Chapter 16

Principles of Reactivity: Chemical Equilibria

OWL Homework Due: 2/26/2008 at 11:50 pm

OWL Quiz Due: 3/2/2008 at 11:50 p.m.

Some Slides Courtesy of Dr. Maria Benavides!

Chemical Equilibrium

Old Chemists Never Die; they just reach

EQUILIBRIUM!

All physical and chemical changes TEND toward a state of equilibrium.

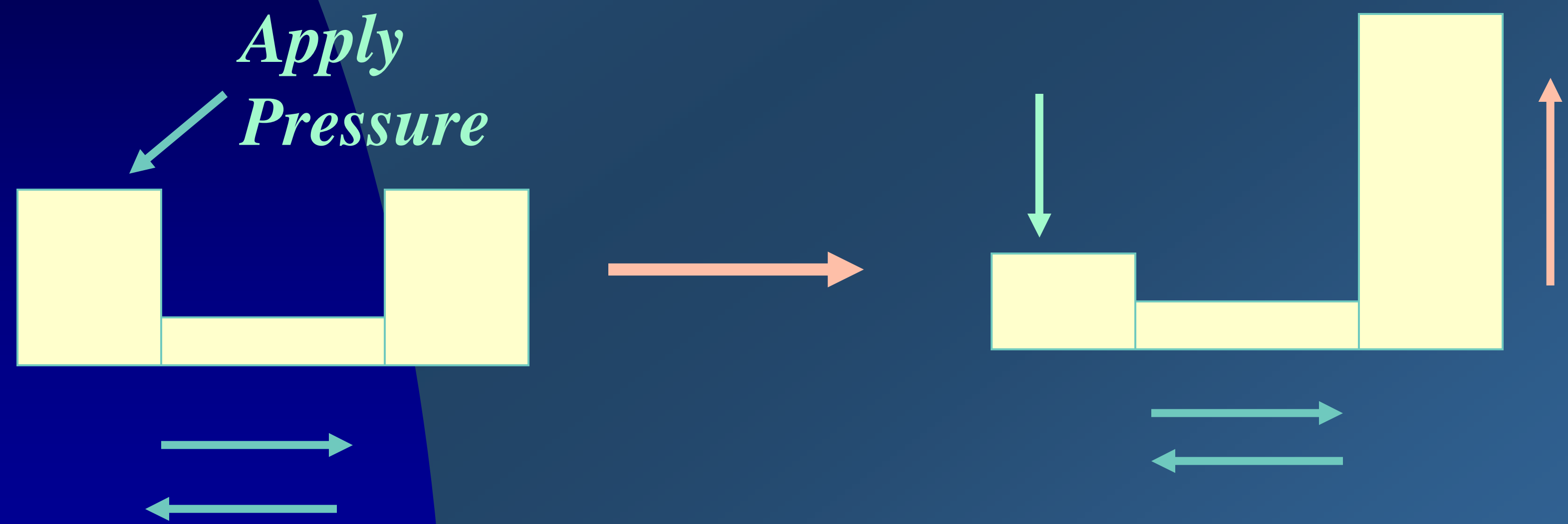
$$A\,(l) \rightleftharpoons A\,(g)$$

$$A\,(s) \rightleftharpoons A\,(l)$$

Dynamic Equilibrium

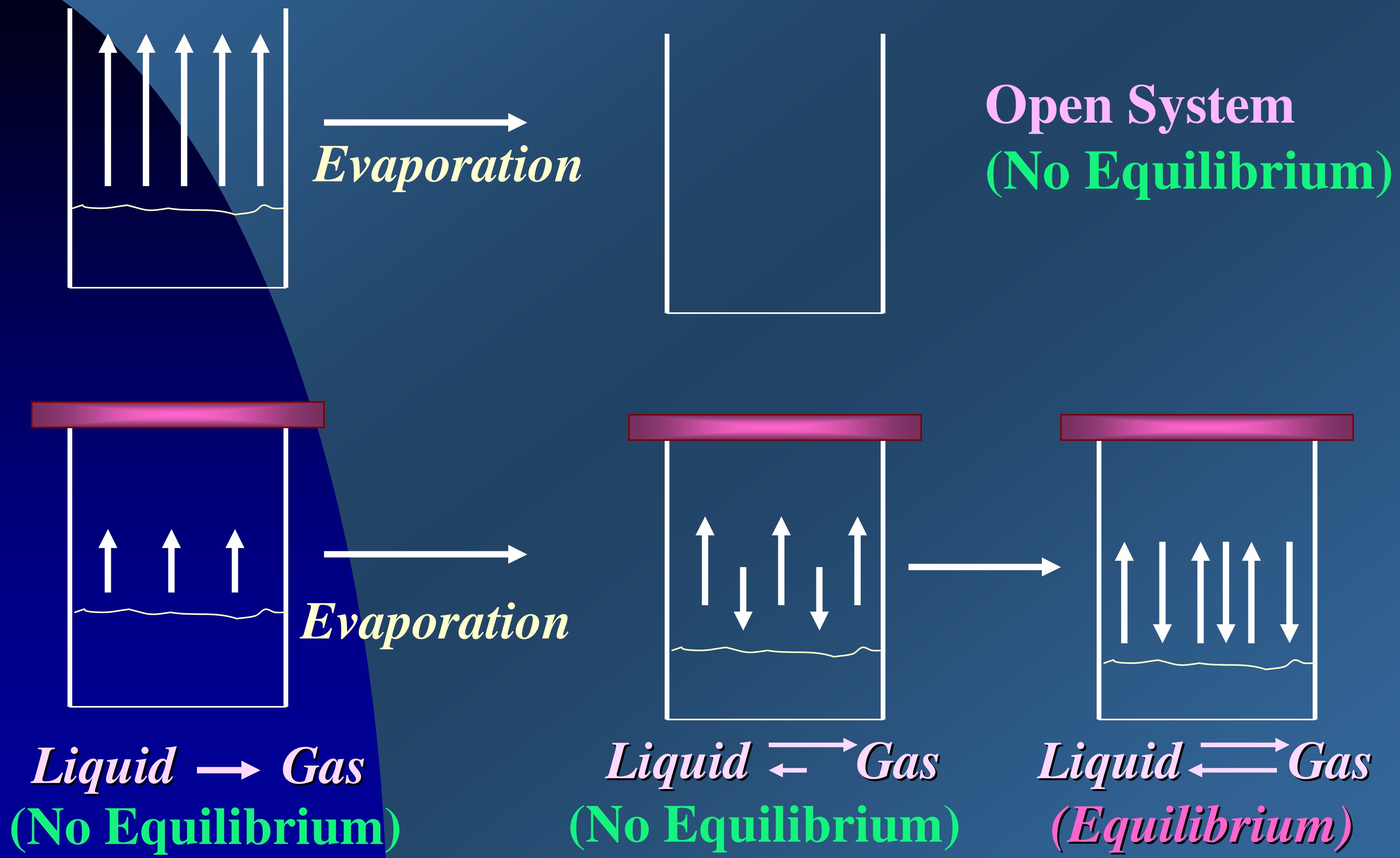
The net result of a dynamic equilibrium is that no change in the system is evident.

Le Chatelier's Principle - ***If a change is made in a system at equilibrium, the equilibrium will shift in such a way so as to reduce the effect of the change.***



Pressure applied to the system at equilibrium caused it to shift until a new equilibrium was established.

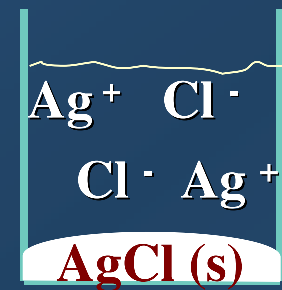
Dynamic Equilibrium



Dynamic Equilibrium

$$Ag^{+} + Cl^{-} \rightleftharpoons AgCl\ (s)$$

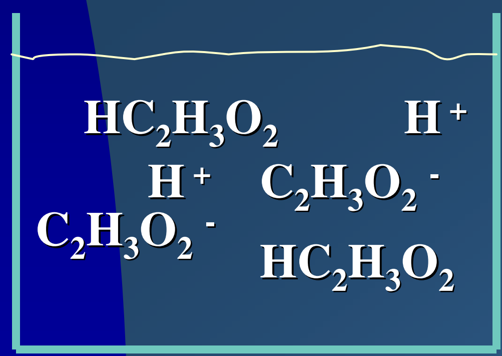
Chemical Equilibrium



Rate of Precipitation = Rate of Dissolving

$$HC_2H_3O_2\ (aq) \rightleftharpoons H^{+} + C_2H_3O_2^{\ -}$$

Rate of dissociation (ionization) = Rate of Association



CHEM 1108 Lab Experiment

Orange — Red

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Blue — Pink

$$[CoCl_4]^{2-} + 6\ H_2O\ (l) \rightleftharpoons Co(H_2O)_6^{2+} + 4\ Cl^-$$

White — Colorless Solution

$$NH_4Cl\ (s) \rightleftharpoons NH_4^+ + Cl^-$$

You can actually "see" the equilibrium shift!

Reversible Reactions

$$N_2O_4\,(g) \xrightarrow{R_1} 2\,NO_2\,(g)$$

$$2\,NO_2\,(g) \xleftarrow{R_2} N_2O_4\,(g)$$

$$N_2O_4\,(g) \underset{R_2}{\overset{R_1}{\rightleftharpoons}} 2\,NO_2\,(g) \qquad [R_1 = R_2]$$

Homogeneous Equilibrium

Reversible Reactions

	$[N_2O_4]_i$	$[NO_2]_i$	$[N_2O_4]_{eq}$	$[NO_2]_{eq}$
Exp. 1	0.0250 M	0.0 M	0.0202 M	0.009 66 M
Exp. 2	0.0150 M	0.0125 M	0.0146 M	0.008 23 M
Exp. 3	0.0 M	0.0250 M	0.0923 M	0.006 54 M

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Reaction Quotient

$$Q_C = \frac{[NO_2]^2}{[N_2O_4]}$$

Equilibrium Constant

$$K_C = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$$

Equilibrium Constants

Equilibrium Constant **- When the rates of the forward and reverse reactions are equal, the system is "at equilibrium" and the reaction quotient = equilibrium constant.**

Experiment 1 $K_C = [0.009\ 66]^2/[0.0202] = 0.004\ 62\ M$

Experiment 2 $K_C = [0.008\ 23]^2/[0.0146] = 0.004\ 64\ M$

Experiment 3 $K_C = [0.006\ 54]^2/[0.009\ 23] = 0.004\ 63\ M$

$$aA + bB \rightleftharpoons cC + dD$$

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

Equilibrium Constants

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

$$Q_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_C = \frac{[HI]^2_{eq}}{[H_2]_{eq}[I_2]_{eq}}$$

Exp.	$[H_2]_{eq}$	$[I_2]_{eq}$	$[HI]_{eq}$	K_C
1	0.00291	0.00171	0.01648	54.58
2	0.00356	0.00125	0.01559	54.62
3	0.00225	0.00234	0.01685	53.93
4	0.00183	0.00313	0.01767	54.51
5	0.00114	0.00114	0.00841	54.42
6	0.00050	0.00050	0.00366	53.58

Median K_C = 54.47

Equilibrium Constants

$$4\ NH_3\ (g)\ +\ 3\ O_2\ (g) \rightleftharpoons 2\ N_2\ (g)\ +\ 6\ H_2O\ (g)$$

$$Q_C = \frac{[NH_3]^4[O_2]^3}{[N_2]^2[H_2O]^6}$$

$$K_C = \frac{[NH_3]_{eq}{}^4[O_2]_{eq}{}^3}{[N_2]_{eq}{}^2[H_2O]_{eq}{}^6}$$

Reaction Quotient vs. Equilibrium Constant

$Q_C < K_C$

$Q_C = K_C$

$Q_C > K_C$

Reaction Quotient vs. Equilibrium Constant

Class Problem 16.1 - *The concentration of N_2O_4 = concentration of NO_2 = 0.0125 M in a reaction vessel. The equilibrium constant for N_2O_4 (g) = 2 NO_2 (g) is 0.004 63. Calculate Q_C and state which direction the reaction will go.*

Class Problem 16.2 - *If $[O_2]$ = 0.21 M and $[O_3]$ = 6.0×10^{-8} M, what is the value of the K_C for the equilibrium, 2 O_3 (g) = 3 O_2 (g)?*

Chemical Equilibrium

Heterogeneous Reaction - *A reaction that takes place in more than one phase or state. These reactions occur at the interface between phases - on the surface of liquids and solids.*

At a constant temperature, the concentration of a solid or liquid component remains constant in a heterogeneous equilibrium. ***WHY?***

Since the concentration is constant, it can be considered a part of the equilibrium constant and, thus, does NOT appear in the K_C expression.

$$C\ (s,\ graphite) + CO_2\ (g) = 2\ CO\ (g)$$

$$K_C = \frac{[CO]^2}{[C][CO_2]} \qquad K_{eq} = \frac{[CO]^2}{[CO_2]}$$

Chemical Equilibrium

Class Problem 16.3 - ***A mixture that was initially 0.005 00 M in H_2 (g) and 0.012 50 M in I_2 (g), and contained no HI (g), was heated at 425.4°C until equilibrium was reached. The resulting equilibrium concentration of I_2 (g) was found to be 0.007 72 M. What is the value of the K_C for this equilibrium at 425.4°C?***

Construct an "ICE" Table:

			425.4°C	
Equation:	H_2 (g)	+ I_2 (g)	→	2 HI (g)
Initial (I) conc., M	0.005 00	0.012 50		0.000 00
Change (C) in conc., M	- 0.004 78	- 0.004 78		+ 0.009 56
Equil. (E) conc., M	- 0.000 22	0.007 72		+ 0.009 56

Chemical Equilibrium

Calculate K_C:

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.009\ 56)^2}{(0.000\ 22)(0.007\ 72)} = 54$$

Class Problem 17.4 - *When 1.000 mol each of H_2O (g) and CO (g) are introduced into an empty 1.000 L vessel at 959 K and allowed to come to equilibrium, the equilibrium mixture contains 0.422 mol H_2O (g). Find K_C for*

$$H_2O\ (g) + CO\ (g) \rightarrow H_2\ (g) + CO_2\ (g)$$

Construct an "ICE" Table……………..→

Chemical Equilibrium

959°C

Equation:	H_2O (g)	+ CO (g)	→ H_2 (g)	+ CO_2 (g)
I	1.000	1.000	0.000	0.000
C	- 0.578	- 0.578	+ 0.578	+ 0.578
E	0.422	0.422	0.578	0.578

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{(0.578)^2}{(0.422)^2} = 1.88$$

Class Problem 16.4 - *Suppose that $[H_2O]_I$ = 2.00 M and $[CO]_I$ = 4.00 M? What are the equilibrium concentrations of the four species?*

Chemical Equilibrium

959°C

Equation:	H_2O (g)	+ CO (g)	→ H_2 (g)	+ CO_2 (g)
I	2.00	4.00	0.00	0.00
C	- x	- x	+ x	+ x
E	2.00 - x	4.00 - x	x	x

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = 1.88 = \frac{x^2}{(2.00-x)(4.00-x)}$$

How are your algebra skills now??

$$x^2 = 1.88\ (2.00 - x)(4.00 - x) = 1.88\ (8.00 - 6x + x^2)$$

$$x^2 = 15.0 - 11.3\ x + 1.88\ x^2$$

$$0 = 0.88\,x^2 - 11.3\,x + 15.0 \quad (ax^2 + bx + c)$$

Dust off the old Quadratic Formula:

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

http://www.freemathhelp.com/algebra-help.html

$$\frac{-(-11.3) \pm [(-11.3)^2 - 4(0.88)(15.0)]^{1/2}}{2(0.88)}$$

= **11 *and* 1.5 !** *Which is RIGHT?*

Chemical Equilibrium

					959°C
Equation:	H_2O (g) +	CO (g)	→	H_2 (g) +	CO_2 (g)
I	2.00	4.00		0.00	0.00
C	- x	- x		+ x	+ x
E	2.00 - x	4.00 - x		x	x

What is 'x'? It is the equilibrium concentration of H_2 and CO_2 at equilibrium! But…you can't have more hydrogen gas than you have of reactants to begin with!

Thus, 11 M can't be right!

1.5 M is the only sensible answer!

Chemical Equilibrium

What if you don't remember the quadratic formula???

You can then use……………

Successive Approximation!