

CHEMISTRY
XL-14A

CHEMICAL
EQUILIBRIA



August 20, 2011

Robert lafe

Unit Overview

2

- Reactions at Equilibrium
- Equilibrium Calculations
- Le Châtelier's Principle
- Catalysts

Reactions at Equilibrium

3

- Reversibility of Reactions
- Law of Mass Action K
- Gas Phase Equilibrium K_p
- Solution Phase Equilibrium K_c
- Extent of Reaction using K
- Direction of Reaction Q vs K

Introduction to Chemical Equilibrium

4

We previously assumed all reactions proceeded to completion

However: many reactions approach a state of equilibrium

Equilibrium – condition of a chemical reaction in which chemical change ceases and no further change occurs spontaneously

Equilibrium – a dynamic equilibrium between reactants and products in a chemical reaction.

At Equilibrium:

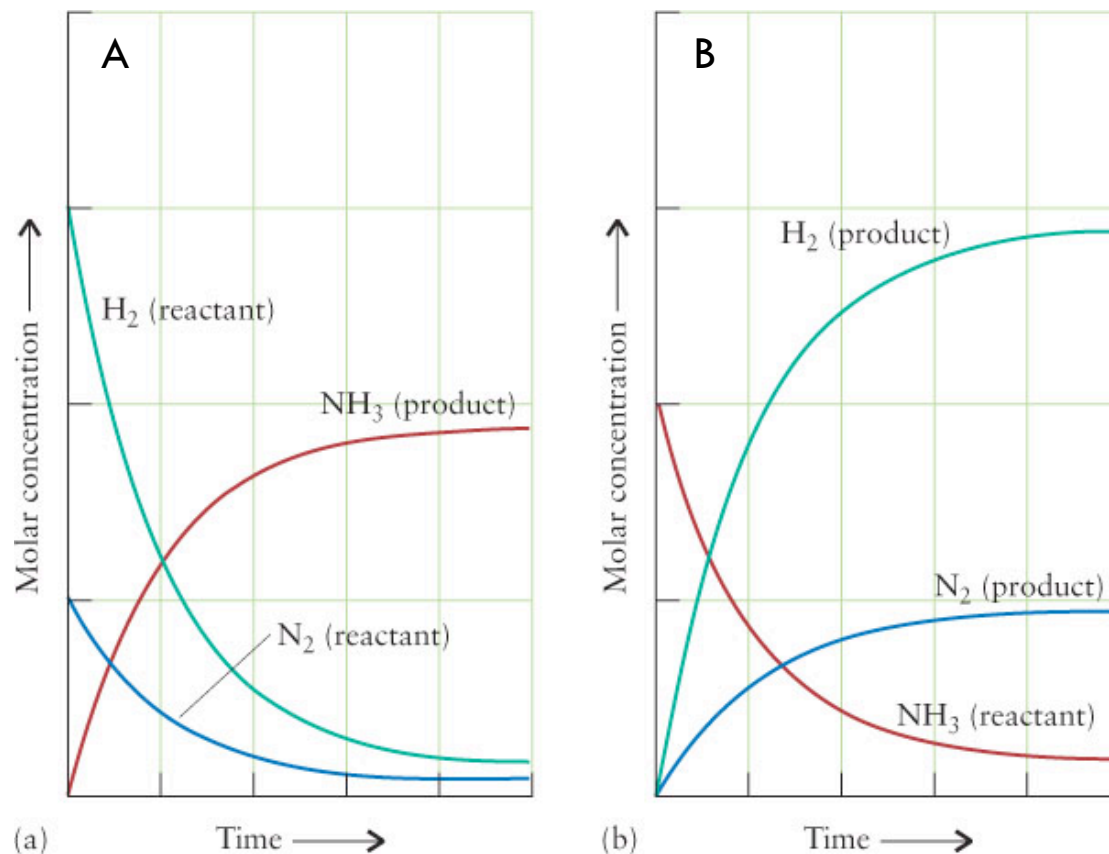
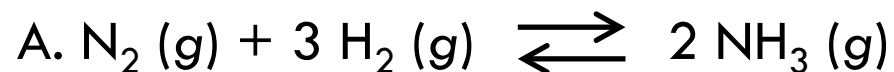
- Forward and reverse reactions simultaneous with equal rates
- No further net conversion of reactants to products unless the experimental conditions have been changed

The equilibrium state is characterized by the

Equilibrium Constant (K_{eq})

Reversibility of Reactions

5



Reversibility of Reactions

6

Dissolve $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in pure water

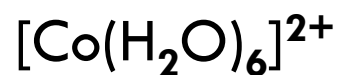
Dissolve in 10 M HCl



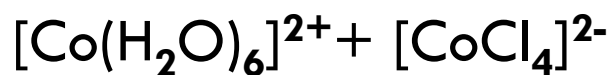
Add conc.
HCl
→



←
Add
H₂O



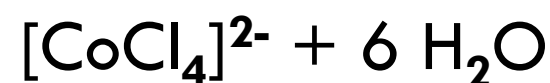
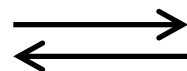
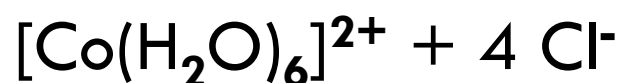
Pink



Purple

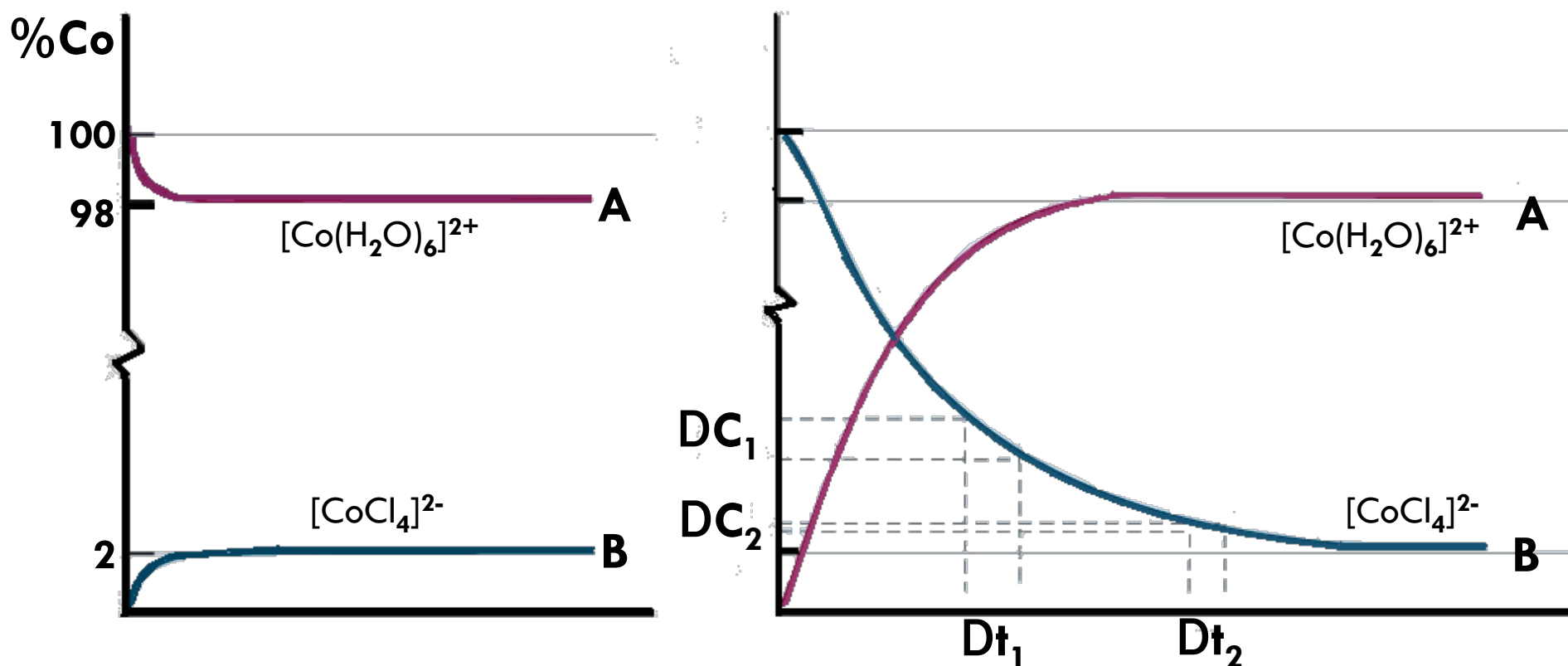
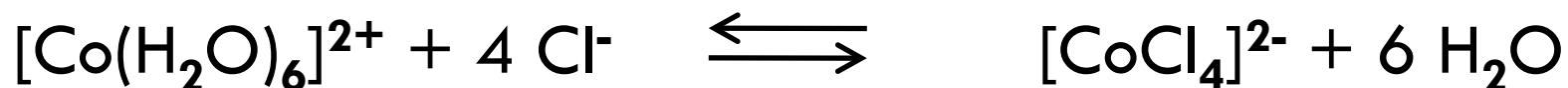


Blue



The Nature of Chemical Equilibrium

7



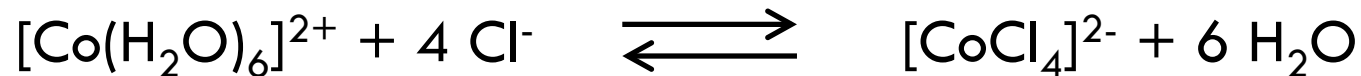
As time progresses, rate = concentration/time slows
When rate(s) = constant, reaction is at equilibrium

The Nature of Chemical Equilibrium

Characteristics of the Equilibrium State

8

1. No Macroscopic Change
2. Reached Spontaneously
3. Dynamic Balance of Forward/Reverse Processes
4. Same regardless of direction of approach



Situations which appear to be equilibrium, but are not:

Steady State – macroscopic concentrations are constant, even though system is not at equilibrium

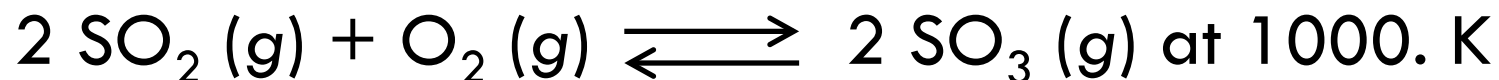
1 process removes species while 2nd process supplies species

Homeostasis – body tries to maintain blood pH, etc...

Equilibrium Data

9

1864: Norwegians Cato Guldberg and Peter Waage discovered the mathematical relationship that summarized the composition of a reaction mixture at equilibrium



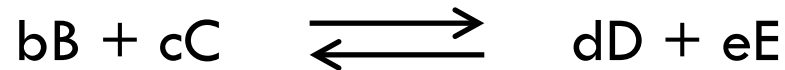
P_{SO_2} (bar)	P_{O_2} (bar)	P_{SO_3} (bar)	K^*
0.660	0.390	0.0840	0.0415
0.0380	0.220	0.00360	0.0409
0.110	0.110	0.00750	0.0423
0.950	0.880	0.180	0.0408
1.44	1.98	0.410	0.0409

*Average K : 0.0413

$$\frac{\left(P_D / P^\circ\right)^d \left(P_E / P^\circ\right)^e}{\left(P_B / P^\circ\right)^b \left(P_C / P^\circ\right)^c} = K$$

The Empirical Law of Mass Action

10



At equilibrium (independent of starting conditions)
the **law of mass action** is constant

$$\frac{a_D^d a_E^e}{a_B^b a_C^c} = K$$

(unitless)

a_B = 'activity' of species B

K = equilibrium constant

Magnitude of K tells us about the equilibrium state

$K \gg 1$, (activities of products) \gg (activities of reactants) at equilibrium

$K \ll 1$, (activities of products) \ll (activities of reactants) at equilibrium

'Activity'

11

$$\frac{a_D^d a_E^e}{a_B^b a_C^c} = K$$

Ideal Gas

$$a_B = \frac{P_B}{P^\circ}$$

$$P^\circ = 1 \text{ bar}$$

Ideal Solution

$$a_B = \frac{[B]}{c^\circ}$$

$$c^\circ = 1 \text{ M}$$

Pure Liquid

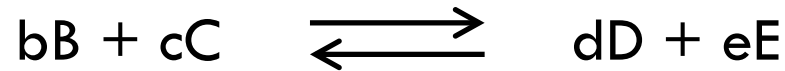
$$a = 1$$

Pure Solid

$$a = 1$$

Gas Phase Reactions

12



$$\frac{a_D^d a_E^e}{a_B^b a_C^c} = K$$

a = activity of reacting species

For ideal gases: $a_B = \frac{P_B}{P^\circ}$ where $P^\circ = 1 \text{ bar}$

$$\frac{\left(P_D/P^\circ\right)^d \left(P_E/P^\circ\right)^e}{\left(P_B/P^\circ\right)^b \left(P_C/P^\circ\right)^c} = K \longrightarrow \frac{P_D^d P_E^e}{P_B^b P_C^c} = K \left(P^\circ\right)^{(d+e-b-c)}$$

$$\frac{P_D^d P_E^e}{P_B^b P_C^c} = K_P \quad K_P = K \left(P^\circ\right)^{(d+e-b-c)}$$

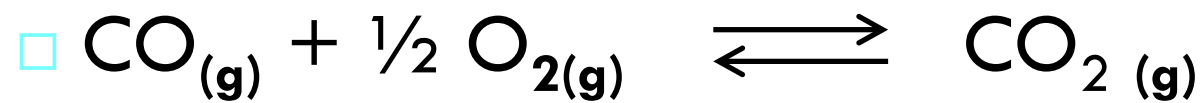
****Note****

Your textbook refers
to K_p as K

Gas Phase Reactions

13

- Write the equilibrium expression for the following reaction:



Molarity

14

- Molarity is a unit commonly used to describe the concentration of a solution
- **Solution** – homogeneous mixture of two or more substances
- **Solute** – one or more minor components in a solution
- **Solvent** – the major component of a solution, medium for solute
- **Molarity** – the number of moles per unit volume (mol/L = M)

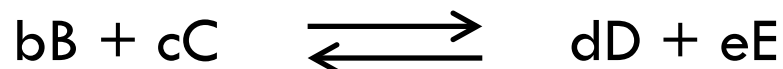
$$Molarity = \frac{n_{solute}}{V_{solution}} \left(\frac{mol}{L} \right) = M$$

- It can also be used to describe the molar volume of a gas

$$Molarity = \frac{n_{gas}}{V_{gas}} \left(\frac{mol}{L} \right) = M$$

Reactions in Solution

15



$$\frac{a_D^d a_E^e}{a_B^b a_C^c} = K$$

a = activity of reacting species

For ideal solutions: $a_B = \frac{[B]}{c^\circ}$ where $c^\circ = 1 \text{ M}$

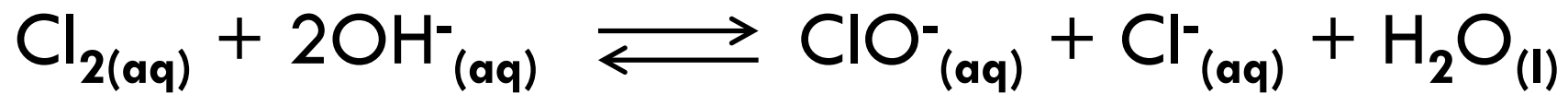
$$\frac{([D]/c^\circ)^d ([E]/c^\circ)^e}{([B]/c^\circ)^b ([C]/c^\circ)^c} = K \longrightarrow \frac{[D]^d [E]^e}{[B]^b [C]^c} = K (c^\circ)^{(d+e-b-c)}$$

$$\frac{[D]^d [E]^e}{[B]^b [C]^c} = K_C \quad K_C = K (c^\circ)^{(d+e-b-c)}$$

Reactions in Solution

16

Write the equilibrium expression for the following reaction:



Pure Substances and Multiples Phases

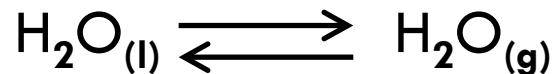
17

$$\frac{a_D^d a_E^e}{a_B^b a_C^c} = K$$

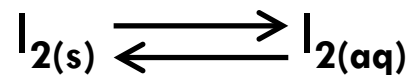
a = activity of reacting species

For solids: $a_{(\text{pure solid})} = 1$

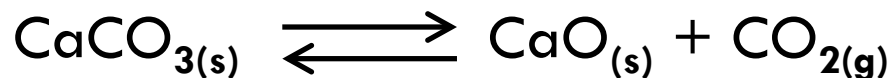
For liquids: $a_{(\text{pure liquid})} = 1$



$$K = P_{\text{H}_2\text{O}}$$



$$K = [\text{I}_2]$$

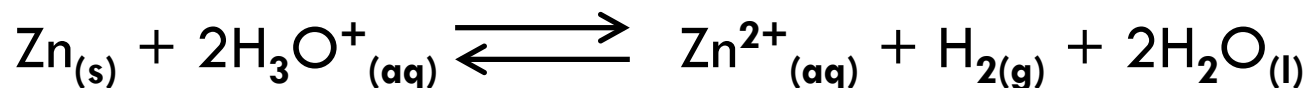


$$K = P_{\text{CO}_2}$$

Mixed Phase Reaction

18

Write the equilibrium expression for the following reaction:



$$K = \frac{a_{\text{Zn}^{2+}_{aq}} a_{\text{H}_2(aq)} a_{\text{H}_2\text{O}(l)}^2}{a_{\text{Zn}(s)} a_{\text{H}_3\text{O}^+_{aq}}^2}$$

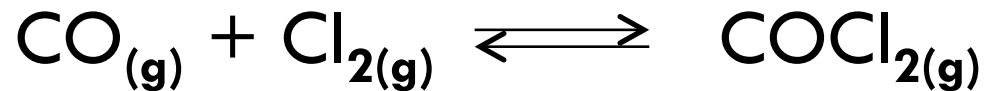
$$K = \frac{([\text{Zn}^{2+}]/1M)(P_{\text{H}_2}/1atm)(1)^2}{(1)([\text{H}_3\text{O}^+]/1M)^2}$$

$$K = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}_3\text{O}^+]^2}$$

Extent of a Reaction

19

Phosgene (COCl_2) is an important intermediate in the manufacture of certain plastics. It is produced by the reaction:



- a) Use the law of mass action to write the equilibrium expression for this reaction
- b) At 600 C, $K = 0.20$. Calculate the partial pressure of phosgene in equilibrium with a mixture of $P_{\text{CO}} = 0.0020$ atm and $P_{\text{Cl}_2} = 0.00030$ atm

Direction of Change in Reactions: Reaction Quotient (Q)

20

To determine the direction of a reaction, use the Reaction Quotient:

$$Q = \frac{P_D^d P_E^e}{P_B^b P_C^c} \quad Q = \frac{[D]^d [E]^e}{[B]^b [C]^c}$$

Q is the same expression as K

Q valid all the time

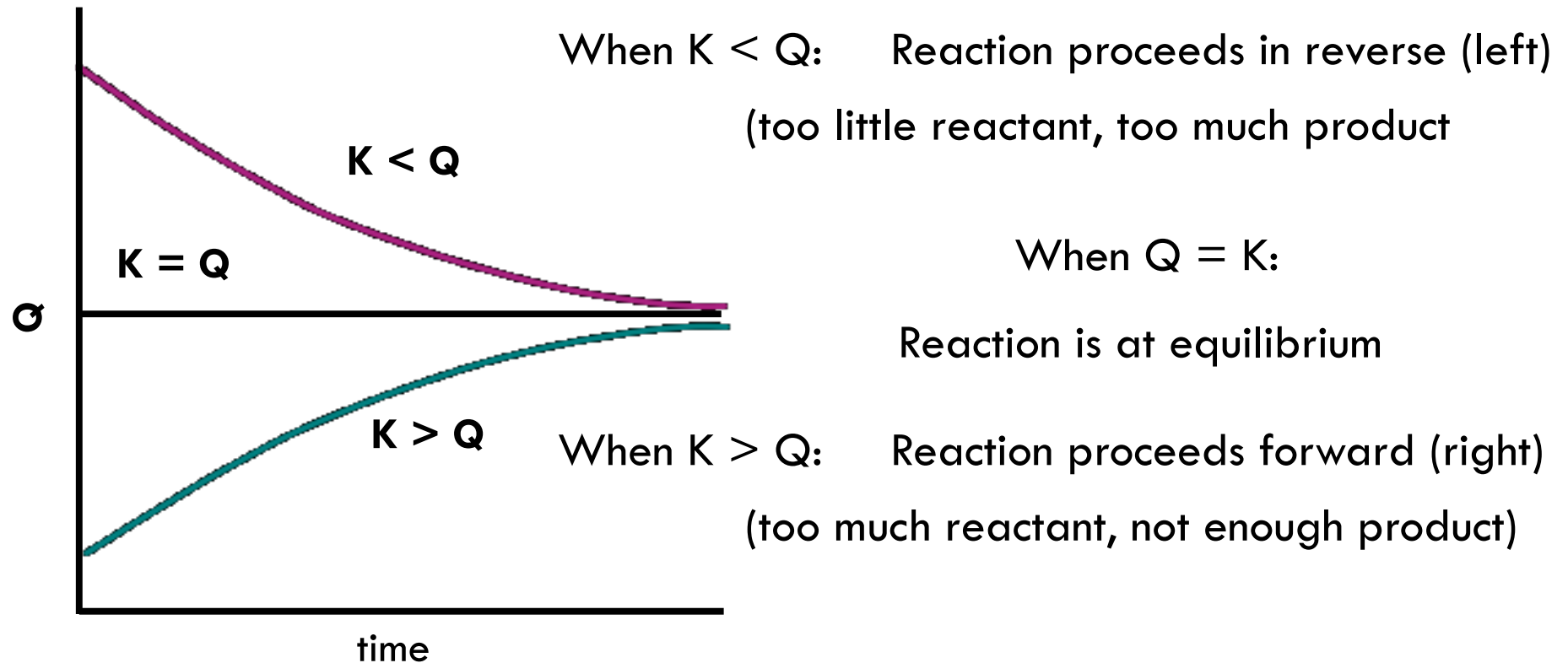
K valid only at equilibrium

The relationship between Q and K will determine the
direction of a reaction

Direction of Change in Reactions:

Q vs K

21



Equilibrium Calculations

22

- K vs K_c
- Relationships between K's of reactions
- Using K and $K_c \rightarrow$ ICE box calculations

K vs K_C

23

$$\frac{[D]_{eq}^d [E]_{eq}^e}{[B]_{eq}^b [C]_{eq}^c} = K_C$$

$$\frac{P_{D,eq}^d P_{E,eq}^e}{P_{B,eq}^b P_{C,eq}^c} = K$$

$$P_X = \frac{n_X RT}{V}$$

$$R = 8.3145 \times 10^{-2} \frac{L \cdot \text{bar}}{\text{mol} \cdot K}$$

$$[X] = \frac{n_X}{V}$$

$$P_X = [X]RT$$

K vs K_C

24

$$\frac{P_{D,eq}^d P_{E,eq}^e}{P_{B,eq}^b P_{C,eq}^c} = K \quad P_X = [X]RT$$

$$K = \frac{P_D^d P_E^e}{P_B^b P_C^c} = \frac{([X_D]RT)^d ([X_E]RT)^e}{([X_B]RT)^b ([X_C]RT)^c}$$

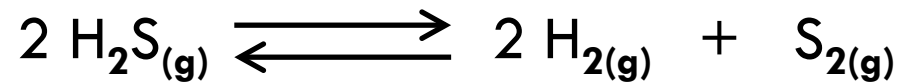
$$K = \frac{[X_D]^d [X_E]^e}{[X_B]^b [X_C]^c} (RT)^{d+e-b-c} = K_c (RT)^{d+e-b-c}$$

$$K = K_c (RT)^{d+e-b-c} \quad R = 8.3145 \times 10^{-2} \frac{L \cdot \text{bar}}{\text{mol} \cdot K}$$

K vs K_C

25

At 1132 °C, for the following reaction:



$K_C = 2.26 \times 10^{-4}$. What is the value of K at this temperature?

$$K = K_c (RT)^{d+e-b-c}$$

$$R = 8.3145 \times 10^{-2} \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}$$

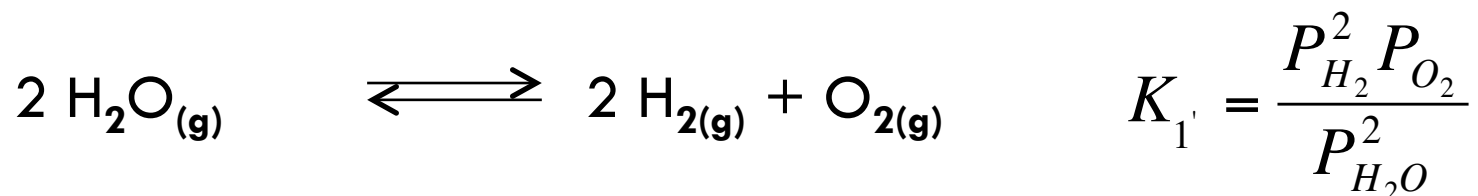
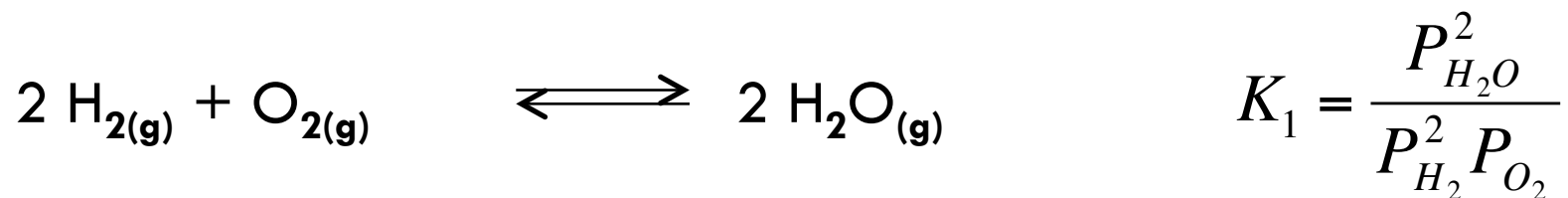
Relationships among Equilibrium Expressions

26

Case 1: Compare forward and reverse reactions

Case 2: Multiply a chemical reaction by a constant x

Case 3: Add or subtract chemical reactions (Hess's Law)



$$K_1 K_{1'} = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} = 1 \quad K_1 = \frac{1}{K_{1'}}$$

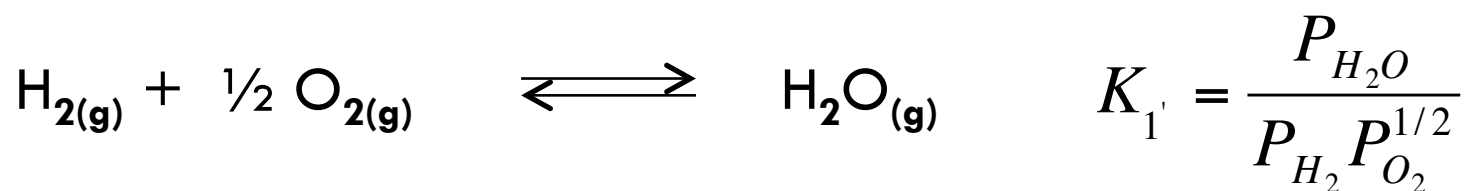
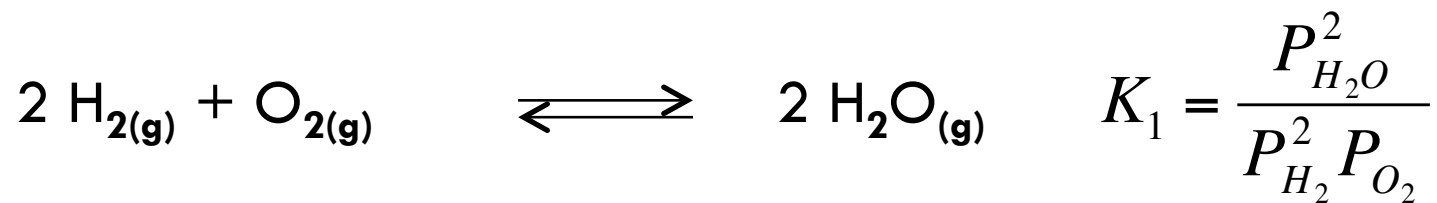
Relationships among Equilibrium Expressions

27

Case 1: Compare forward and reverse reactions

Case 2: Multiply a chemical reaction by a constant x

Case 3: Add or subtract chemical reactions (Hess's Law)



$$K_{1'} = \sqrt{\frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} = \sqrt{K_1} \quad K_{1'} = K_1^x$$

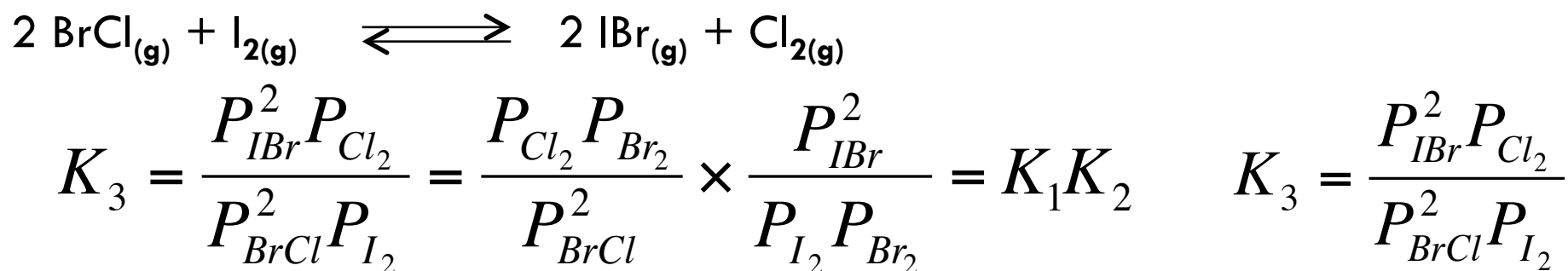
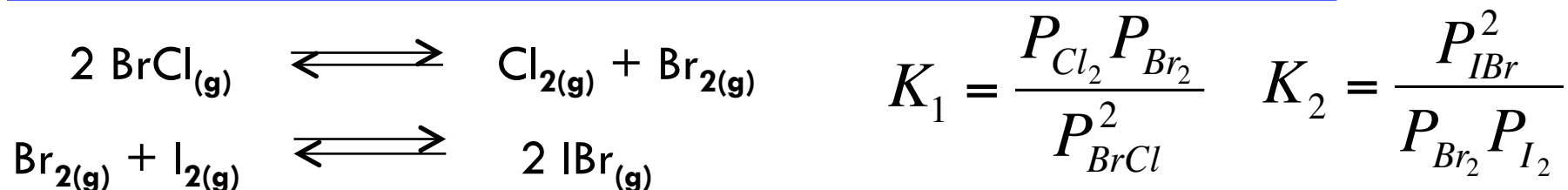
Relationships among Equilibrium Expressions

28

Case 1: Compare forward and reverse reactions

Case 2: Multiply a chemical reaction by a constant x

Case 3: Add or subtract chemical reactions (Hess's Law)



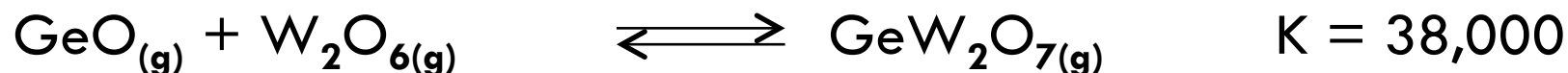
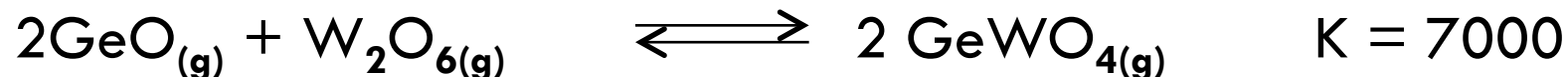
If adding reactions: $1 + 2 \rightarrow K_3 = K_1 \times K_2$

If subtracting reactions: $1 - 2 \rightarrow K_3 = K_1 / K_2$

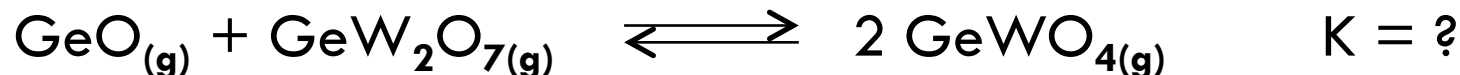
Relationships among Equilibrium Expressions

29

At 1330 K, germanium(II) oxide (GeO) and tungsten(VI) oxide (W_2O_6) are both gases. The following two equilibria are established simultaneously:



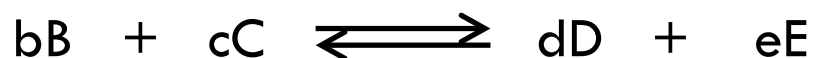
Compute K for the reaction:



Equilibrium Calculations: (R)ICE Box

30

For a Chemical Reaction:



Reaction	bB	+	cC	\rightleftharpoons	dD	+	eE
Initial P_a	1 atm		1 atm		0 atm		0 atm
Change in P_a	-bx		-cx		+ dx		+ex
Equilibrium P_a	1 - bx		1 - cx		0 + dx		0 + ex

$$K = \frac{P_D^d P_E^e}{P_B^b P_C^c} \quad K = \frac{(dx)^d (ex)^e}{(1 - bx)^b (1 - cx)^c}$$

Evaluating K from Reaction Data

31

At 600 °C, a gas mixture of CO and Cl₂ has initial partial pressures of P_(CO) = 0.60 atm and P_(Cl₂) = 1.10 atm. At equilibrium, the P_(COCl₂) = 0.10 atm. Calculate K for this reaction:

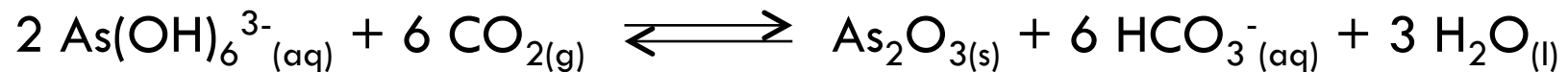
	CO _(g)	+ Cl _{2(g)}	⇌	COCl _{2(g)}
Initial P _a	0.60 atm	1.10 atm		0 atm
Change in P _a	-0.10	-0.10		+0.10
Equilibrium P _a	(0.60 - 0.10) atm	(1.10 - 0.10) atm		0.10 atm

$$K = \frac{P_{\text{COCl}_2}}{P_{\text{CO}}P_{\text{Cl}_2}} = \frac{(0.10)}{(0.60 - 0.10)(1.10 - 0.10)} = \frac{0.10}{(0.50)(1.00)} = 0.20$$

Evaluating K from Reaction Data

32

Must take into account stoichiometric coefficients:



	$2 \text{As}(\text{OH})_6^{3-}(\text{aq}) + 6 \text{CO}_2(\text{g})$		\rightleftharpoons	$\text{As}_2\text{O}_3(\text{s}) + 6 \text{HCO}_3^-(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$	
I [A]	1 M	1 M	-	1 M	-
C in [A]	-2x	-6x		+6x	
E [A]	1 M - 2x	1 M - 6x		1 M + 6x	

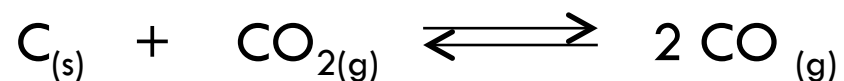
$$K_C = \frac{[\text{HCO}_3^-]^6}{[\text{As}(\text{OH})_6^{3-}]^2 [\text{CO}_2]^6}$$

$$K_C = \frac{[1 + 6x]^6}{[1 - 2x]^2 [1 - 6x]^6}$$

Evaluating K from Reaction Data

33

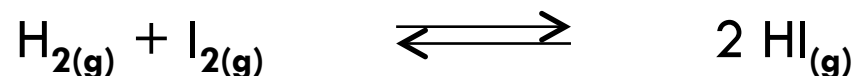
Graphite (solid carbon) is added to a vessel that contains $\text{CO}_{2(g)}$ at a pressure of 0.824 atm. The pressure rises during the reaction. The total pressure at equilibrium is 1.366 atm. Calculate the equilibrium constant:



Calculating Equilibrium Compositions

34

$\text{H}_{2(g)}$ and $\text{I}_{2(g)}$ are sealed in a flask with partial pressures: $P(\text{H}_2) = 1.980$ atm and $P(\text{I}_2) = 1.710$ atm. The sealed flask is heated to 600 K, and the gases quickly reach equilibrium. $K_{600\text{ K}} = 92.6$



Calculate the equilibrium partial pressures of H_2 , I_2 and HI at 600 K

Can solve this 3 ways:

- 1) Solve exactly using quadratic equation
- 2) Solve by approximation
- 3) Solve by successive approximation if 2 doesn't work

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Le Châtelier's Principle

35

- Adding and Removing Reagents
- Changing Pressure
- Effect of Temperature on Equilibrium
- Effect of Temperature on K
- Catalysts

Direction of Change in Reactions: Le Châtelier's Principle

36

Le Châtelier's Principle: A system in equilibrium that is subjected to a stress will react in a way that tends to counteract the stress

At equilibrium, the macroscopic properties of a system remain constant

When you perturb the equilibrium, the system will counteract the perturbation

- Changing the concentration of a reactant or product
- Changing the Volume or Pressure
- Changing the Temperature

Can maximize the yield by perturbing the system

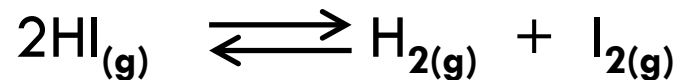
Le Châtelier's Principle

Adding or Removing Reagent

37

Change the concentration (or Partial Pressure) of a reagent

Consider how the change in concentration affects Q



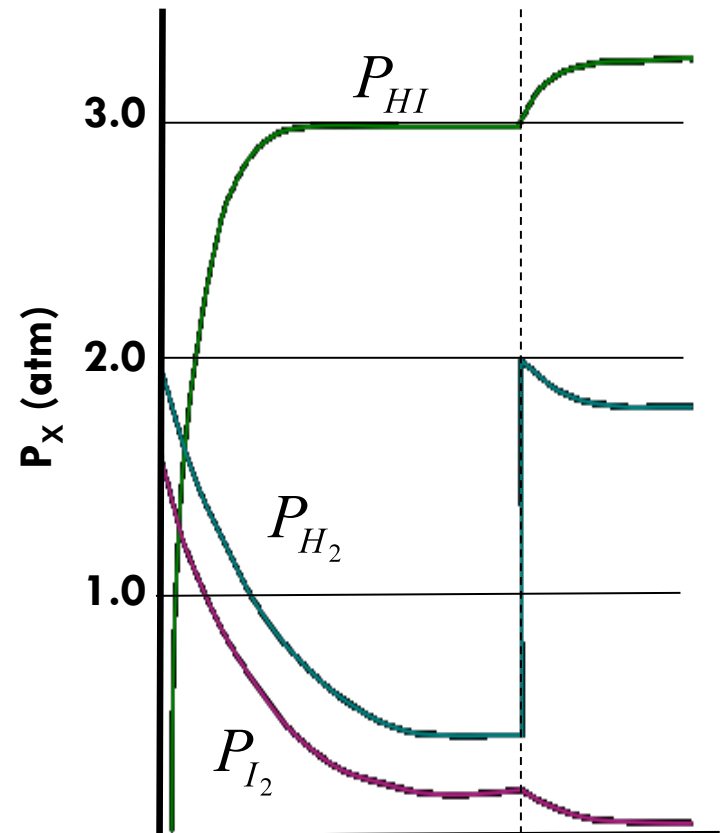
$$Q = \frac{P_{\text{H}_2} P_{\text{I}_2}}{P_{\text{HI}}^2}$$

Increase a Product (decrease a Reactant)

$Q > K$ Reverse (to the left)

Increase a Reactant (decrease a Product)

$Q < K$ Forward (to the right)

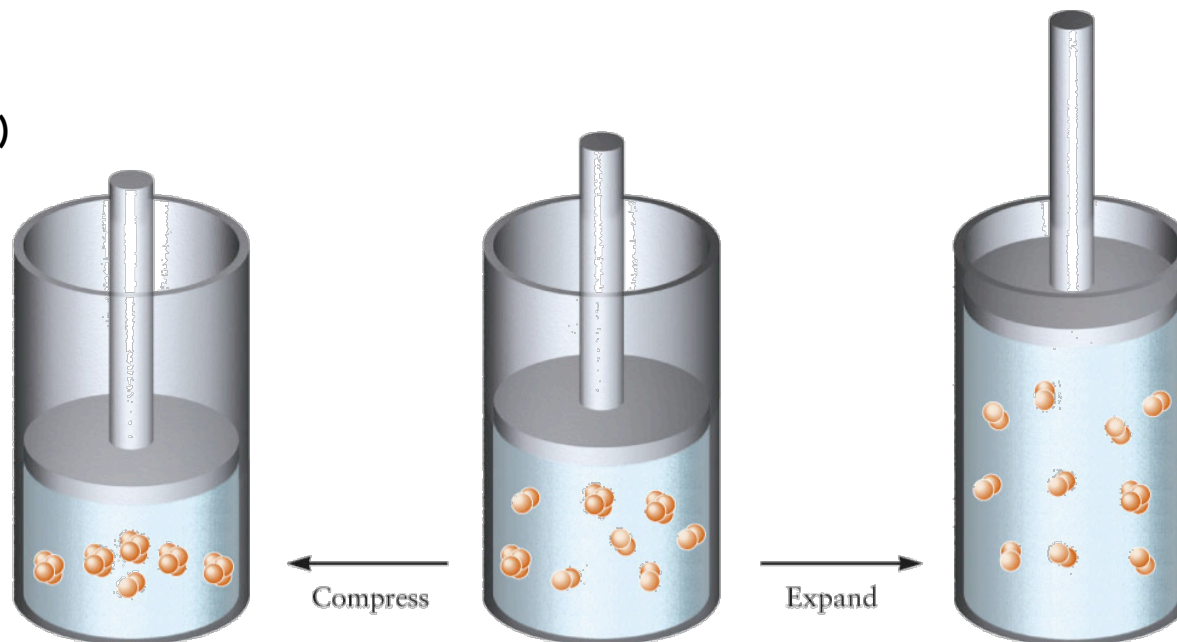
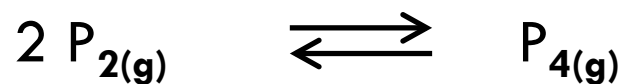


Le Châtelier's Principle

Changing Volume or Pressure

38

Specific to gas phase reactions



Increase V (decrease P)

Reaction \rightarrow direction with greater n_{gas}

Increase P (decrease V)

Reaction \rightarrow direction with fewer n_{gas}

Le Châtelier's Principle

Changing the Temperature

39

Endothermic or Exothermic reactions

Endothermic Reaction – absorbs heat

Exothermic Reaction – gives off heat

Increase T (“adding heat”)

Reaction will proceed endothermically

Trying to absorb excess heat

Increase T

Endothermic reaction → forward

Exothermic reaction → reverse

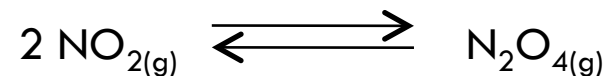
Decrease T

Endothermic reaction → reverse

Exothermic reaction → forward



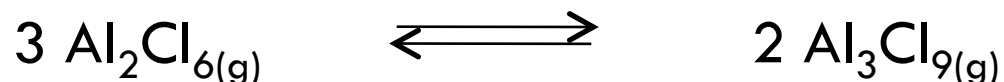
© 2007 Thomson Higher Education



$\Delta H < 0 \rightarrow$ exothermic

Direction of Change in Reactions: Le Châtelier's Principle

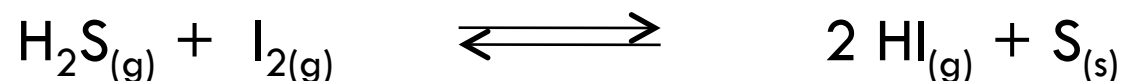
40



Increase $P(\text{Al}_2\text{Cl}_6)$

Increase Volume

Decrease Temperature (assume $\Delta H < 0$)



The equilibrium constant at 110 °C is $K = 0.0023$

For the following conditions, calculate Q and determine the direction of the reaction:

a) $P(\text{I}_2) = 0.461 \text{ atm}$, $P(\text{H}_2\text{S}) = 0.050 \text{ atm}$, $P(\text{HI}) = 0.1 \text{ atm}$

b) $P(\text{I}_2) = 0.461 \text{ atm}$, $P(\text{H}_2\text{S}) = 0.050 \text{ atm}$, $P(\text{HI}) = 1.0 \times 10^{-3} \text{ atm}$

Temperature Dependence of K

41

Van't Hoff Equation

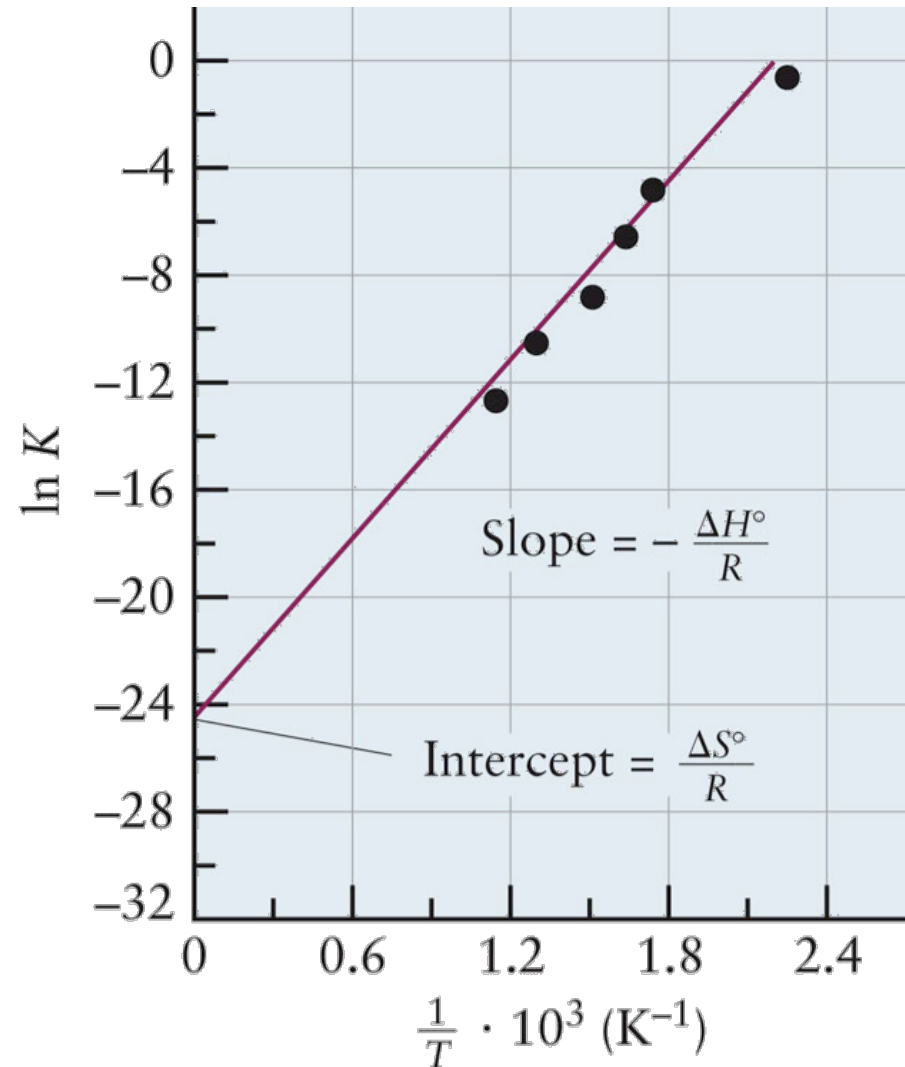
$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

ΔH° is the Enthalpy of a Reaction

$\Delta H^\circ < 0$ – Exothermic

$\Delta H^\circ > 0$ – Endothermic

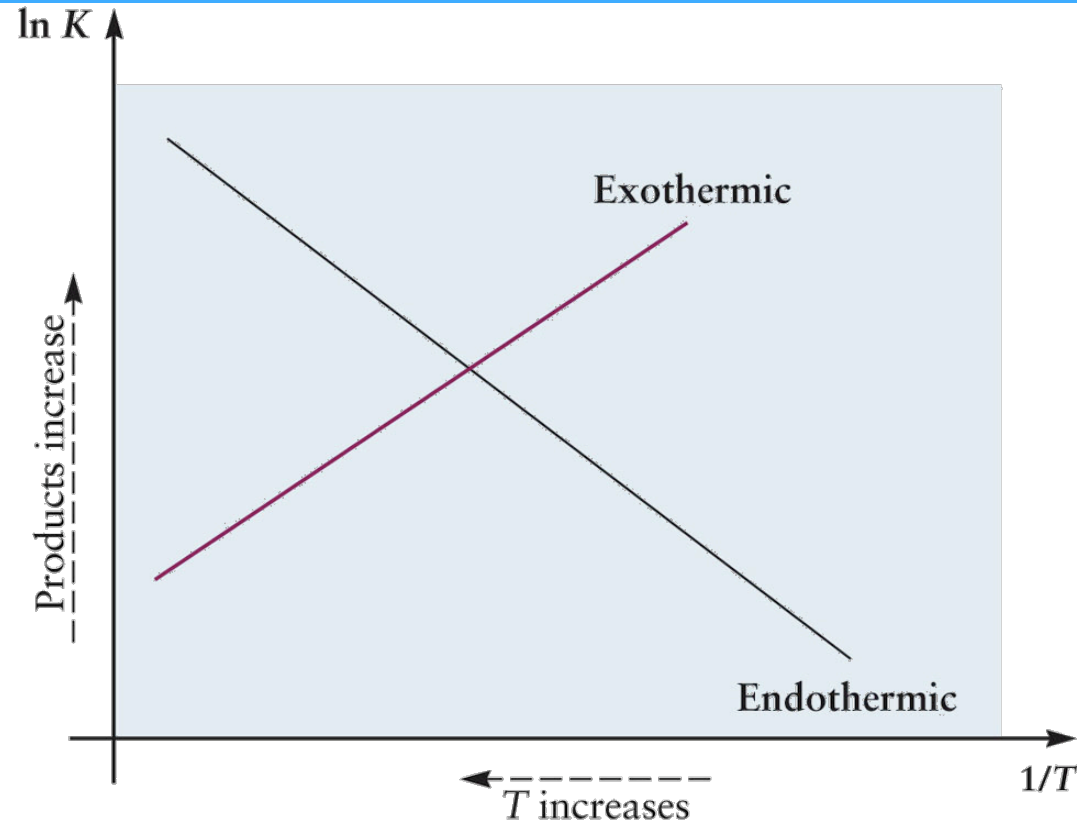
$R = 8.31451 \text{ J/mol K}$



Temperature Dependence of K

42

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



© 2007 Thomson Higher Education

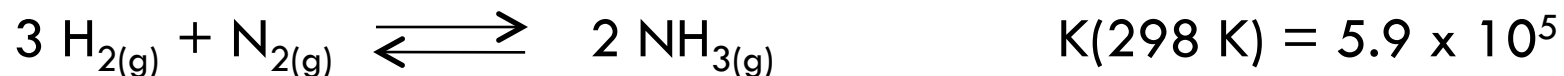
If $\Delta H < 0$ (exothermic reaction), then Increase in T reduces K

If $\Delta H > 0$ (endothermic reaction), then Increase in T increases K

Direction of Change in Reactions: van't Hoff Equation

43

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



If $\Delta H^\circ = -92.2 \text{ kJ/mol}$, calculate K at $T = 600 \text{ K}$

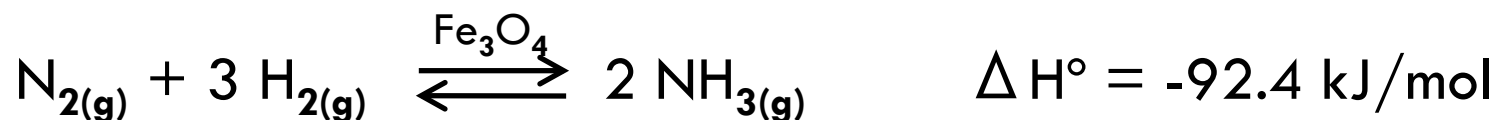
Catalysts

44

A **Catalyst** is a substance that increases the rate of a chemical reaction and is not consumed in the net reaction

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

Haber Process:



Catalysts do not affect the equilibrium composition

They only change the path

Catalysts speed up both the forward and reverse reactions

You will learn more about catalysts in 14B when you study Reaction Kinetics