THE IDIOT'S GUIDE TO EQUILIBRIUM!

I. Consider the reversible reaction

$$aA + bB \overset{\downarrow}{\rightleftharpoons} cC + dD .$$

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

As more C & D products form, the reverse (←) 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 - Keq

Ⓐ

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

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 Keq is always written with PRODUCTS OVER REACTANTS.

→ ONLY INCLUDE (aq) AND (g) SPECIES in the Keq expression!! Leave out solids(s) and liquids(l).

The value of Keq is TEMPERATURE-DEPENDENT! If T changes, Keq changes.

(II, continued)

(B) How Keq changes with temperature depends on the ΔH°_{rxn}; the relationship is expressed in the van't Hoff equation:

$$\boxed{\ln \frac{K_{eq_2}}{K_{eq_1}} = \frac{\Delta H^\circ_{rxn}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

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

where K_{eq_2} is at T_2,
K_{eq_1} is at T_1,
ΔH°_{rxn} is the enthalpy change in $\frac{\text{Joules}}{\text{mole}}$
and R is the Gas Constant; $8.315 \frac{\text{J}}{\text{mol}\cdot\text{Kelvin}}$

(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. ($B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$)
*K_c : Any Keq expressed in terms of MOLARITIES of reactants & products.

c stands for Concentration

*K_p : Keq 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} : Keq for solubility equilibria involving so-called "insoluble" ionic compounds:

$$AB_{(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} A^+_{(aq)} + B^-_{(aq)}$$

$K_w := [H^+][OH^-]$
The equilibrium constant for the autoionization of water molecules:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

At 25°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 Keq expressions as either Partial Pressures or Molar concentrations, both forms of the → page ②

(II Ⓒ cont.) Keq can be written for gas-phase equilibria. However, K_p is not necessarily equal to K_c for the same reaction! The relationship between the K_p and the K_c for the same gas phase equilibrium reaction is:

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

Where R = gas constant
T = Kelvin Temp
and Δn is the difference between the total moles of gaseous PRODUCTS minus the total moles of gaseous REACTANTS, as shown by the balanced reaction equation.

$$\Delta n = \begin{pmatrix}\text{Total}\\ \text{moles of}\\ \text{gaseous}\\ \text{products}\end{pmatrix} - \begin{pmatrix}\text{Total}\\ \text{moles of}\\ \text{gaseous}\\ \text{reactants}\end{pmatrix}$$

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

III. Manipulating the Keq

When you:

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

example: $A + B \rightleftharpoons 2C$ $\quad$ $K_{eq} = 0.5$

multiply by 3: $3A + 3B \rightleftharpoons 6C$ $\quad$ $K_{eq} = (0.5)^3$ cube Keq

multiply by $\frac{1}{2}$: $\frac{1}{2}A + \frac{1}{2}B \rightleftharpoons C$ $\quad$ $K_{eq} = \sqrt{0.5}$ square root Keq (i.e. raise to $\frac{1}{2}$ power)

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

example:

1. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ $\quad$ $K_{sp} = 1.8 \times 10^{-10}$
2. $Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)^+_{2(aq)}$ $\quad$ $K_f = 1.6 \times 10^{7}$

overall rxn: $AgCl_{(s)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+ + Cl^-_{(aq)}$

$\underline{K_{eq}\ \text{overall}} = (K_{sp})(K_f) = (1.8\times10^{-10})(1.6\times10^{7}) = \underline{2.9\times10^{-3}}$

(III, cont.)

Ⓒ REVERSE an equilibrium rxn, take the INVERSE of the Keq to get the new Keq:

example: $A + B \rightleftharpoons 2C \quad K_{eq} = 0.5$

$2C \rightleftharpoons A + B \quad K_{eq} = 1/0.5 = 2$

IV. WHAT VALUES OF Keq MEAN

Ⓐ When Keq >>> 1, there will be FAR MORE PRODUCT(S) than REACTANT(S) at equilibrium; the rxn. is said to be "PRODUCT-FAVORED".

Ⓑ When Keq <<< 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)

Ⓐ "Q" is the value obtained when the NON-EQUILIBRIUM concentrations of species are plugged into the Keq expression:

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

where [A], [B], [C], and [D] are NOT NECESSARILY the equilibrium concentrations of A, B, C, and D.

Ⓑ 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.

(V (B) cont.)

a) IF $Q = K_{eq}$, rxn. is at equilibrium.

b) IF $Q < K_{eq}$, rxn. is not at equilibrium, and must proceed in the FORWARD (→) direction to reach it.

c) IF $Q > K_{eq}$, rxn. is not at equilibrium and must proceed in the REVERSE (←) 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:	THE SYSTEM WILL:
1.	Add more reactant	Shift right (toward products)
2.	Add more product	Shift left (toward reactants)
3.	Add heat (i.e, raise temperature)	if ΔH°_{rxn} is (−) (exothermic), shift left if ΔH°_{rxn} is (+) (endothermic) shift right
4.	Decrease volume (i.e, increase pressure) on a gas-phase equilibrium	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!!

VII : CALCULATING WITH Keq - The ICETABLE

example : For the reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$ at 760 Kelvin,

$K_c = 33.3$.

If 1.50g of $PCl_{5(g)}$ and 15.0g of $PCl_{3(g)}$ 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:

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

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

Initial Concentration of Cl_2 = 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 $\rightleftharpoons$	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 Keq 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:

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

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.)

FINAL ANSWERS

So, if $x = 0.181\,M$, $[Cl_2]$ at equilibrium $= x = \boxed{0.181\,M\,Cl_2}$

$[PCl_5]$ at equilibrium $= 0.198\,M - x = \boxed{0.017\,M\,PCl_5}$

$[PCl_3]$ " " $= 3.01 + x = \boxed{3.19\,M\,PCl_3}$

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?)

carbon monoxide

$$O_2Hb_{(aq)} + CO_{(g)} \rightleftharpoons COHb_{(aq)} + O_{2\,(g)}$$

Keq at body temp. = 200. i.e, very product favored!

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

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

Bonus Question for all you phuture 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 $P_{O_2} > 1.0$ atm)?

Example ② : At 450°C, 3.60 mol NH_3 is placed in a 2.00L vessel and allowed to decompose into its elements: $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

Uh Oh - K_c is too large to avoid using quadratic here.

K_c at 450°C = 6.3. Calculate the equilibrium concentrations for all species.

	$2NH_{3(g)}$	$\rightleftharpoons N_{2(g)}$	$+ 3I_{2(g)}$
I	3.60mol/2.00L	θ	θ
C	$-2x$	$+x$	$+3x$
E	$\frac{3.60\text{mol}}{2.00\text{L}} - 2x$	x	$3x$

note that this is $-2x$

note that this is $3x$

$$6.3 = K_c = \frac{[N_2][I_2]^3}{[NH_3]^2} = \frac{(x)(3x)^3}{\left(\frac{3.60}{2.00} - 2x\right)^2}$$

← 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: $\sqrt{6.3} = \sqrt{\frac{27x^4}{1.80-2x}}$

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

$\boxed{x = 0.567\text{ M}} = [N_2]$.

$[H_2] = \boxed{3x = 1.70\text{ M}}$; $[NH_3] = \boxed{1.80 - 2x = 0.67\text{ M}}$

Example ③

K_p for the rxn. $N_2O_{4(g)} \rightleftharpoons 2\ NO_{2(g)} = 0.15$. At equilibrium, the pressure of N_2O_4 is 0.85 atm.

What is the total pressure of both gases at equilibrium?

$$K_p = 0.15 = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \quad \text{let } x = P_{NO_2}$$

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

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

∴ Total pressure = 0.36 atm + 0.85 atm

= $\boxed{1.21\text{ atm}}$

* 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 Keq 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.

VIII.A. cont.

EXAMPLE

① For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, the experimentally-determined rate expression is $k[H_2][I_2]$.

Does the following proposed mechanism satisfy this rate law?

step 1 (fast, reversible) : $I_2 \rightleftharpoons 2I$

step 2 (fast, reversible): $I + H_2 \rightleftharpoons IH_2$

step 3 (slow) : $IH_2 + I \rightarrow 2HI$

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

Then, write Keq expressions for the two equilibrium steps, and write the rate expression for the slow (rate-determining) step:

step 1: $K_{eq_1} = \dfrac{[I]^2}{[I_2]}$

step 2: $K_{eq_2} = \dfrac{[IH_2]}{[I][H_2]}$

step 3 (slow): rate $= k[IH_2][I]$

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

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

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:

rate expression for rate-determining step | Uh-oh... | overall rate expression (given)

$k[IH_2][I] \neq k[H_2][I_2]$

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

Rearrange the Keq expressions for steps 1 and 2 to get [I] and [IH$_2$]:

step 1: $[I] = \sqrt{K_{eq_1}[I_2]}$

step 2: $[IH_2] = K_{eq_2}[I][H_2]$

Substituting these into the rate expression for step 3 ($k\underbrace{[IH_2]}_{}\underbrace{[I]}_{}$), we get:

$$\text{rate} = k \cdot K_{eq_2}\underbrace{[I]}_{}[H_2]\sqrt{K_{eq_1}[I_2]}$$

$$= k \cdot K_{eq_2}\sqrt{K_{eq_1}[I_2]}\,[H_2]\sqrt{K_{eq_1}[I_2]}$$

$$= \underline{k \cdot K_{eq_2} \cdot K_{eq_1}}[I_2][H_2]$$

the product of 3 constants = a constant; so

rate = $k'[I_2][H_2]$. IT <u>DOES</u> WORK!