A; i.e., percentage wise A does not change much, only B, so the rate will be influenced mostly by [B], the limiting reagents.

(III) MUTLIPLE STEPS AND INCLUDING BACK REACTIONS:

More interesting then these elementary steps are the combinations.

E.g., a reaction Y_2+X→ XY+Y which proceeds as:

$$X + Y_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} XY_2$$

$$XY_2 \xrightarrow{k_2} XY + Y$$

A few comments:

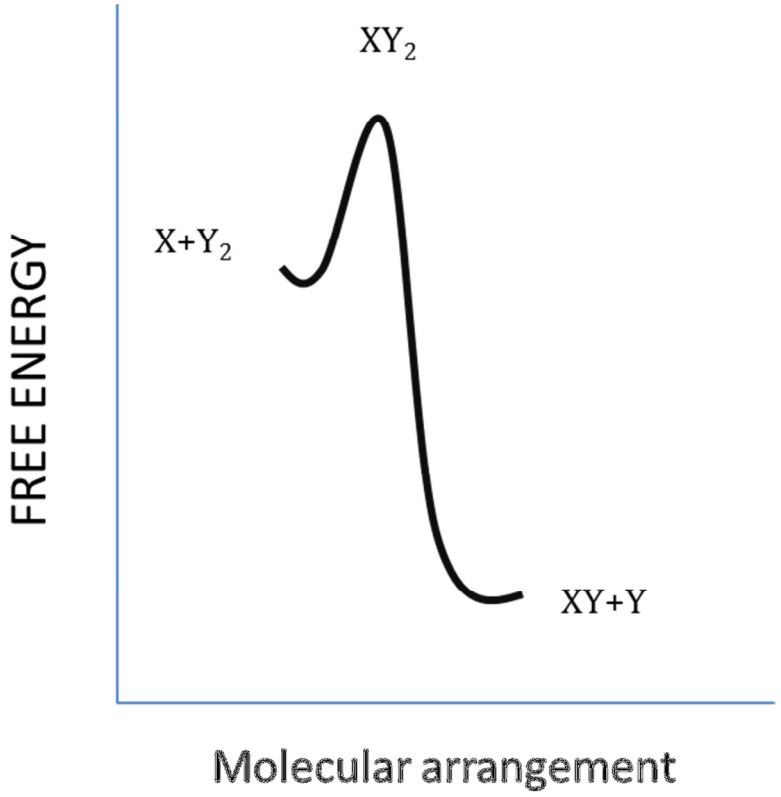
1) The overall reaction is

   $X+Y_2 \leftrightarrow XY+Y$

   It looks like a single-step bimolecular reaction but is really made from two individual elementary steps.

2) The reaction involves a "transition states", i.e., unstable states of a molecules. The state here is: XY_2.
   Sometime we will put a * or a # subscript to emphasize that we consider a transition state.

   Schematically, see the figure below:



XY_2 is a transition state, i.e., a state of the molecules which lives for a short time.

3) Let's write the math; for each compound we need to consider all the reactions (with correct signs) that make or destroy it

$$X + Y_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XY_2$$

$$XY_2 \xrightarrow{k_2} XY + Y$$

$d[X]/dt = -k_1[X][Y_2] + k_{-1}[XY_2]$

$d[Y_2]/dt = -k_1[X][Y_2] + k_{-1}[XY_2]$

$d[XY_2]/dt = k_1[X][Y_2] - k_{-1}[XY_2] - k_2[XY_2]$

$d[XY]/dt = k_2[XY_2]$

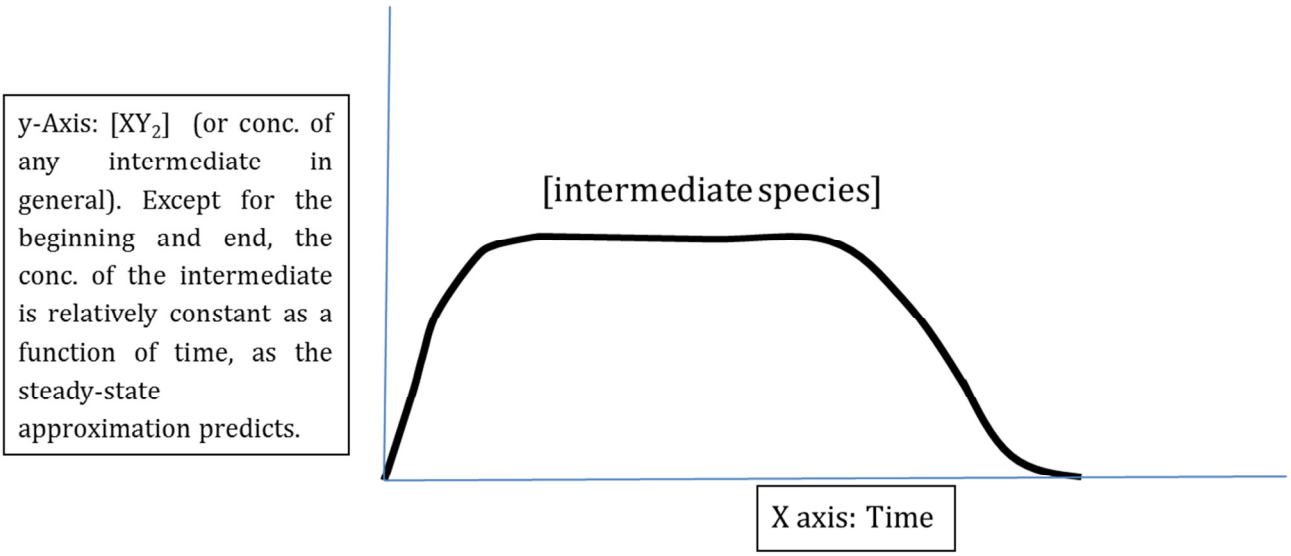
$d[Y]/dt = k_2[XY_2]$

Note that we have two reactants, two products, and one intermediate (XY_2).

We could solve these eqs. numerically, or for more insight apply meaningful approximations. The most important one is:

IV. Approximations: First, Steady State Approximation

In the steady-state approx., we assume that the concentrations of the intermediates are essentially fixed as a function of time (except for the early times, when there are no products, and at late times, when the reaction is almost over; see **picture)**;



In our case the steady state approximation means that

$0 \sim d[XY_2]/dt = k_1[X][Y_2] - k_{-1}[XY_2] - k_2[XY_2]$

So:

$$[XY_2] \sim \frac{k_1[X][Y_2]}{k_{-1} + k_2}$$

So that the rate of production of the product will be:

$$\frac{d[Y]}{dt} = k_2[XY_2] = \frac{k_1}{k_{-1} + k_2}[X][Y_2]$$

Note a qualitative feature: to make Y the system goes "twice forward" (rate proportional to k_2k_1)

(V) EQUILIBRIUM

The stage step in a reaction is when it is over (or approaching completion). The result is boring if it is only a forward reaction, i.e., no reactants remain, only products (though it could be quite interesting if we have several option for different products, and the details of the react. determine which of the possible products is made). However, in many cases there will be some reactants and some products rmeaining, so then we'll like to use the rates to tell us the concentrations

Before considering the equilibrium let's do one change – allow products to back-react, otherwise in equilibrium we'll only have products. I.e., we'll modify the reaction to be:

$$X + Y_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} XY_2 \qquad \text{(I)}$$

$$XY_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} XY + Y \qquad \text{(II)}$$

With a rate constant "k_{-2}" to go back from the products XY+Y to the transition state.

Let's only concentrate on reaction I, reactants to transition state.

Now at equilibrium the amount of reactants does not change

$$0 = (at\ equi.)\ \frac{d[X]}{dt} \quad = \quad -k_1\,[X][Y_2] \;+\; k_{-1}[XY_2]$$

So the concentration of the transition state is

$$[\boldsymbol{XY_2}] = \frac{\boldsymbol{k_1}}{\boldsymbol{k_{-1}}}[\boldsymbol{X}][\boldsymbol{Y_2}]$$

So we can use a thermodynamic relation like we had before

$$\frac{[\boldsymbol{XY_2}]}{[\boldsymbol{X}][\boldsymbol{Y_2}]} = \boldsymbol{K_I}$$

Where we defined an "equilibrium constant",

$$\boldsymbol{K_I = \frac{k_1}{k_{-1}}}$$

Let's define a ""Free energy of the transition state",

$$G^* \equiv G_m(XY_2)$$

which will be calculated by imposing the K vs. G relation that we derived earlier

$$\boldsymbol{K_I \sim \exp\left(-\frac{G^* - G_{reactants}}{RT}\right)}$$

Put differently G^* will be <u>defined</u> so as to fulfill this relation above, i.e., I is defined as

$$G^* = G_{reactants} + RTln(K_I)$$

Also, $G_{reactnats} = G_m(X) + G_m(Y_2)$,

(One word of caution: the reason for having a $\sim$ sign is that we ignore terms like RT/P which are necessary when we go from K to K_c, as we learned earlier. For this reason we are "missing units", i.e., K as we defined it has units of 1/density, so it cannot be an exponent unless we divide by another quantity with the same units; but for our qualitative discussion this is OK).

And we can summarize this as:

$$\boldsymbol{\frac{k_1}{k_{-1}} = \frac{[XY_2]}{[X][Y_2]} = \exp\left(-\frac{(G^* - G_{reactants})}{RT}\right)}$$

So the lesson is that **there is a relation (the yellow-highlighted eqs. above) between the forward and backward rate constant; they are related by the exponential of the free energy difference between the transition state and the initial state.**

This shows you that if the transition state free energy is much larger than RT, than the forward rate, k_1, has to be very small (as "K" will be very small). I.e., to get a high occupation of the transition state, which will allow you to have fast

reaction, you need to lower the free energy of the transition state, which will make k_1 higher.

Now let's briefly consider the second reaction, i.e.,. transition state to products. Using exactly the same mathematics, we will get

$$\frac{\boldsymbol{k_{-2}}}{\boldsymbol{k_2}} = \frac{[\boldsymbol{XY_2}]}{[\boldsymbol{XY}][\boldsymbol{Y}]} = \mathbf{exp}\left(-\frac{(\boldsymbol{G^* - G_{products}})}{\boldsymbol{RT}}\right)$$

(Note that now k_2 is at the denominator, since it refers to reacting away from the transition state, just like k_{-1}).

Let's divide the last two highlighted equations, so we get:

$$\frac{\boldsymbol{k_{-2}k_{-1}}}{\boldsymbol{k_2k_1}} = \frac{[\boldsymbol{XY}][\boldsymbol{Y}]}{[\boldsymbol{X}][\boldsymbol{Y_2}]} = \mathbf{exp}\left(-\frac{(\boldsymbol{G_{products} - G_{reactants}})}{\boldsymbol{RT}}\right)$$

Note that we get the mass-reaction law – i.e., the densities are related by a constant.

$$\frac{[XY][Y]}{[X][Y_2]} = K_c$$

where

$$K_c = \frac{k_2k_1}{k_{-2}k_{-1}}$$

Note that this is the mass reaction law, derived from rate kinetics!

(VI) The dependence of the rate constants on T

We can understand how the rate constant depends on T qualitatively (for elementary reactions). Let's consider a typical bimolecular elementary reaction case where the transition state could be quite high (e.g., our X+Y_2→ XY_2 → XY+Y reaction diagrammed above); t

Ten, let's say that a pair of molecules (X and Y_2) needs to have relative kinetic energy above , ΔG^* to react (where, at least approximately, $\Delta G^* = G^* - G_{reactants}$, i.e., the difference in free energy between the transition state and the reactants).

ΔG^* is the **activation free-energy** (it is similar to $\bar{E}$ in the book)

Then, from the |Boltzmann distribution we know that at least approximately, the fraction of molecules with molar energy above ΔG^* (i.e., those molecules that can react) is

(Fraction with E higher than $\bar{E}$) ~ exp(-$\Delta G^*/(R\,T)$)

And therefore we expect that the forward rate will be proportional to

$k_1 \sim \exp(-\Delta G^*/(RT))$

Note that the rate will then be very small at low T (as we saw in the earlier section);

So then k_{-1} ~ constant (any molecule in the transition state breaks easily), and

$$\frac{k_1}{k_{-1}} \sim \exp\left(-\frac{\Delta G^*}{R\,T}\right)$$

Note that this is the same as the expression we derived in the previous section,

$$\frac{k_1}{k_{-1}} \sim \exp\left(-\frac{G^* - G_{reactants}}{RT}\right)$$

Arrhenius plot

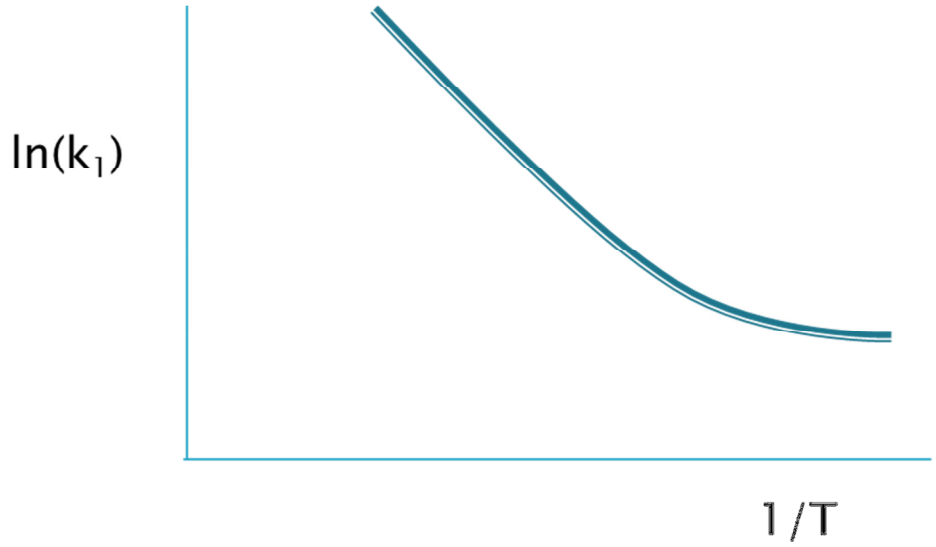
Further, if ΔG^* is made from two components, an energy term and an entropy term,

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

We can find we find them by plotting ln(k_1) vs. -1/T , this is called an "Arrhenius plot (and is similar to what we did earlier with general transitions, as you'll recall)

$$\ln(k_1) = -\frac{\Delta H^*}{R} \bullet \frac{1}{T} + \frac{\Delta S^*}{R}.$$

See the book for examples, and the figure below



Arrhenius plot:
slope of ln(k_1) vs. 1/T gives -E(transition state);

At very low temperatures
(~50–100K for H–exchange reaction, ~10K or lower otherwise) k flattens due to Q.M. tunneling

(Note that some small number of important reactions, especially involving hydrogen, can "penetrate through a barrier" by quantum mechanical tunneling so then then ln(k_1) will remain flat even when T is reduced)

Also note that this only applies to reactions with barrier, i.e., typically to the reactions leading to the transition state; in the opposite direction, i.e., for the

breakup **from** the transition state, the temperature dependence (of k_{-1} or k_2 in our example) will be very weak, since all molecules in the transition state will break without barrier

(VII) ENZYMES:

Final kinetics topic. Important in biochem.!

Covered clearly in Oxtoby, so just a summary: the enzyme is a catalyst, enabling the reaction (other kinds of catalysts, typically metal surfaces, are also covered).

The reactions are

$$E(enzyme) + S(subtrate) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \text{ (bound enzyme, transition state)}$$

$$ES \xrightarrow{k_2} E + P(product)$$

Note that the total enzyme (defined as $[E_0]$) is conserved, i.e., it could be either unbound E or bound ES, i.e.,

$$[E_0] = [E][S] + [ES]).$$

The product formation rate is

$$\frac{d[P]}{dt} = k_2[ES]$$

using the steady state approximation, which says that the formation of the ES transition state intermeidiary is essentially balanced by its consumption, we get

$$0 \sim \frac{d[ES]}{dt} = k_1[E][S] - (k_2 + k_{-1})[ES] = k_1([E_0] - [ES])[S] - (k_2 + k_{-1})[ES]$$

(where we used $[E_0] = [E][S] + [ES]$)so

$$[ES] \sim \frac{k_1[E_0][S]}{k_1[S] + k_2 + k_{-1}}, \quad \text{i.e.,}$$

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2 k_1[E_0][S]}{k_1[S] + k_2 + k_{-1}}$$

Note that for small enzyme substrate concentration([S]) the enzyme will be mostly free, and then the rate of production of products will be proportional to

the concentration of the substrate (i.e., the denominator in the expression above will be k_2+k_{-1}, i.e., constant);

But if there is a lot of enzyme, so that the denominator will be dominated by the substrate form ($k_1[S] >> k_2+k_{-1}$) then

$$d[P]/dt \sim k_2 [E_0],$$

i.e., at high substrate concentration the reaction will look zeroth order in the substrate density – this makes sense since then the reaction will be limited by the amount of enzyme, not substrate.

Part 13. Raul's Law and Colligative properties (if time permits!)

Physical properties of solution diff. from pure solvent:

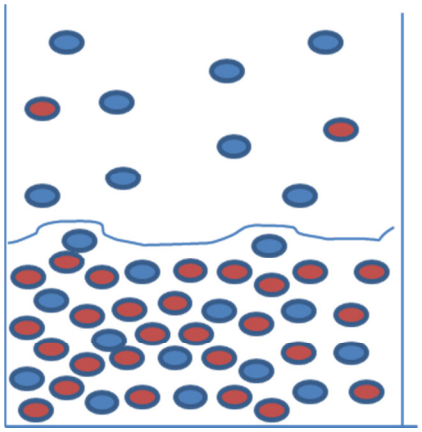
Diff. boiling point (b.p.), vapor pressure, melting point (m.p.)

Most importantly: solutions exhibit a range of temperatures where, at the same pressure, there's equilibrium between liquids and vapors! This is the basis for distillation, i.e., purifying solutions making them richer in one compound or another, as we'll see.

Start: **Vapor pressure**

Add: two liquid compounds, "1" and "2" (I label them "A" and "B" or "1" and "2", interchangeably) to form a solution;

Seal this solution in a fixed volume container so there will be equilibrium between the compounds in their liquid and vapor phases



Schematic drawing of a vapor-liquid equilibrium for a 2-compound mixture; is the less volatile compound, is the more volatile one. The vapor is richer in than the solution is. (In the example, is benzene, is toluene.)

How is vapor pressure (v.p., denoted as P_A, P_B) of compounds affected?

Let's concentrate on species "A", for example.

Think of: mole fraction x_A (L) of A(in Liquid!).

We know what happens at the extremes

$x_A(L)=1$ → pure "1" → $P_A = P_A^*$ where * denotes pure solvent

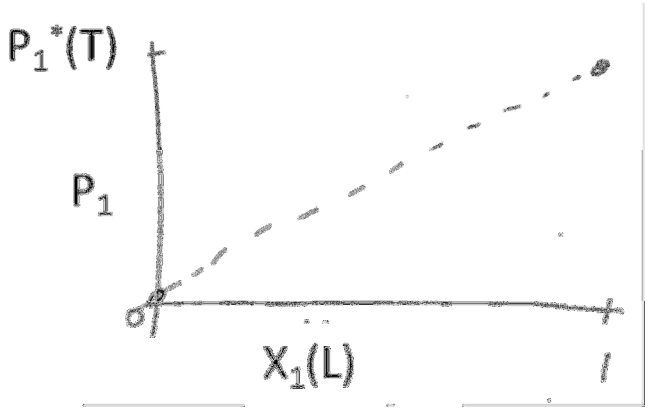
$x_A(L)=0$ → no "1" → $P_A=0$.

That's always true. What's in between?

If "A" and "B" are "PHYSICALLY SIMILAR liquids that interact in similar ways, will be called "ideal mixture", then

For ideal mixtures, **Raul's law** obeyed:

$$P_A = x_A(L)\, P_A^*(T)$$



Physically, reason that in Raul's law vapor pressure relates to the molar fraction in the liquid is due to equilibrium;

I.e., Raul's law $P_A = x_A(L)\, P_A^*(T)$, is really the same (up to an overall function multiplying both sides) the same as:

$$rate(vapor \rightarrow liquid) = rate(liquid \rightarrow vapor)$$

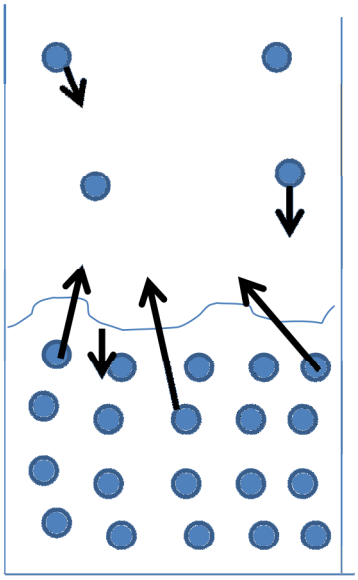
Left: Pressure term, particles coming from vapor to liquid come at a rate which is determined by the pressure (higher pressure → more vapor particles impinge on the liquid);

Right: represents tendency of "A" particles to leave liquid and go to vapor. This tendency is reduced when there is a solution, as there is more disorder (each A now can be surrounded by only As, or B and several A's, or 2B & several As, etc.).

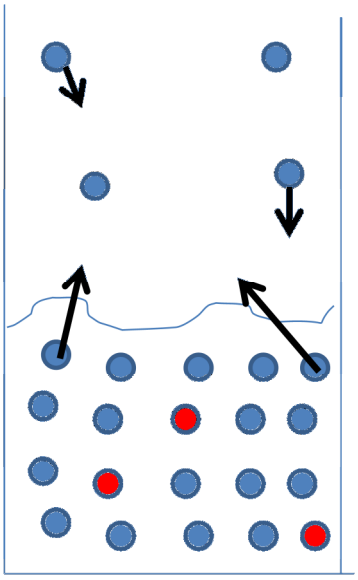
More disorder → more stability (particles love higher entropy, as it leads to lower free energy).

Notice "Left=Right" : since in equilibrium # of particles leaving solution is same as # of particles entering it from vapor.

Graphical explanation for why solvent vapor pressure is reduced when there is a solute:



Pure solvent: particles leaving and joining liquid continuously, creating equilibrium between pure solvent liquid and vapor at P_1^*



In presence of solute ● , the solvent particles ● have less of a tendency to leave the liquid (due to entropy) creating equilibrium between liquid and vapor at a reduced pressure, $P_1 < P_1^*$

In solutions, vapor's composition will be different than Liquid:

Let's see this for ideal solutions, where we can work the numbers. If the solution is ideal, we have Raul's law

$$P_A = x_A(L)\, P_A^*(T)$$

$$P_B = x_B(L)\, P_B^*(T)$$

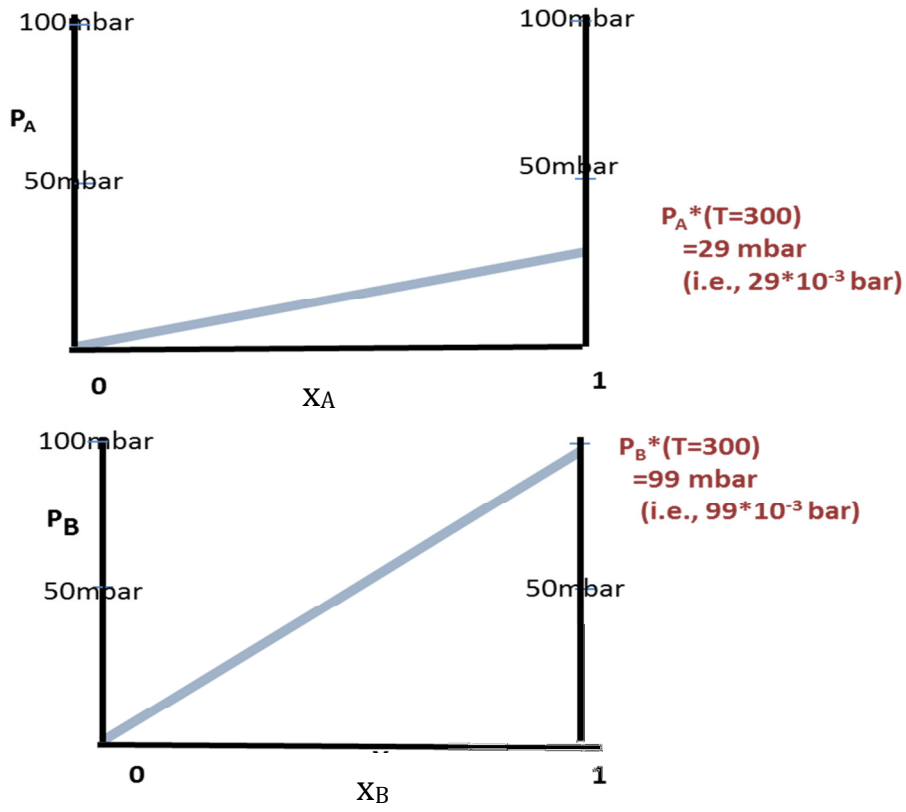
E.g., "A"=toluene (methyl-benzene) , "B"=benzene, T=300K:

$$P_A^*(T = 300K) = 29mbar$$

$$P_B^*(T = 300K) = 99mbar$$

Note that toluene is less volatile than benzene (slightly bigger molecule, vdW interactions more effective, holding the liquid slightly more together, everything else the same).

Graphically:



Example:

Solution of toluene and benzene, 60% of liquid is "A" (toluene); the solution is in a container and there's equilibrium between vapor and liquid.

Question.

(i) What's the vapor pressures of "A" and "B"

(ii) What's the mole fraction of "A" and "B" in vapor.

Answer:

. (i) $P_A = x_A(L)\ P_A^* = 0.60*29\text{mbar} = 17.4\ \text{mbar}$

$P_B = x_B(L)\ P_B^* = 0.40*99\text{mbar} = 39.6\ \text{mbar}$

(ii) $\frac{n_A}{n_{tot}} = \frac{P_A}{P_{tot}} = \frac{17.4}{39.6+17.4} = 30\% = 0.30$

Note that solution is 60% toluene, but vapor only 30% toluene!

Reason – toluene is much less volatile.:

We can use the difference in composition of vapor and liquid for:

Distillation:

Scrape the vapor; richer in one compound (above, vapor richer in Benzene).

Then repeat: Cool down vapor till it liquefies, scrape vapor; that vapor is even richer in benzene, and continue for a few more steps.

Colligative properties

Next, **specialize to non-volatile solutes (e.g., salt in water, or sugar in water).**

The reduction of vapor pressure for a **solvent** upon inclusion of a **non-volatile** solute, leads to**: colligative properties i.e., properties that depend on # of dissolved solute, not on identity of such species.**

First:

Vapor pressure lowering:

- Boiling temp. elevation (e.g., salty water boils at > 100^0C)
- Freezing point depression:
  (Salty water freeze at temp. as low as -18 ^{0}C [0 Fahrenheit], depending on conc.)
- Osmotic pressure (see later).

Important prelude on Raul's law: it is always valid for solvents.

I.e., we said that Raul's law is only valid for "ideal" mixtures; but for solvent-solute mixtures, i.e., if one compound is much more abundant than the other, **Raul's law is valid for the solvent when any solute is inserted**, as long as the concentration of the solute is small;

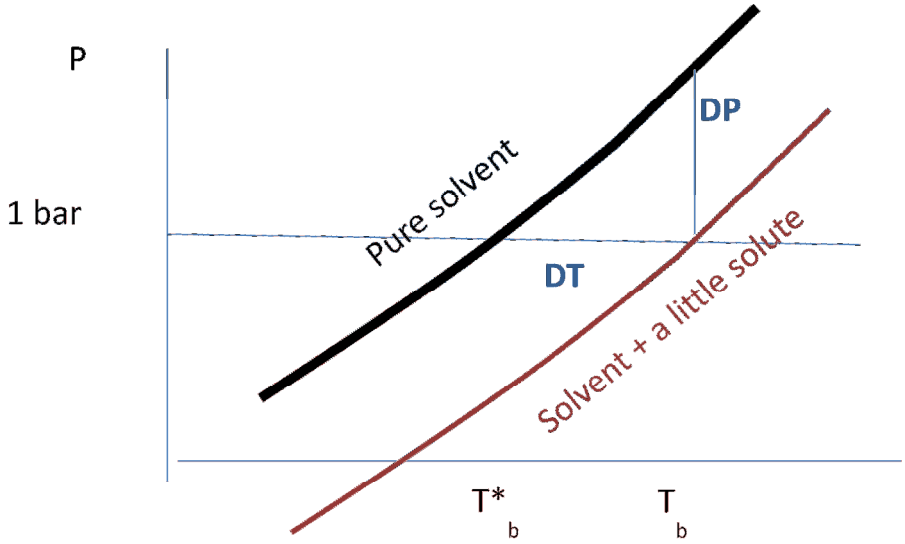
So in general: $P_{solvent} = x_{solvent}(L)\, P^*_{solvent}(T)$

Physically: the solvent molecules "like" to remain liquid a little more due to the presence of the solute – the solvent molecules therefore will have lower vapor pressure

Now we can understand colligative properties. Start with:

Boiling point elevation.

Consider vapor pressure vs. T figure:



First: boiling without solute.

Thick black line: vapor pressure vs. T.

Say the external pressure is, say, 1bar. When the vapor pressure reaches the external pressure (i.e., the thick black line crosses the 1bar line) then boiling occurs; that temperature is denoted as T_b^*

(Reminder: Reason for bubbles in boiling: when the compound reaches even slightly above T_b^*, then any vapor that's formed pushes away the air around it; that lowers its pressure, so more liquid turns to vapor, and so forth – causing boiling. Boiling occurs only because the container is open and the external pressure is fixed. In a closed flask, there is no bubbly boiling – as we raise T, p increases.)

Next: solute added;

The solvent's concentration decreases → its pressure is reduced; and if only the solvent is volatile (e.g., when the solute is salt, nonvolatile), then the total pressure is made from the solvent's pressure, i.e. at the same temperature,

equilibrium between the mixture as liquid and as vapor will happen at lower P once the non-volatile solute is added. (See picture).

Analogously, from the picture, we will need a higher T to reach equilibrium with vapor at the same pressure.

Finally, without doing the math, you see from the picture that if the original curve of P vs. T for pure solvent is "flatter" , then we will need a larger temperature to affect the boiling – i.e., the boiling point elevation will happen at higher T.

Mathematically: we write

$$dT_B = K_B X_{solute}$$

Where K_B (not Kelvin, and not related to the other K's we used!) is the boiling-point increase parameter, which depends on solvent and the temperature.

Technical points

1): we used X_{solute}. Note that if we have salts, e.g.,

$$NaCl \rightarrow Na^+ + Cl^-$$

Then, 1mol of salt in water solution gives 2mol solutes (Na^+, Cl^-)

Example, 1mol of salt in 1800g of water gives

$$X_{solute} = \frac{n_{solute}}{n_{tot}} = \frac{2mol}{100mol + 2mol} \sim 0.02,$$

where the 100 mol comes from the water, 1 mol comes from Na+, and 1mol from Cl-; so the total # of moles is 102mol, and of which 2mol is solution. So the answer is about 2%, not 1%, since the salt gives 2 contributions – one from positive ions, one from the negative ones.

2) It is important to note that in practice when we use this equation we need to measure the concentration in molality, as K_b is usually given in units of K/molality. (i.e., $\frac{Kelvin}{\frac{mol\ solute}{Kg\ solvent}}$]

I would have preferred the concentration, but for experimentalists it is more convenient, at least historically, to use Molality.

The experimental number for water is $K_b \sim 0.5\ \frac{\text{K Kg}}{\text{mol}}$. It is possible to estimate this number theoretically.

Now we can turn to a completely similar phenomena:

Freezing point depression

Similar; since liquid solvent is made "more stable" by presence of solute, then freezing temperature is lowered. For example, if we add salt to water, then, whereas it would have frozen at 0 Celsius before, now it will freeze at a lower temperature, as low as -18 Celsius if we add salt (and even lower for some forms of "antifreeze").

Formally, if the amount of solute is not too much, we write the same equation as before

$$dT_f = -K_f X_{solute}$$

Where, as mentioned, X_{solute} now stands for the Molality and not the mole fraction.

Also, the negative sign is since the freezing point depresses (liquid is more stable than solid);

For water :

$$K_b = 0.5\ \text{K Kg /mol}$$
$$K_f = 1.8\ \text{K} \cdot \text{Kg/mol}$$

Physically, K_f is larger since solids & liquids are quite similar (strongly interacting molecules) and differ only in whether the molecules are ordered.

Therefore, the increased stability of the liquid in the presence of the solute can cause a big effect on freezing.

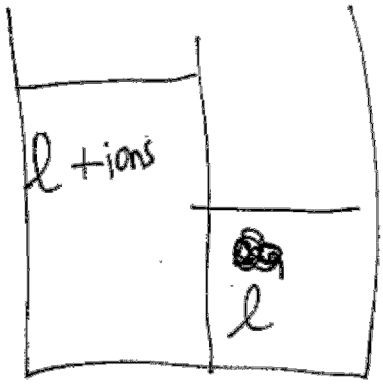
In contrast, for gas-liquid (boiling) transition, the difference between liquid and gas is quite large, so the extra stability of the solvent is not going to affect the transition temperature strongly.

The last colligative effect is:

Osmotic Pressure

Take a semi-permeable membrane that just lets water pass through, but not a solute.

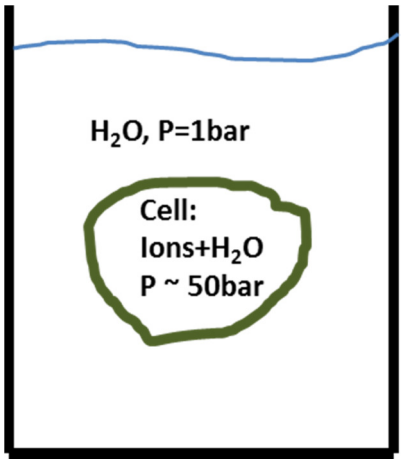
Use it to separate water into two compartments – e.g., in the left one put solute, and in the right one pure water (labeled "l" for "liquid" in the figure).



Then the liquid which contains ions is more stable → water will move into the left region, as solvent prefers region with higher stability, i.e., with more solute ' the extra water in the left compartment will create a higher pressure (so the water column will rise on the left).

Analogously, in biological cells: the cells have ions, and cell wall which is permeable to water; within the cell there will be higher P as water moves into

the cell. Can be as high as 50bar (as the work of several professors in ULCA demonstrated!)



In summary: P higher in region with more solutes!

We can prove (Chem. 110A) that:
There is an equation **ostensibly** (**and only ostensibly!!!)** resembling ideal-gas law:

$$P_{extra}V = n_{solute}RT$$ (proof: difficult; 110A)

where:

P_{extra} is extra pressure in region with solutes;
n_{solute} : number of moles of solute.
V: volume of region with solutes
R, T : usual meaning.

Note the appearance of R, gas constant; it is the <u>only time</u> we'll see R, relating to gas, in equations relating to <u>liquid</u>. **Otherwise, R never enters equations for liquids.**

Osmotic pressure: useful to extract molecular weight.

Take measured mass, m_{solute} of solute;

Do osmotic pressure measurement; From P_{extra} get n_{solute} ;

Molecular weight: m_{solute}/n_{solute}!

END OF NOTES.

GOOD LUCK IN THE EXAM!