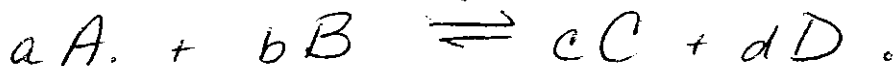


# THE IDIOTS' GUIDE TO EQUILIBRIUM!

I. Consider the reversible reaction



In a CLOSED SYSTEM, beginning with reactants A and B only, the rxn. will proceed in the forward ( $\rightarrow$ ) direction.

As more C & D products form, the reverse ( $\leftarrow$ ) rxn will commence; at some point the rates of the forward and reverse rxns will become EQUAL. This is the state of DYNAMIC EQUILIBRIUM:

Both forward & reverse rxns proceed simultaneously at the SAME RATE, and as a result the concentrations of the reactants and products STOP CHANGING.

EQUILIBRIUM can only be established in a CLOSED SYSTEM where at least some amount of EVERY SPECIES of reactant & product is present.

## II. The EQUILIBRIUM CONSTANT - $K_{eq}$

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where  $[X]^x =$   
X's concentration  
in  $\frac{\text{moles}}{L}$  AT EQUILIBRIUM,  
raised to the power of its  
coefficient (x) from the  
balanced equation.

Note that  $K_{eq}$  is always  
written with PRODUCTS  
OVER REACTANTS.

$\rightarrow$  ONLY INCLUDE (aq) AND (g) SPECIES  
in the  $K_{eq}$  expression!! Leave out solids(s)  
and liquids(l).

The value of  $K_{eq}$  is TEMPERATURE-DEPENDENT!  
If T changes,  $K_{eq}$  changes.

(II, continued)

(B) How  $K_{eq}$  changes with temperature depends on the  $\Delta H_{rxn}^\circ$ ; the relationship is expressed in the van't Hoff equation:

$$\ln \frac{K_{eq2}}{K_{eq1}} = \frac{\Delta H_{rxn}^\circ}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Bears a striking resemblance to the Clausius-Clapyron and Arrhenius equations, huh?

where  $K_{eq2}$  is at  $T_2$ ,  
 $K_{eq1}$  is at  $T_1$ ,  
 $\Delta H_{rxn}^\circ$  is the enthalpy change in Joules/mole  
and  $R$  is the Gas Constant;  $8.315 \frac{J}{mol \cdot Kelvin}$

### (C) Types of Equilibrium Constants

$K_a$ : for weak acid equilibria ( $HA_{(aq)} \rightleftharpoons H_{(aq)}^+ + A_{(aq)}^-$ )

$K_f$ : for the formation of complex ions

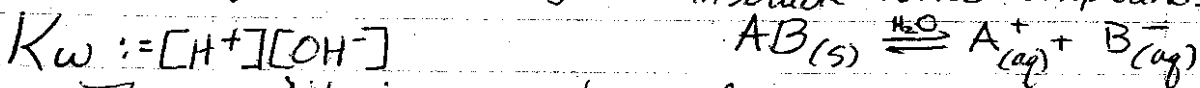
$K_b$ : for weak base equil. ( $B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB_{(aq)}^+ + OH_{(aq)}^-$ )

a. stands for Concentration

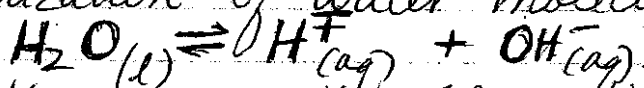
\*  $K_c$ : Any  $K_{eq}$  expressed in terms of MOLARITIES of reactants & products.

\*  $K_p$ :  $K_{eq}$  for gas-phase equilibria, expressed in the terms of PARTIAL PRESSURES:  $K_p = \frac{(P_c)^c (P_d)^d}{(P_a)^a (P_b)^b}$

$K_{sp}$ :  $K_{eq}$  for solubility equilibria involving so-called "insoluble" ionic compounds:



The equilibrium constant for the autoionization of water molecules:



At  $25^\circ C$ ,  $K_w = 1.0 \times 10^{-14}$ . This equilibrium is in effect wherever liquid water is present, and is the basis for the pH scale.

\* Relationship between  $K_p$  and  $K_c$ : Since gases can be included in  $K_{eq}$  expressions as either Partial Pressures or Molar concentrations, both forms of the  $\rightarrow$  page 2

(II) cont.)

Keq can be written for gas-phase equilibria. However, Kp is not necessarily equal to Kc for the same reaction! The relationship between the Kp and the Kc for the same gas phase equilibrium reaction is:

$$K_p = K_c (RT)^{\Delta n}$$

where R = gas constant  
T = Kelvin Temp  
and  $\Delta n$  is the difference between the total moles of gaseous PRODUCTS minus the total moles of gaseous REACTANTS, as shown by the balanced reaction equation.

$$\Delta n = \left( \begin{array}{c} \text{Total} \\ \text{moles of} \\ \text{gaseous} \\ \text{products} \end{array} \right) - \left( \begin{array}{c} \text{Total} \\ \text{moles of} \\ \text{gaseous} \\ \text{reactants} \end{array} \right)$$

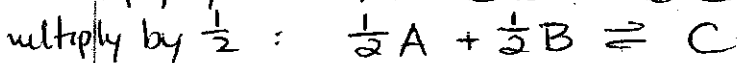
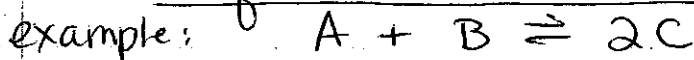
difference between the total moles of gaseous PRODUCTS minus the total moles of gaseous REACTANTS, as shown by the balanced reaction equation.

Note that if  $\Delta n = 0$ ,  $K_p = K_c$ .

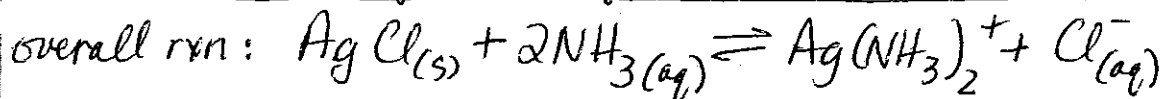
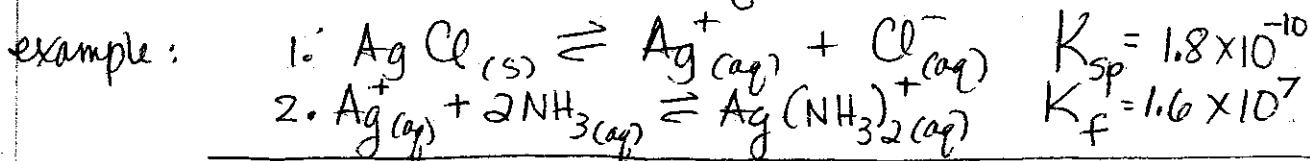
### III: Manipulating the Keq

When you:

(A) MULTIPLY THE COEFFICIENTS by some number in an equilibrium reaction, you RAISE the Keq TO THAT POWER to obtain the new Keq:



(B) ADD TWO EQUILIBRIUM REACTIONS TOGETHER to obtain an overall reaction, the overall Keq is the PRODUCT of each individual rxn's Keq's:

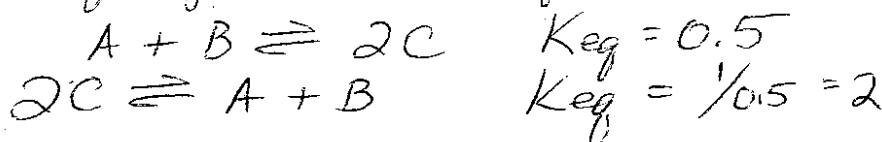


$$K_{eq \text{ overall}} = (K_{sp})(K_f) = (1.8 \times 10^{-10})(1.6 \times 10^7) = 2.9 \times 10^{-3}$$

(III, cont.)

(C) REVERSE an equilibrium rxn, take the INVERSE of the  $K_{eq}$  to get the new  $K_{eq}$ :

example:



#### IV. WHAT VALUES OF $K_{eq}$ MEAN

(A) When  $K_{eq} \gg 1$ , there will be FAR MORE PRODUCT(S) than REACTANT(S) at equilibrium; the rxn. is said to be "PRODUCT-FAVORED".

(B) When  $K_{eq} \ll 1$ , the opposite is true - there will be FAR MORE REACTANT(S) than PRODUCT(S) at equilibrium, and the rxn. is "REACTANT-FAVORED".

#### V. REACTION QUOTIENT (Q)

(A) 'Q' is the value obtained when the NON-EQUILIBRIUM concentrations of species are plugged into the  $K_{eq}$  expression:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{where } [A], [B], [C], \text{ and } [D] \text{ are NOT NECESSARILY the equilibrium concentrations of } A, B, C, \text{ and } D.$$

(B) The value of Q will indicate

- 1) whether the rxn. is at equilibrium or not, and, if not,
- 2) which direction (forward or reverse) the reaction must go in order to reach equilibrium.

(cont.) page 4

## (V(B) cont.)

- IF  $Q = K_{eq}$ , rxn. is at equilibrium.
- IF  $Q < K_{eq}$ , rxn. is not at equilibrium, and must proceed in the FORWARD ( $\rightarrow$ ) direction to reach it.
- IF  $Q > K_{eq}$ , rxn. is not at equilibrium and must proceed in the REVERSE ( $\leftarrow$ ) direction in order to achieve it.

VI. LE CHATELIER'S PRINCIPLE: Once a system has reached equilibrium, a change in any of the factors that effect the equilibrium (i.e., Temp., pressure, concentrations, volume, etc.) will cause the system to respond in a way that will reduce or counteract the effect of that change. The system will attempt to establish a NEW equilibrium state where, even though concentrations or pressures have changed, the value of  $K_{eq}$  does not change.

### A. EFFECTS OF DISTURBANCE ON A CHEMICAL EQUILIBRIUM

#### IF YOU:

- Add more reactant
- Add more product
- Add heat (i.e., raise temperature)
- Decrease volume (i.e., increase pressure) on a gas-phase equilibrium

#### THE SYSTEM WILL:

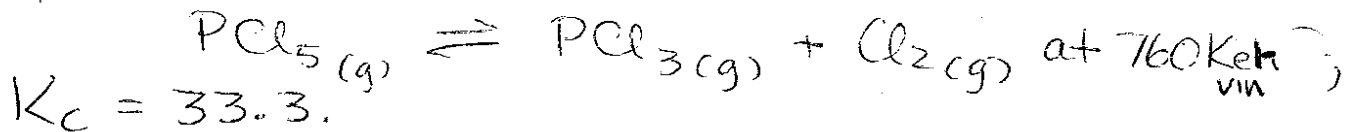
- Shift right (toward products)
- Shift left (toward reactants)
- if  $\Delta H_{rxn}^{\circ}$  is (-) (exothermic), shift left
- if  $\Delta H_{rxn}^{\circ}$  is (+) (endothermic) shift right
- Shift to whichever side has FEWER total moles of gas

The opposite actions above will have the opposite effect (i.e., removing a reactant will cause a shift to LEFT.)

➔ NOTE that, if a reactant or product IS NOT INCLUDED in the  $K_{eq}$  EXPRESSION, adding or removing it will have NO EFFECT on the equilibrium!! (page 5)

# VII : CALCULATING WITH $K_{eq}$ - The ICE TABLE

example: For the reaction



If 1.50g of  $PCl_5$  and 15.0g of  $PCl_3$  are placed in a 36.3 mL flask and are allowed to react until equilibrium is reached, what will be the molar concentrations of all 3 species at equilibrium?

Answer: Step ①: Find initial concentrations (in  $\frac{mol}{L}$ ) for all species:

$$\frac{1.50g PCl_5}{36.3 mL} \left| \frac{1000 mL}{1 L} \right| \frac{1 mol PCl_5}{208.239g PCl_5} = 0.198 M PCl_5$$

$$\frac{15.0g PCl_3}{36.3 mL} \left| \frac{1000 mL}{1 L} \right| \frac{1 mol PCl_3}{137.333g PCl_3} = 3.01 M PCl_3$$

Initial Concentration of  $Cl_2 = \text{zero}$ .

Step ②: Set up an ICE table (ICE means Initial, Change, Equilibrium) of: what concentrations are initially; as the reaction proceeds ('change'); and at equilibrium:

	$PCl_5$	$PCl_3$	$Cl_2$
I →	0.198 M	3.01 M	0 M
C →	-x*	+x*	+x*
E →	(0.198-x) M	(3.01+x) M	x M

\*As the reaction begins and proceeds to equilibrium, some amount "x" of the  $PCl_5$  will be consumed. Since the mole-to-mole ratios from the balanced equation are all 1:1, the same amount "x" of  $PCl_3$  will form, and also "x" amount of  $Cl_2$  will form. (If the mole-to-mole ratios were 1:2, then "x" amount of reactant consumed would form "2x" amount of product, etc.)

Step ③: Solve for "x" using the equilibrium concentrations and plugging them into the  $K_{eq}$  expression:

$$K_{eq} = 33.3 = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(3.01+x)(x)}{0.198-x}$$

Continued

Note that it appears necessary to use the Quadratic formula to solve for  $x$ :

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}; \quad x = 0.181M.$$

However, there is a way to weasel out of having to use it! Pay close attention in class to the lecture to learn this critical short-cut!! (or, see the bottom of page 2 of 3 in your Teacher's Tools packet.)

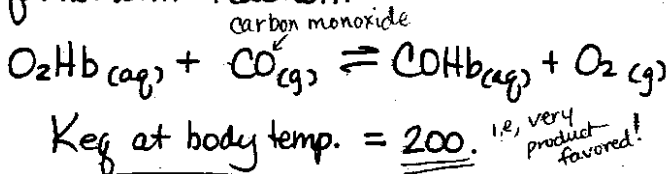
So, if  $x = 0.181M$ ,

FINAL ANSWERS	
$[Cl_2]$ at equilibrium = $x =$	$0.181M Cl_2$
$[PCl_5]$ at equilibrium = $0.198M - x =$	$0.017M PCl_5$
$[PCl_3]$ " " = $3.01 + x =$	$3.19M PCl_3$

Example (1)

Hemoglobin (a high-molecular-mass protein that we will refer to as simply "Hb") is the molecule that binds with  $O_2$  and carries oxygen from our lungs to our tissues. Unfortunately, CO will displace  $O_2$  from Hb according to the following equilibrium reaction:

(This problem is a frequent occurrence in the news during winter months - why?)



If the ratio of  $O_2Hb : COHb$  in our blood approaches 1:1, death is probable.

What partial pressure of CO in air is likely to be fatal to us? The partial pressure of  $O_2$  in air is 0.20 atm.

Answer: Fatality occurs when conditions are as follows: let  $x =$  Partial pressure CO

$$K_{eq} = 200 = \frac{[COHb][O_2]}{[O_2Hb][CO]} = \frac{[1][0.2]}{[1][x]}$$

1:1 ratio

$$200x = 0.2 \quad \boxed{x = 0.001 \text{ atm}}$$

Bonus Question for all you future physicians:

Would treating a person suffering from CO poisoning with pure  $O_2$  be helpful?

Explain. (hint: see what increasing  $[O_2]$  would do to the other concentrations in the Keq expression... remember that COHb is BAD.)

How about hyperbaric  $O_2$  (ie, at  $P_{O_2} > 1.0 \text{ atm}$ )?

Example (2): At  $450^\circ\text{C}$ ,  $3.60\text{ mol NH}_3$  is placed in a  $2.00\text{ L}$  vessel and allowed to decompose into its elements:  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

Uh oh -  $K_c$  is too large to avoid using quadratic here.  $K_c$  at  $450^\circ\text{C} = 6.3$ . Calculate the equilibrium concentrations for all species.

note that this is  $-2x$

	$2\text{NH}_3(\text{g})$	$\rightleftharpoons$	$\text{N}_2(\text{g})$	$+$	$3\text{H}_2(\text{g})$
C	$3.60\text{ mol} / 2.00\text{ L}$		$0$		$0$
E	$\frac{3.60\text{ mol}}{2.00\text{ L}} - 2x$		$+x$		$+3x$

note that this is  $3x$

$$6.3 = K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{(x)(3x)^3}{\left(\frac{3.60}{2.00} - 2x\right)^2}$$

yes, you still cube it, in addition to putting the coefficient 3 in front.

Simplify:  $\frac{27x^4}{(1.80 - 2x)^2} = 6.3$ ; take square root of both sides:  $\sqrt{6.3} = \frac{\sqrt{27x^4}}{1.80 - 2x}$

$5.20x^2 + 5.02x - 4.52 = 0$ . Use quadratic formula to find  $x$ .

$$x = 0.567\text{ M} = [\text{N}_2]$$

$$[\text{H}_2] = 3x = 1.70\text{ M}; [\text{NH}_3] = 1.80 - 2x = 0.167\text{ M}$$

Example (3)

$K_p$  for the rxn.  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) = 0.15$ .  
At equilibrium, the pressure of  $\text{N}_2\text{O}_4$  is  $0.85\text{ atm}$ .

What is the total pressure of both gases at equilibrium?

$$K_p = 0.15 = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} \quad \text{let } x = P_{\text{NO}_2}$$

$$\text{so } x^2 = (0.15)(0.85\text{ atm})$$

$$x = \sqrt{(0.15)(0.85)} = 0.36\text{ atm}$$

$$\therefore \text{Total pressure} = 0.36\text{ atm} + 0.85\text{ atm} = 1.21\text{ atm}$$

\* Flashback to Kinetics! Remember how sometimes an intermediate would show up in the rate law for the slow step in a mechanism?

### VII. EQUILIBRIUM STEPS IN REACTION MECHANISMS:

A. In testing a proposed mechanism for a given reaction, it is important that the rate expression for the slow (rate-determining) elementary step matches the experimentally-determined rate expression for the overall rxn.

However, if the rate expression for the elementary step contains a reaction intermediate, we must somehow eliminate the intermediate from the rate expression\*. This can be done by substitution, using an elementary step that is an equilibrium rxn. and its  $K_{eq}$  expression.

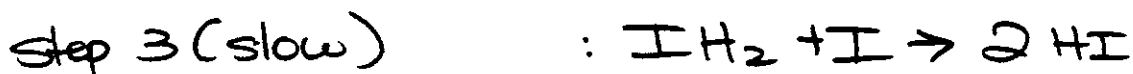
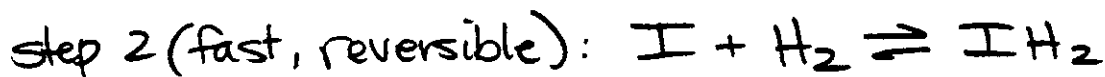
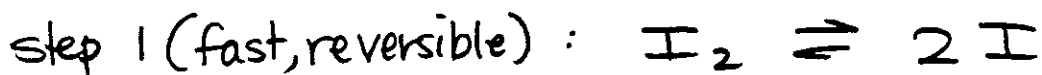
See the example on the next page.

\* Otherwise, it's impossible to compare the rate law for the slow step to the rate law for the overall rxn to see if they match.

EXAMPLE

① For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ ,  
the experimentally-determined rate  
expression is  $k[\text{H}_2][\text{I}_2]$ .

Does the following proposed mechanism  
satisfy this rate law?



Solution: first, make sure the steps all  
add up to the overall reaction  
as written. (They do).

Then, write  $K_{\text{eq}}$  expressions for the  
two equilibrium steps, and write  
the rate expression for the slow  
(rate-determining) step:

step 1:  $K_{\text{eq}_1} = \frac{[\text{I}]^2}{[\text{I}_2]}$

step 2:  $K_{\text{eq}_2} = \frac{[\text{IH}_2]}{[\text{I}][\text{H}_2]}$

step 3 (slow): rate =  $k[\text{IH}_2][\text{I}]$

with me so far? Good - keep going....

Note that these  
are both intermediates  
that don't appear  
in the overall rxn.

VIII A.1. cont.

OK. So... to know if this mechanism works, we have to see if the rate expression for the rate-determining step matches the experimentally-determined rate expression for the overall rxn:

$$\frac{\text{rate expression for rate-determining step}}{k [\text{IH}_2][\text{I}]} \neq \frac{\text{overall rate expression (given)}}{k [\text{H}_2][\text{I}_2]}$$

BUT: if we can get rid of the reaction intermediates by substitution, maybe they DO match.... hmmmm.....

Rearrange the  $K_{eq}$  expressions for steps 1 and 2 to get  $[\text{I}]$  and  $[\text{IH}_2]$ :

$$\text{step 1: } [\text{I}] = \sqrt{K_{eq1} [\text{I}_2]}$$

$$\text{step 2: } [\text{IH}_2] = K_{eq2} [\text{I}][\text{H}_2]$$

Substituting these into the rate expression for step 3 ( $k [\text{IH}_2][\text{I}]$ ), we get:

$$\begin{aligned} \text{rate} &= k \cdot K_{eq2} [\text{I}][\text{H}_2] \sqrt{K_{eq1} [\text{I}_2]} \\ &= k \cdot K_{eq2} \sqrt{K_{eq1} [\text{I}_2]} [\text{H}_2] \sqrt{K_{eq1} [\text{I}_2]} \\ &= k \cdot K_{eq2} \cdot K_{eq1} [\text{I}_2][\text{H}_2] \end{aligned}$$

The product of 3 constants = a constant, so

$$\text{rate} = k' [\text{I}_2][\text{H}_2]. \text{ IT DOES WORK!}$$