

CHEM 206 section 01

LECTURE #17

Fri. March 7, 2008

LECTURE TOPICS:

TODAY'S CLASS: sect.19.7 & start Ch.16

NEXT CLASS: finish Ch.16

(1)

Magnitude of equilibrium constant describes rxn

Large $K \Rightarrow$ product-favoured rxn (eqm "positions" are mostly products)

Small $K \Rightarrow$ reactant-favoured rxn (eqm positions are mostly reactants)

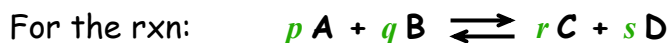
Reaction	Equilibrium Constant K (at 25 °C)
Table 16.1	
<i>Combination Reactions of Nonmetals</i>	
$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g})$	3.2×10^{81}
$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	3.5×10^8
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$	1.7×10^{-3} (at 2300 K)
<i>Ionization of Weak Acids and Bases</i>	
$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ acetic acid	1.8×10^{-5}
$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ carbonic acid	4.2×10^{-7}
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ ammonia	1.8×10^{-5}
<i>Dissolution of "Insoluble" Solids</i>	
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	3.4×10^{-9}
$\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	1.8×10^{-10}

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16.2: Equilibrium constants "Law of Mass Action"

Experimental observations of many many equilibria show:

- for **ANY** eqm system (single *OR* multistep...)
- we can use balanced chemical equation to write expression for the **equilibrium** constant (*recall: for rate constants, must know mechanism*)



Eqm expression:
$$K = \frac{[C]^r [D]^s}{[A]^p [B]^q}$$



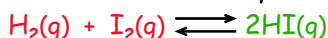
$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$

To determine a reaction's equilibrium constant via experiment:

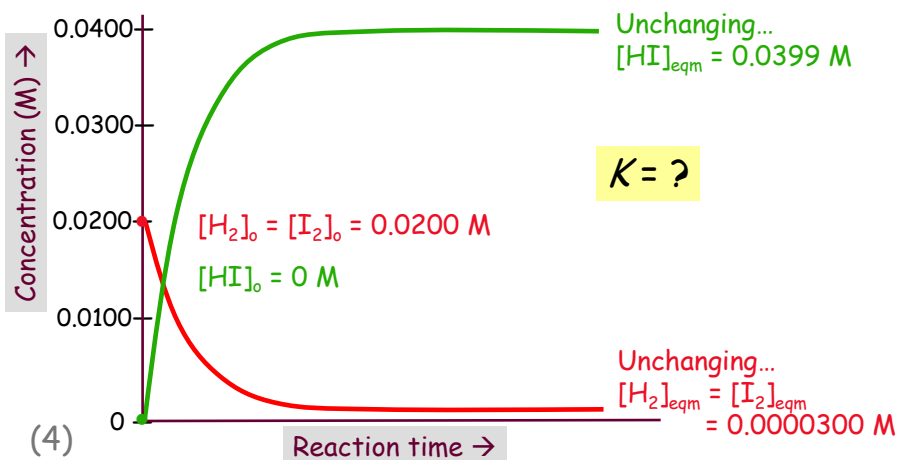
- mix reactants; be sure rxn has sufficient thermal E to proceed
- wait until []s of all species stop changing**, then measure them
- sub #s into K expression (as above) \Rightarrow calculate value of K
 \Rightarrow K is a constant, applicable to that rxn at that temp.

Ex.: Determining a rxn's equilibrium constant via experiment

Reaction under study at 425°C:



- Ensure rxn eqn is balanced
- Write K expression
- Allow rxn mixture to equilibrate
- Measure concentrations
- Calculate K using []_{eqm} values



If K is known: can find eqm conc'ns...using eqm data...

At 500K, $K = 6.9 \times 10^5$ for: $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$
 If have 0.0010M O_2 & 0.050M NO at eqm, what is $[\text{NO}_2]_{\text{eqm}}$?

An "ICE" table:

	$2\text{NO}(g)$	+	$\text{O}_2(g)$	\rightleftharpoons	$2\text{NO}_2(g)$
<u>I</u> nitial	---		---		---
<u>C</u> hange	---		---		---
<u>E</u> qm	0.050 M		0.0010 M		x

$$K = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

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$$= 1.3 \text{ M (2SF)}$$

$$= [\text{NO}_2]_{\text{eqm}}$$

Gas-phase equilibria: two related forms of eqm constant

For eqm: $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

= the "usual" K
 = 3.5×10^8 at 25°C

For gas-phase rxns:
 can also use partial pressures to define a K
 (yields a different # value)

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

Since $PV = nRT$ for any gas: $[] = \frac{n}{V} = \frac{P}{RT}$

\Rightarrow Thus: $K_c = \frac{(P_{\text{NH}_3}/RT)^2}{(P_{\text{N}_2}/RT)(P_{\text{H}_2}/RT)^3}$

$$= \frac{(P_{\text{NH}_3})^2(RT)^{-2}}{(P_{\text{N}_2})(RT)^{-1}(P_{\text{H}_2})^3(RT)^{-3}}$$

$$= \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \times \frac{(RT)^{-2}}{(RT)^{-1}(RT)^{-3}}$$

K_p $\frac{1}{(RT)^{-2}} = (RT)^{-(-2)}$

$$K_p = K_c(RT)^{\Delta n_{\text{gases}}}$$

← same...

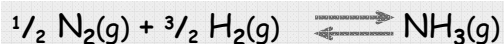
$$K_c = K_p \times (RT)^{-\Delta n_{\text{gases}}}$$

where Δn_{gases} = sum of coefficients of gaseous products minus sum of coefficients of gaseous reactants

For this example: $K_p = K_c \times [(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298\text{K})]^{-2} = 5.9 \times 10^5$

LINKING THERMODYNAMICS & EQUILIBRIUM...

Calculate the equilibrium constant for the formation of 1.00 mol of ammonia from hydrogen and nitrogen at 25°C.



What is the reaction's standard driving force?

$$\Delta G^\circ = -RT \ln K \Rightarrow K = e^{(-\Delta G^\circ/RT)}$$

⇔ "thermodynamic eqm constant"

= K_p ...derived from ΔG° for std. state gases (1 atm each)

$$\Rightarrow K_p = 738 = \frac{P_{\text{NH}_3}}{(P_{\text{N}_2})^{0.5} (P_{\text{H}_2})^{1.5}}$$

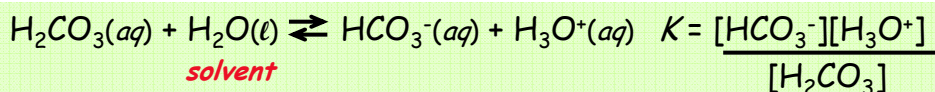
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The Law of Mass Action & Heterogeneous Equilibria

If substance's concentration will NOT change, don't include it.

(e.g., pure solids, liquids, & solvents...)

WHY?



WHY ARE SOLIDS & PURE LIQUIDS "IGNORED"?

Pure substances have constant [], no matter the quantity:

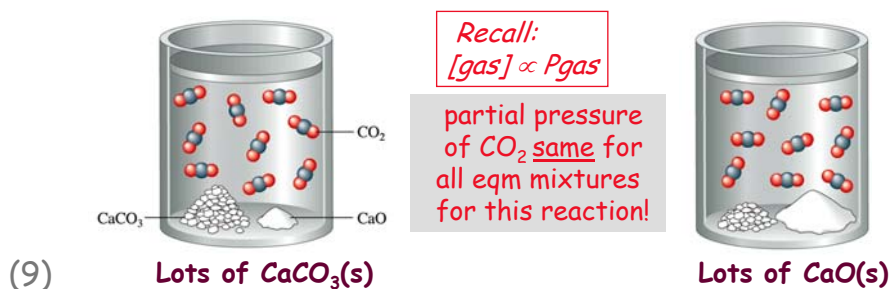
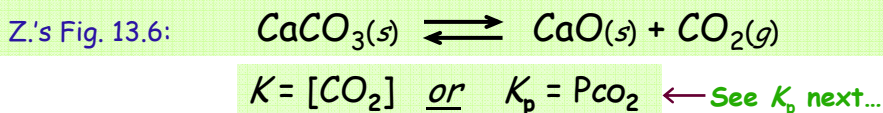
- Pure liquids: [] determined by liquid's density (a constant)
- Solvent: in excess, so even if involved in rxn, [] doesn't change much
- Solids: [] of molecules fixed by solid's density
heterogeneous rxns occur only at surfaces...thus: complicated...
BUT EVEN SO: exp'ts show that amount is unimportant!
- **So:** imagine [*s or l*] as multiplied into value of K (*rather than ignored*)
- **In reality:** strict definition of K seen in advanced courses leads to [*s or l*] being ~factored out (*so, it appears to be ignored!*)

⇒ Net effect: the link between values of K & $\Delta G^\circ_{\text{rxn}}$ remains!

Heterogeneous Equilibria: rxns involving multiple phases
i.e., gases vs. solids & pure liquids (including H₂O(l) as solvent)

AS LONG AS SOME OF EACH PHASE IS PRESENT...
 the position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present

⇒ **Pure solids & pure liquids are NOT included in K expressions.**



Since K expression is written based on rxn's stoichiometry...
 ...the way the rxn is written is important! (see 16.5)

- The equilibrium expression for a rxn (K_1) is the reciprocal of that for the rxn written in reverse:

$$K_{-1} = 1/K_1$$

- If the equation for a rxn is multiplied by some factor n (e.g., all stoich. coeff.'s scaled up...):

$$K_{\text{new}} = (K_{\text{original}})^n$$

- If two eqm processes occur in sequence (i.e., net rxn is sum of two rxns), then the overall eqm constant for the process is the product of the two individual eqm constants:

$$K_{\text{rxn}(1+2)} = K_1 \times K_2$$

The units for K depend on the rxn being considered (like rate constants)
BUT: conventionally, units are not given for eqm constants

Coupled reactions: using 1 rxn to drive another fwd...

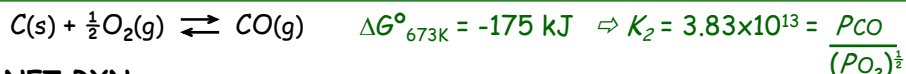
If we want to convert copper(I) oxide into copper metal (at 673K):

- in one step: $\Delta G^\circ > 0 \Rightarrow K = e^{-\Delta G^\circ/RT} \ll 1 \Rightarrow$ thermodynamics is against us

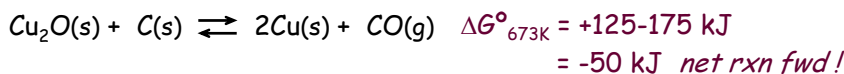


However, if we add a 2nd step that uses a product of the 1st rxn:

- Le Chatelier's principle says: should drive 1st eqm to the right (fwd)
- K expression rules say: net rxn's equilibrium constant $K_{\text{net}} = K_1 \times K_2$
- Thermodynamically: like a Hess's law combination of rxns
 \Rightarrow free energy released in exergonic 2nd step drives 1st step to occur



NET RXN:



$$\begin{aligned} \text{Now, forming copper metal is favoured!} \Rightarrow K_{\text{net}} &= 7.60 \times 10^3 \quad \checkmark \\ &= K_1 \times K_2 \text{ (very close: } 7.62 \times 10^3) \\ &= \frac{P_{\text{CO}}(\text{PO}_2)^{\frac{1}{2}}}{(\text{PO}_2)^{\frac{1}{2}}} \\ &= P_{\text{CO}} \text{ (matches rxn equation...)} \end{aligned}$$

Recall: Bronze Age metallurgists' method

The many uses of equilibrium constants...

$$m \text{ reactant} \rightleftharpoons n \text{ product} \quad K = \frac{[\text{product}]^n_{\text{eqm}}}{[\text{reactant}]^m_{\text{eqm}}}$$

1.) Can judge **extent** of rxn: how far rxn goes before reaches eqm

Small K reactant-favoured	$10^{-3} < K < 10^3$ lots of both	Large K product-favoured
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2.) Can predict **direction** of rxn: net rxn until eqm is reached...

$Q < K$ proceeds fwd	$Q = K$ already at eqm	$Q > K$ proceeds reverse
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3.) Can calculate **concentrations** of species present at eqm starting with ANY initial concentrations...

(NEXT)

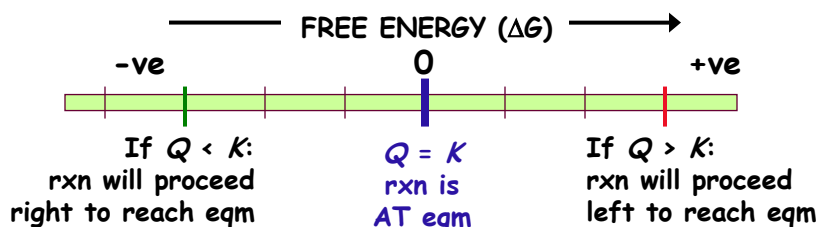
2.) Predicting whether or not an observable rxn will occur
i.e., is the system already at eqm?

PRACTICAL QUESTION:

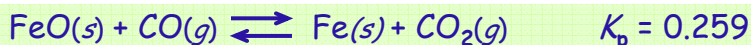
When you mix some substances together, do your initial []'s already correspond to eqm situation, or will a net rxn occur?

Calculate reaction quotient Q ...
...& compare it to rxn's known
value for K at that temp.!

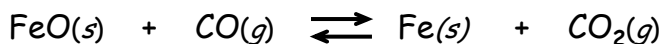
$$Q = \frac{[\text{products}]_o^n}{[\text{reactants}]_o^m}$$



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If initially $P_{\text{CO}} = 1.000$ atm & $P_{\text{CO}_2} = 0.500$ atm, is the system at equilibrium? If not, which direction will the reaction proceed until it reaches equilibrium?



Initial	present	1.000 atm	present	0.500 atm
Change				
Eqm	present		present	

Which way will rxn proceed until reaching equilibrium?

$$Q = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \text{ using initial conditions...} \quad Q = \frac{0.500 \text{ atm}}{1.000 \text{ atm}} = 0.500 > 0.259 = K_p$$

Conclusion: free energy available to drive rxn LEFT...

...making P_{CO} larger & P_{CO_2} smaller until $Q \rightarrow K$

(14)

3.) Determining what your eqm mixture will look like ...16.4-5 Solving Equilibrium Problems...

- ➔ **1** Write the balanced equation for the reaction. **ALWAYS!**
- ➔ **2** Write the equilibrium expression using the law of mass action. + **find/calculate K**
- ➔ **3** List the initial concentrations.
- ➔ **4** Calculate Q , and determine the direction of the shift to equilibrium. Not REQUIRED... but ensures you've THOUGHT about your answer!
- ➔ **5** Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
- ➔ **6** Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
- ➔ **7** Check your calculated equilibrium concentrations by making sure they give the correct value of K .

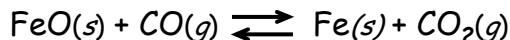
SUMMARY: YOUR "TO DO" LIST

- Balance rxn equation
- "ICE" table: initial, change & eqm ['s
- Eqm expression ($K = \dots$)
- THINK...

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Finding eqm concentrations... (or partial pressures) ...knowing initial conditions and K

At 1000K, this rxn involved in making steel has $K_p = 0.259$:



What are the eqm partial pressures of CO and CO₂

if initially have $P_{\text{CO}} = 1.000$ atm & $P_{\text{CO}_2} = 0.500$ atm?

...assume both solids are present at the end

(or else won't be at equilibrium!)

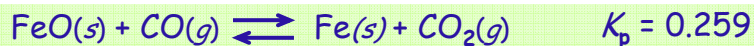
1. Rxn equation
2. "ICE" table
3. Eqm expression
4. THINK...

Same example as seen earlier...

...now in a more typical problem setting.

Recall: we already showed that this rxn will proceed LEFT ($Q > K$) as it approaches equilibrium...

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Assuming some FeO & Fe remain, what are $P_{\text{eqm CO}}$ & $P_{\text{eqm CO}_2}$ if initially $P_{\text{CO}} = 1.000 \text{ atm}$ & $P_{\text{CO}_2} = 0.500 \text{ atm}$?

So, at eqm: $P_{\text{CO}} = 1.000 + 0.191 = 1.191 \text{ atm}$
 $P_{\text{CO}_2} = 0.500 - 0.191 = 0.309 \text{ atm}$

Note: you don't NEED to find Q 1st! Can put "-x" for reactants and "+x" for products & the algebra takes care of the signs. Try it for yourself....

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.19.7,
Ch.16 up to section 16.4

+ WORK ON Problems from Ch.19, Ch.16