### CHAPTER 17. CHEMICAL EQUILIBRIUM

#### Section 17.1 Equilibrium State and Equilibrium Constant

Chemical reactions do NOT go to completion (100% products) - even those that look like they do. Reactions instead reach a point (called equilibrium) after which the amount of reactants and products no longer change with time. This is because <u>all reactions are reversible</u>.

**Example:**  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  ( $\rightleftharpoons$  means the reaction goes in both directions) --- Add some colorless  $N_2O_4(g)$  to an empty flask and then watch it with time - the gas will slowly go more and more brown as  $N_2O_4(g)$  converts to brown  $NO_2(g)$ . --- After a few minutes, no further color change occurs - "the reaction has reached equilibrium". The gas contains <u>both</u>  $N_2O_4$  and  $NO_2$ . Why doesn't it keep giving more  $NO_2$ and going more brown? Because the rate at which  $N_2O_4$  is giving more  $NO_2$  is now the same as the rate of the reverse reaction ( $2NO_2$  combining to give  $N_2O_4$ ). Thus the  $[N_2O_4]$  and  $[NO_2]$  concs do not change (Figure 17.1). We can see this in a conc ([]) vs time (t) plot (Figure 17.3)



 $\begin{array}{l} \underline{At \ any \ given \ time \ t:} \\ \text{Rate (forward) = } k_{fwd}[N_2O_4] &= -\Delta[N_2O_4]/\Delta t \\ \text{Rate (reverse) = } k_{rev}[NO_2]^2 &= -\Delta[NO_2]/\Delta t \\ (\text{Note: (i) assume reaction is elementary.} \\ & (ii) \ we'll \ define \ what \ Q \ is \ soon.) \\ \hline After \ a \ certain \ time, \ the \ concs \ of \ all \ species \ do \ not \\ change \ any \ more. \ The \ reaction \ has \ reached \\ equilibrium. \ This \ is \ a \ "dynamic \ equilibrium", \ which \\ means \ reactions \ are \ still \ occurring, \ but \ no \ overall \\ change \ in \ the \ []'s. \end{array}$ 

## Figure 17.1 Reaching equilibrium on the macroscopic and molecular levels.



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#### At equilibrium: rate (forward) = rate (reverse) $\therefore k_{fwd}[N_2O_4] = k_{rev}[NO_2]^2$

 $k_{fwd}/k_{rev} = [NO_2]^2/[N_2O_4] = K$ 

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 $K = [NO_2]^2 / [N_2O_4]$ 

K is the **Equilibrium Constant** for the reaction.

(do NOT confuse equil constant K (capital K) with rate constants  $k_{fwd}$  /  $k_{rev}$  (small k).

The equilibrium constant (K) is <u>a number</u> (no units) that depends on the relative amounts of products and reactants at equilibrium:

Note (i) \*\*Only temperature, T, can change the value of K (see later)\*\*

(ii) "reactants" are <u>defined</u> as the things on the left, and "products" as the things on the right of the balanced equation.

If K very large:  $[NO_2] \gg [N_2O_4]$  - we say "the equilibrium lies far to the right" i.e. mainly products (things on the right of equation)

If K very small:  $[NO_2] \ll [N_2O_4]$  - we say "the equilibrium lies far to the left" i.e. mainly reactants (things on the left of equation)

Note: If K very, very small, we can say "there is no reaction"

If K very, very large, we can say "reaction has gone to completion" (Fig 17.2)

Both these statements are, however, not correct, just reasonable approximations. Chemical reactions NEVER go exactly 0% or 100%. They are ALWAYS equilibria

#### Figure 17.2 The range of equilibrium constants.



small *K* The reaction mixture contains mostly reactants.



large *K* The reaction mixture contains mostly products.



intermediate K



#### Section 17.2 Reaction Quotient (Q) and Equilibrium Constant (K)

Consider again the reaction equation:  $N_2O_4(g) \approx 2NO_2(g)$ 

At equilibrium:  $[NO_2]^2/[N_2O_4] = K$ 

But, if the reaction is not at equilibrium:  $[NO_2]^2/[N_2O_4] = Q$  **Q is the "reaction quotient" or "mass-action expression"** As the reaction proceeds, Q is changing. When the reaction reaches equilibrium, Q = K. **Remember this! At equilibrium, Q = K** 

Writing Q and K for any reaction<br/>Considera A + b B = c C + d D $Q_c = [C]^c[D]^d$ <br/> $[A]^q[B]^p$ a, b, c, d are coefficients in balanced eqn.<br/> $(Q_c means Q expressed in []'s).<br/>At equilibrium, <math>Q_c = K_c$ So, all we have to do is:<br/>1) Write reaction equation<br/>2) Balance it !<br/>3) Write down Q and KAt equilibrium,  $Q_c = K_c$ **Example:** $N_2(q) + 3H_2(q) = 2NH_3(q)$ check: it is balanced

 $\therefore$  Q<sub>c</sub> = [NH<sub>3</sub>]<sup>2</sup>/[N<sub>2</sub>][H<sub>2</sub>]<sup>3</sup> (= K<sub>c</sub> if at equilibrium)



## Sample problem 17.1 (b):

 $C_{3}H_{8}(g) + O_{2}(g) = CO_{2}(g) + H_{2}O(g)$ 

check: not balanced, so we must balance it first!

$$C_{3}H_{8}(g) + 5O_{2}(g) = 3CO_{2}(g) + 4H_{2}O(g)$$

 $\therefore Q_c = [CO_2]^3 [H_2O]^4 \qquad (= K_c \text{ if at equilibrium})$ 

[C<sub>3</sub>H<sub>8</sub>] [O<sub>2</sub>]<sup>5</sup>

**Note:** (i) Q and K are unitless numbers, because each conc is divided by standard conc = 1.00 M, so the units (M) cancel. (ii) Q and K refer to <u>balanced</u> reaction as written (important! see below)

(iii) Doesn't matter how many steps reaction involves to get to products: all we need are Q and K for the <u>overall</u> balanced eqn (see below)



### DIFFERENT FORMS OF Q and K

#### <u>1) Equation written in the opposite direction</u>

Q and K refer to a particular equation! - if the equation is written differently, Q and K change.

(a)  $2SO_2(\tilde{g}) + O_2(g) = 2SO_3(g)$ (b)  $2SO_3(g) = 2SO_2(g) + O_2(g)$   $Q_{(a)} (or K_{(a)}) = [SO_3]^2 / [SO_2]^2 [O_2]$  $Q_{(b)} (or K_{(b)}) = [SO_2]^2 [O_2] / [SO_3]^2$ 

 $\therefore$  Q<sub>(a)</sub> = 1/Q<sub>(b)</sub> and K<sub>(a)</sub> = 1/K<sub>(b)</sub>

2) Overall reaction of more than one step.

 ${\bf Q}$  and  ${\bf K}$  of overall reaction are related to  ${\bf Q}$  and  ${\bf K}$  of individual steps by the relationships

$$Q_{\text{overall}} = Q_1 \times Q_2 \times Q_3 \times \dots$$
$$K_{\text{overall}} = K_1 \times K_2 \times K_3 \times \dots$$

#### Example:

<u>Overall</u> reaction is  $N_2(g) + 2O_2(g) = 2NO_2(g)$   $\therefore$   $Q_c = [NO_2]^2/[N_2][O_2]^2$ 

But this reaction has two steps;

$$\begin{array}{rcl} (a) \ N_2(g) + O_2(g) &=& 2NO(g) & & \therefore \ Q_{c \ (a)} = [NO]^2 / [N_2][O_2] \\ (b) \ 2NO(g) + O_2(g) &=& 2NO_2(g) & & \therefore \ Q_{c \ (b)} = [NO_2]^2 / [NO]^2[O_2] \\ \therefore \ Q_{c \ (a)} \times \ Q_{c \ (b)} = \underline{[NO]^2} & \times & \underline{[NO_2]^2} &=& \underline{[NO_2]^2} \\ [N_2][O_2] & [NO]^2[O_2] & & [N_2][O_2]^2 \end{array}$$

 $\therefore$  when writing  $Q_c$  or  $K_c$ , only the overall balanced equation is needed. It doesn't matter whether the reaction is one-step or multi-step.



#### 3) Coefficients multiplied by a common factor.

4) Reactions involving pure liquids and solids.

 $CaCO_3(s) \Rightarrow CaO(s) + CO_2(g)$ Concs of solids or liquids are constant  $\therefore$  in such a heterogeneous reaction, only the substances whose concs can change are included.

$$\therefore Q_c = [CO_2]$$
 (Fig 17.4)



# Figure 17.4 The reaction quotient for a heterogeneous system depends only on concentrations that change.





Section 17.3. Q and K Expressed as Pressures It is often convenient to use pressures (p) rather than concs ([]). pV = nRT : p = (n/V)RT = (conc)RT (since n/V = conc) For a mixture of gases 1, 2, 3, etc total pressure (P) =  $p_1 + p_2 + p_3 \dots = \Sigma p_i = nRT/V$   $p_i = partial pressure of gas i$ Consider again  $aA(q) + bB(q) \Rightarrow cC(q) + dD(q)$  $Q_p = p_c^c p_D^d / p_A^a p_B^b = K_p \text{ at equilibrium}$ **Example**:  $CO(g) + 3 H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$  at 927 °C  $Q_{p}$  (or  $K_{p}$ ) =  $p_{CH4} p_{H20} / p_{C0} p_{H2}^{3}$ **Relationship between K\_c and K\_p** Since p = (conc)RT from above:  $K_{p} = \frac{p_{C}^{c} p_{D}^{d}}{p_{A}^{a} p_{B}^{b}} = \frac{[C]^{c}(RT)^{c}}{[A]^{a}(RT)^{a}} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}. (RT)^{c+d-a-b}$  $\therefore K_p = K_c (RT)^{\Delta n}$   $\Delta n = c + d - a - b = change in total number of moles of gas$ <u>total number of moles</u> of gas. : if there is no change in the moles of gas (i.e.  $\Delta n = 0$ ),  $K_p = K_c$ For above example: CO (g) + 3 H<sub>2</sub> (g)  $\rightleftharpoons$  CH<sub>4</sub> (g) + H<sub>2</sub>O (g) at 927 °C  $\therefore \Delta n = 1 + 1 - 1 - 3 = -2$   $\therefore K_p = K_c (RT)^{-2} = K_c / (RT)^2$ At 927 °C,  $K_c = 3.93$   $\therefore K_p = (3.93) / {(0.082 L. atm/mol. K)(1200K)}^2$ (use R in these units)

: 
$$K_p = 4.04 \times 10^{-4}$$





#### Section 17.4 Predicting Reaction Directions: Comparing Q and K

First, remember that the size of K tells us the relative amounts of reactants (things on the left) and products (things on the right) at equilibrium.

- If K >> 10 products favored ("equilibrium lies to the right") K << 0.1 reactants favored ("equilibrium lies to the left")
- 0.1 < K < 10 both reactants and products in significant amounts

If Q does not equal K, reaction is not at equilibrium. Net reaction will occur until equilibrium is reached.

If Q > K reaction proceeds from right-to-left to reach equil

- Q < K reaction proceeds from left-to-right to reach equil
- Q = K reaction at equilibrium  $\therefore$  no change to concs occurs

#### Sample Problem 17.6.

 $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$   $K_c = 0.21 \text{ at } 100 \text{ }^{\circ}C$ Question: at a certain time, the  $[N_2O_4] = 0.12 \text{ M}$  and  $[NO_2] = 0.55 \text{ M}$ . Has the reaction reached equil? If not, in which direction is it going? Answer: calculate  $Q_c$  and compare with  $K_c$ .

 $Q_c = [NO_2]^2 / [N_2O_4] = (0.55)^2 / (0.12) = 2.5$ 

 $\therefore Q_c > K_c \quad \therefore$  the reaction shifts from the right (products) to the left (reactants). As this occurs,  $[NO_2] \downarrow$  (decreases) and  $[N_2O_4] \uparrow$  (increases) until  $Q_c = K_c = 0.21$ 17-11

### Sample Problem 17.5

 $A(g) \rightleftharpoons B(g)$ 

At equilibrium:  $[A] = 2.8 \times 10^{-4} M$  and  $[B] = 1.2 \times 10^{-4} M$ .

At the times below (not in order), does the reaction shift to the right or left or not at all for each mixture to reach equilibrium?



- 1.  $Q_c > K_c$ ; reaction shifts to the left.
- 2.  $Q_c = K_c$ ; no net change.
- 3.  $Q_c > K_c$ ; reaction shifts to the left.
- 4.  $Q_c < K_c$ ; reaction shifts to the right.



#### Section 17.5. Solving Equilibrium Problems

Two main types of calculations:

(A) Calculate K from provided information

(B) Use K to calculate one of the concentrations (or pressures)

(A) Calculating  $K_c$  from equilibrium concentrations <u>Sample Problem 17.7</u>  $2HI(g) \Rightarrow H_2(g) + I_2(g)$ A 2.00 L flask is filled with 0.200 mol of HI and allowed to reach equilibrium. At equilibrium, [HI] = 0.078 M. Calculate  $K_c$ .

Answer: set up reaction table (ICE table) to follow the changes.

	2HI (g)	$\Rightarrow$ H <sub>2</sub> (g)	+	I <sub>2</sub> (g)
[ <b>I</b> nitial]	0.100 M	0		0
[Change]	-2x	+X		+X
[ <b>E</b> quil]	(0.100-2x)	×		×

(Note: M units are omitted from the table above to make it clearer, but remember these numbers are all concs).

initial [HI] = n/V = 0.200 mol/2.00L = 0.100 M ∴ at equilibrium: [HI] = 0.078M = (0.100 -2x) ∴ x = 0.011 M

$$\therefore K_{c} = [H_{2}][I_{2}] = x \cdot x = (0.011)(0.011) = 0.01988 = 0.020$$

$$[HI]^{2} (0.100 - 2x)^{2} = (0.078)^{2}$$



## (B) Calculating equilibrium concentrations from $K_c$ .

\*\* See Problems 17.8 and 17.9 on pages 692/693 of textbook \*\*

Another Example: In a 50.0 L vessel, 1.00 mol of CO and 1.00 mol of  $H_2O$  at high temp are allowed to reach equilibrium. Calculate the concs of all species if  $K_c = 0.58$ 

CO(g) +  $H_2O(g) = CO_2(g) + H_2(g)$ 1.00 mol 1.00 mol 0 n(initial) 0 0.0200 M 0.0200 M 0 [initial] 0 [change] -x -X +X +X  $K_{c} = \frac{[CO_{2}][H_{2}]}{[CO][H_{2}O]} = \frac{x^{2}}{(0.0200-x)^{2}} = 0.58$ [equil] X square-rooting both sides:  $x = \pm \sqrt{0.58} = \pm 0.76$ (0.0200-x) Two solutions x = 0.0152 - 0.76xAND x = -0.0152 + 0.76xx = 0.0086 Mx = -0.063 M∴ x = 0.0086 M negative [] : reject  $\therefore$  equilibrium concs are [CO] = [H<sub>2</sub>O] = 0.0114 M  $[CO_2] = [H_2] = 0.0086 \text{ M}$ If the question had asked for moles rather than concs;  $n(CO) = n(H_2O) = (0.0114 \text{ M})(50.0 \text{ L}) = 0.570 \text{ mol}$  $n(CO_2) = n(H_2) = (0.0086 \text{ M})(50.0 \text{ L}) = 0.43 \text{ mol}$ 



#### Using the quadratic formula to calculate x

In many calculations, we can't square-root both sides, and therefore have to solve for x using the quadratic formula.

For the equation  $ax^2 + bx + c = 0$ 

\*\* See textbook example (page 694 of 6<sup>th</sup> edition) for yourselves \*\*

#### Another example:

1.00 mol H<sub>2</sub> and 2.00 mol I<sub>2</sub> are placed in a 1.00 L vessel at 458 °C. Calculate the moles of each substance at equilibrium.  $K_c = 49.7$ 

	$H_{2}(g) +$	$I_2(g) \rightleftharpoons$	2HI (g)
n(initial)	1.00 mol	2.00 mol	0
[initial]	1.00 M	2.00 M	0
[change]	-x	-X	+2x
[equil]	(1.00-x)	(2.00-x)	2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.00-x)(2.00-x)} = \frac{4x^2}{(2-3x+x^2)} = 49.7$$

$$\therefore 4x^{2} = 49.7x^{2} - 149.1x + 99.4$$
  

$$45.7x^{2} - 149x + 99.4 = 0$$
 (di  

$$x^{2} - 3.26x + 2.17 = 0$$

(divide by 45.7 for convenience)



x <sup>2</sup> - 3.26x + 2.	17 = 0	
∴ x = -b ± √(b²-4ac) 2a	= -(-3.26) ±	√{(-3.26)2 - 4(1)(2.17)} 2
∴ x = 2.33 M (not possible: max [HI]=2.00M)	OR	x = 0.93 M correct x

Finally, use x to calculate all concs:  $[H_2] = (1.00 - 0.93) = 0.07 \text{ M}$   $[I_2] = (2.00 - 0.93) = 1.07 \text{ M}$ [HI] = 2(0.93) = 1.86 M

if the question had asked for number of moles instead of concs:  $n(H_2) = (0.07 \text{ M})(1.00 \text{ L}) = 0.07 \text{ mol}$   $n(I_2) = (1.07 \text{ M})(1.00 \text{ L}) = 1.07 \text{ mol}$ n(HI) = (1.86 M)(1.00 L) = 1.86 mol



#### **APPROXIMATION**

Sometimes, an approximation can be used that avoids the need to use the quadratic expression. If K is small, (say K << 1), the reaction lies to the left, therefore x is small (i.e. not much product forms at equilibrium), and the [equil]  $\approx$  [initial] of reactants.

Everyday analogy to get the idea across: you weigh yourself on a bathroom scale and you are 160 lb. You then take off a ring from your finger, and within the accuracy of the scale, you still weigh 160 lb. The weight of the ring is so small compared to the weight of your body that it can be neglected. ... final body weight  $\approx$  initial body weight

**Example:**  $I_2(g) \rightleftharpoons 2I(g) at 500 K.$ Initial conc of  $I_2$  is 0.45 M. What is [I] at equil?  $K_c = 5.6 \times 10^{-12}$ 

	$I_2(g) \rightleftharpoons$	2I (g)
[initial]	0.45 M	0
[change]	-X	+2x
[equil]	(0.45-x)	2x

 $K = 5.6 \times 10^{-12} = (2x)^{2} \approx (2x)^{2}$  because x <<< 0.45, since K is tiny (0.45 - x) 0.45Solving: x = 7.9 x 10<sup>-7</sup> Therefore, [I] = 2x = 1.6 x 10<sup>-6</sup> M

\*\* Rule of Thumb: if [initial] > 400 K, the approximation is valid \*\*



## Section 17.6. Le Chatelier's Principle.

If a system in equilibrium is disturbed, it will then adjust in a way that reduces the effect of the disturbance and returns to equilibrium.

(A) Change in Concentration (Note: this DOES NOT change  $K_c$  or  $K_p$ )

$$A + B \rightleftharpoons C + D$$
  $\therefore K_c = [C][D]$   
[A][B]

If [C] or [D] are increased (for example, by dissolving more C or D in a solution), the equilibrium is disturbed. The change in [C] or [D] causes  $Q \neq K$ , and the reaction adjusts to return to equilibrium. How? Since there is now too much [C] or [D], the reaction proceeds right-to-left until it is back to equilibrium.

i.e. if  $[D] \uparrow$  reaction proceeds right-to-left  $\therefore [D] \downarrow [C] \downarrow [A] \uparrow [B] \uparrow$ i.e. if  $[D] \downarrow$  reaction proceeds left-to-right  $\therefore [A] \downarrow [B] \downarrow [C] \uparrow [D] \uparrow$ 

<u>The reaction does what is necessary to recover from the disturbance,</u> <u>and re-establish equilibrium.</u>



### Figure 17.7 The effect of a change in concentration.

#### To predict how a reaction will respond:

(A) Consider how  $Q_c$  is affected by the disturbance, and compare to  $K_c$  or (B) See how the reaction "rolls"!!!





<u>To help us understand and remember this</u>, let's make up an example with convenient numbers. Consider the reaction:

 $A (aq) = B (aq) + C (aq) \text{ with } K_c = 100$ If [A] = 4.00M, [B] = 40.00M and [C] = 10.00M ∴ Q\_c = [B][C]/[A] = (40)(10)/4 = 100 Since Q\_c = K\_c, <u>the reaction is at equil.</u>

Now, let's add more C to make new [C] = 20M, i.e., we double [C]. New  $Q_c = (40.00)(20.00)/4.00 = 200 \neq K_c$ 

 $\therefore$  <u>reaction no longer at equilibrium</u>.  $Q_c > K_c \therefore$  reaction shifts to the left until it returns to equilibrium  $\therefore$  more A forms i.e. [A] $\uparrow$ , [B] $\downarrow$ and [C] $\downarrow$ 

When[A] = 4.00M[B] = 40.00M[C] = 20.00M $Q_c = 200 \neq K_c$ [A] = 5.00M[B] = 39.00M[C] = 19.00M $Q_c = 148 \neq K_c$ [A] = 5.50M[B] = 38.50M[C] = 18.50M $Q_c = 130 \neq K_c$ [A] = 6.00M[B] = 38.00M[C] = 18.00M $Q_c = 114 \neq K_c$ [A] = 6.30M[B] = 37.70M[C] = 17.70M $Q_c = 106 \neq K_c$ [A] = 6.50M[B] = 37.50M[C] = 17.50M $Q_c = 101 \neq K_c$ [A] = 6.55M[B] = 37.45M[C] = 17.45M $Q_c = 100 = K_c$ 

∴ reaction at equilibrium again, with new [A] = 6.55 M, new [B] = 37.45 M, new [C] = 17.55M (we started with [A] = 4.00M, [B] = 40.00M and [C] = 10.00M)

 $Q_c = [B][C]/[A] = (37.45)(17.55)/(6.55) = 100 = K_c$ 



### (B) Change in Pressure (Note: this DOES NOT change K<sub>p</sub>)

Consider three ways of changing pressure:

(i) change in p of one gas involved in the reaction: reaction responds as in (A)

(ii) <u>addition of an inert gas (one not involved in the reaction</u>): the total pressure (P) increases but the partial pressures (p) of the gases involved in the reaction stay the same  $\therefore$  no change to the equilibrium in any way because Q = K still.

(ii) <u>change in the volume of the vessel</u>: this changes the total pressure (P)  $\therefore$  the partial pressures (p) of the gases involved in the reaction also change  $\therefore$  the reaction proceeds in the direction that opposes this, but <u>only if the equilibrium has been disturbed and  $Q_p \neq K_p$ .</u>

e.g. consider volume decreased ( $\therefore$  P increased) in the following reactions

$N_2 + 3H_2 \Rightarrow 2NH_3$	$Q_{p} < K_{p}$ $\therefore$ reaction proceeds $L \rightarrow R$
$2O_3 \Rightarrow 3O_2$	$Q_n > K_n $ $\therefore$ reaction proceeds $R \rightarrow L$
$N_2 + O_2 \approx 2NO$	$Q_p^r = K_p^r \therefore$ no change

\*\* If number of moles of gas on the two sides of the equation is the same, changing the volume has no effect on the equilibrium. \*\*



# Figure 17.9 The effect of a change in pressure (volume) on a system at equilibrium.

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Shifts to left Increases moles of gas Shifts to right decreases moles of gas





# Sample Problem 17.13Predicting the Effect of a Change in Volume<br/>(Pressure) on the Equilibrium Position

**PROBLEM:** How would you change the volume of each of the following reactions to *increase* the yield of the products?

(a)  $CaCO_3(s) \iff CaO(s) + CO_2(g)$ 

**(b)** 
$$S(s) + 3F_2(g) \implies SF_6(g)$$

(c)  $\operatorname{Cl}_2(g) + \operatorname{I}_2(g) \Longrightarrow 2\operatorname{ICl}(g)$ 

**PLAN:** Whenever gases are present, a change in volume causes a change in concentration. For reactions in which the number of moles of gas changes, a decrease in volume (pressure increase) causes an equilibrium shift to lower the pressure by producing fewer moles of gas. A volume increase (pressure decrease) has the opposite effect.



(C) Change in Temperature (Note: this DOES change K)  $K = k_{fwd}/k_{rev}$  Since k's change with T, K also changes with T. Rule: (i) endothermic reactions ( $\Delta H^{\circ}$  positive); as T  $\uparrow$ , reaction L  $\rightarrow$  R, K  $\uparrow$ endothermic reactions ( $\Delta H^{\circ}$  positive); as  $T \downarrow$ , reaction  $R \rightarrow L$ ,  $K \downarrow$ (ii) exothermic reactions, ( $\Delta H^{\circ}$  negative); as T  $\downarrow$ , reaction L  $\rightarrow$  R, K  $\uparrow$ exothermic reactions, ( $\Delta H^{\circ}$  negative); as T  $\uparrow$ , reaction R  $\rightarrow$  L, K  $\downarrow$ **Proof**: think of heat as a component of the reaction (i) endothermic ( $\Delta H^{\circ}$  positive) A + heat = B As T  $\uparrow$ , heat  $\uparrow$  $\therefore$  reaction shifts  $L \rightarrow R$   $\therefore$  K gets bigger (ii) exothermic ( $\Delta H^{\circ}$  negative)  $A \Rightarrow B + heat$  As  $T \uparrow$ , heat  $\uparrow$  $\therefore$  reaction shifts  $R \rightarrow L$   $\therefore$  K gets smaller The van't Hoff Equation.

This tells us mathematically how the K is affected by changes in the temperature (T).  $\frac{\ln \frac{K_2}{K_1} = -\frac{\Delta H^{\circ}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$ 

\*\* This tells us how K changes from  $K_1$  to  $K_2$  on going from  $T_1$  to  $T_2$  \*\*

Note: (i) the change in K with T depends only on the ΔH° (= ΔH°<sub>rxn</sub>) (ii) the van't Hoff equation looks similar to the Arrhenius equation for the change in the rate constant k of a reaction as the T is changed (see Chapter 16).



Sample Problem 17.14

Predicting the Effect of a Change in Temperature on the Equilibrium Position

- **PROBLEM:** How does an *increase* in temperature affect the equilibrium concentration of the red substance and *K* for each of the following reactions?
  - (a)  $CaO(s) + H_2O(l) \implies Ca(OH)_2(aq) \quad \Delta H^\circ = -82 \text{ kJ}$
  - (b)  $CaCO_3(s) \implies CaO(s) + CO_2(g) \quad \Delta H^\circ = 178 \text{ kJ}$
  - (c)  $SO_2(g) \implies S(s) + O_2(g)$   $\Delta H^\circ = 297 \text{ kJ}$
  - (a) An increase in temperature will shift the reaction to the left, so [Ca(OH)<sub>2</sub>] and K will decrease.
  - (b) An increase in temperature will shift the reaction to the right, so [CO<sub>2</sub>] and K will increase.
  - (c) An increase in temperature will shift the reaction to the right, so [SO<sub>2</sub>] will decrease and K will increase.



(D) Addition of a Catalyst (Note: this does not change K)

Catalysts speed up the rates of reactions, but do not affect the equilibrium constant (K). Therefore, a catalyst will speed up the rate at which a reaction reaches equilibrium, but it will NOT affect the equilibrium position.

**Note**: the rates of reactions are affected by the activation energy barrier that must be overcome for the reaction to occur. We say the rates of reaction involve "KINETICS". The equilibrium constant (K) is not affected by activation energy barriers: it depends instead on thermodynamic quantities (such as  $\Delta H^{\circ}$ , and others ---- see later when we do chapter 20). We say the equilibrium constant involves "THERMODYNAMICS".

#### KINETICS controls reaction rates THERMODYNAMICS controls equilibrium position

Thus, a reaction  $A \rightarrow B$  might be very slow (i.e. slow kinetics) but it might still lie far to the side of product B (i.e. large K).

**\*\*** <u>Finally:</u> let us repeat one more time - the ONLY change that will alter the value of K is to change the temperature T. The other changes can affect the relative concentrations or pressures of the reactants and products, but they do NOT change the value of K. See **Table 17.4 \*\*** 



## Table 17.4Effects of Various Disturbances on a System at<br/>Equilibrium

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Disturbance	Effect on Equilibrium Position	Effect on Value of <i>K</i>
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase P (decrease V)	Toward formation of fewer moles of gas	None
Decrease P (increase V)	Toward formation of more moles of gas	None
Increase P (add inert gas, no change in V)	None; concentrations unchanged	None
Temperature		
Increase T	Toward absorption of heat	Increases if $\Delta H^{\circ}_{rxn} > 0$ Decreases if $\Delta H^{\circ}_{rxn} < 0$
Decrease T	Toward release of heat	Increases if $\Delta H^{\circ}_{rxn} < 0$ Decreases if $\Delta H^{\circ}_{rxn} > 0$
Catalyst added	None; forward and reverse rates increase equally; equilibrium attained sooner	None

