CHAPTER 14 CHEMICAL EQUILIBRIUM

MANY REACTIONS DO NOT COMPLETELY GO TO PRODUCTS

INSTEAD, PRODUCTS RE-REACT TO FORM REACTANTS

THESE REACTIONS ARE REVERSIBLE

FOR EXAMPLE

$$CO(g) + 3H_2(g) \underset{CAT}{\overset{CAT}{\rightleftharpoons}} CH_4(g) + H_2O$$

THESE ARE IMPORTANT REACTIONS IN COAL GASIFICATION

CHEMICAL EQUILIBRIUM (DYNAMIC EQUILIBRIUM) IS A STATE REACHED BY A REACTION MIXTURE WHEN THE RATES OF FORWARD AND REVERSE REACTIONS ARE EQUAL

INITIALLY, THE FORWARD REACTION WILL BE FAST AND THE REVERSE REACTION SLOW.

AFTER SOME TIME; EQUILIBRIUM WILL BE REACHED

STOICHIOMETRY CAN BE APPLIED TO THE EQUILIBRIUM MIXTURE

EX. INITIALLY, 1 MOLE OF CO AND 3 MOLES H_2 ARE PLACED IN A REACTION VESSEL. AT EQUILIBRIUM, 0.387 MOLES H_2O ARE PRESENT. WHAT IS THE MOLAR COMPOSITION OF THE EQUILIBRIUM MIXTURE?

AMOUNT (MOLES)	CO	+ $3H_2$	$\rightleftharpoons$ CH_4	+ H_2O
START	1.000	3.000	0	0
CHANGE	−.387		+ 0.387	+ 0.387
EQUILIBRIUM	0.613	1.84	0.387	+ 0.387

THE EQUILIBRIUM CONSTANT

THE AMOUNT OF EACH SUBSTANCE PRESENT IN THE EQUILIBRIUM DEPENDS ON THE INITIAL AMOUNT OF REACTANTS.

THE RELATIVE AMOUNTS OF EACH SUBSTANCE PRESENT ARE RELATED BY THE EQUILIBRIUM CONSTANT.

IN GENERAL:

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

where: A, B, C and D are reactants and products

and: a, b, c, d are coefficents in the balanced reaction

THE EQUILIBRIUM CONSTANT K_c IS AN EXPRESSION OBTAINED BY MULTIPLYING THE CONCENTRATIONS OF PRODUCTS, DIVIDING BY THE CONCENTRATIONS OF REACTANTS, AND RAISING EACH TERM TO A POWER EQUAL TO THE COEFFICIENT IN THE CHEMICAL EQUATION

$$K_c = \frac{[\;]\;[\;]}{[A]^a\,[B]^b}$$

THE LAW OF MASS ACTION STATES THAT THE VALUES OF THE EQUILIBRIUM-CONSTANT EXPRESSION K_c ARE CONSTANT FOR A PARTICULAR REACTION AT A GIVEN TEMPERATURE, WHATEVER EQUILIBRIUM CONCENTRATIONS ARE SUBSTITUTED

FOR THE COAL GASIFICATION REACTION

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

EXAMPLES

WRITE EQUILIBRIUM CONSTANT EXPRESSION

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

$$K_c =$$

WRITE BALANCED EQUATION

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

THE KINETICS ARGUMENT FOR EQUILIBRIUM CONSTANTS

$$A \rightarrow B$$

$$rate = k_F[A]$$ $K_F = K_{FORWARD}$

$$B \rightarrow A$$

$$rate = k_R[B]$$ $K_R = K_{REVERSE}$

AT EQUILIBRIUM $K_F = K_R$

$$K_F[A] = K_R[B]$$ DIVIDE BY K_R AND $[A]$

$$\frac{K_F}{K_R} = \frac{[B]}{[A]} = K_c$$

$$K_c = \frac{K_F}{K_R}$$

THE EQUILIBRIUM CONSTANT IS THE RATIO OF RATE CONSTANTS

EQUILIBRIUM CONSTANTS FOR THE SUM OF REACTIONS

DEFINITION:

IF A GIVEN CHEMICAL EQUATION CAN BE OBTAINED BY TAKING THE <u>SUM</u> OF OTHER EQUATIONS, THE EQUILIBRIUM CONSTANT FOR THE GIVEN EQUATION EQUALS THE <u>PRODUCT</u> OF THE EQUILIBRIUM CONSTANTS OF THE OTHER EQUATIONS

EXAMPLE:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad K_1 = 3.92$$

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g) \quad K_2 = 3.3 \times 10^4$$

SUM

$$CO_g + 2H_2S_g \rightleftharpoons CS_2(g) + H_2(g) + H_2O(g) \quad K_3 = K_1 \times K_2$$

$$K_1 = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \qquad K_2 = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

$$K_1 \times K_2 = \frac{\cancel{[CH_4]}[H_2O]}{[CO]\cancel{[H_2]^3}} \times \frac{[CS_2][H_2]^{\cancel{4}}}{\cancel{[CH_4]}[H_2S]^2}$$

$$K_1 \times K_2 = \frac{[H_2O][CS_2][H_2]}{[CO][H_2S]^2}$$

THIS IS THE EQUILIBRIUM EXPRESSION FOR THE OVERALL REACTION

MODIFYING K_c

1) IF A REACTION IS REVERSED, K_c FOR THE REVERSE REACTION IS THE INVERSE OF K_c FOR THE FORWARD REACTION

$$K_F = \frac{1}{K_R} \quad \text{OR} \quad K_R = \frac{1}{K_F}$$

2) IF THE COEFFICIENTS OF A CHEMICAL EQUATION ARE MULTIPLIED BY A FACTOR N, OBTAIN THE NEW K_c BY RAISING THE ORIGINAL K_c TO THE POWER N

EXAMPLE

$$2A + B \rightleftharpoons A_2B \quad K_c = 1 \times 10^{10}$$

MULTIPLY COEFFICIENTS BY ½

$$A + \tfrac{1}{2}B \rightleftharpoons \tfrac{1}{2}A_2B \quad K_c = (1 \times 10^{10})^{1/2} \text{ OR } 1 \times 10^5$$

3) K_p IS RELATED TO K_c BY:

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

WHERE ΔN = THE CHANGE IN THE NUMBER OF MOLES OF GAS

4) K_c FOR THE SUM OF REACTIONS IS EQUAL TO THE PRODUCT OF EACH REACTIONS K_c

5) REMEMBER THAT THE RATE OF A REACTION IS NOT ALWAYS RELATED TO K_c

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \quad K = 10^{83}$$

BUT....

THE MIXTURE OF GASSES REACTS QUITE SLOWLY (KINETIC CONTROL) UNLESS A SPARK IS APPLIED AND AN EXPLOSION RESULTS (THERMODYNAMIC CONTROL)

EXAMPLE OF CALCULATING K_c FROM EQUILIBRIUM CONCENTRATIONS

FOR THE REACTION:

$$2\,NOBr_{(g)} \rightleftharpoons 2\,NO_{(g)} + Br_2(g)$$

IF 2.00 moles NOBr IN A 1L FLASK 9.4% OF NOBr DISSOCIATES INTO PRODUCTS. CALCULATE K_c

	NOBr	NO	Br_2
INITIAL	2.00	0	0
CHANGE	−0.188	+.188	+0.094
FINAL	1.812	0.188	0.094

$.094 \times 2.00 = 0.188$

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

$$K_c = \frac{0.188^2 \times 0.094}{1.812^2}$$

$$K_c = \frac{.00332}{3.283} = 0.00101$$

$$K_c = 1.01 \times 10^{-3}$$

IF REACTANTS AND PRODUCTS EXIST IN MORE THAN 1 PHASE, (IF THERE IS A <u>PURE</u> SOLID OR LIQUID PRESENT) IN A GAS PHASE REACTION, THE REACTION IS CALLED HETEROGENEOUS.

THE "CONCENTRATION" OF A PURE SOLID OR LIQUID IS DEFINED AS EQUAL TO <u>ONE</u>. THEREFORE, THESE TERMS ARE <u>OMITTED</u> FROM THE EQUILIBRIUM CONSTANT EXPRESSION

EXAMPLE:

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4\,(s)} + 4H_{2\,(g)}$$

$$K_c = \frac{[H_2]^4}{[H_2O]^4}$$

THIS IS BECAUSE THE "CONCENTRATION" OF THE SOLIDS REMAINS CONSTANT

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

$$K_c =$$

USING THE EQUILIBRIUM CONSTANT

SOME EASY AND USEFUL APPLICATIONS OF K_c

1) QUALITATIVE USE

SIMPLY LOOKING AT THE MAGNITUDE OF K_c TELLS IF PRODUCTS OR REACTANTS ARE FAVORED

2) PREDICTING THE DIRECTION NON-EQUILIBRIUM MIXTURES WILL TAKE

3) CALCULATING EQUILIBRIUM CONCENTRATIONS

QUALITATIVE USE OF K_c

IF K_c IS LARGE, PRODUCTS ARE FAVORED

IF K_c IS SMALL, REACTANTS ARE FAVORED

IF K_c IS NEAR 1, NEITHER ARE FAVORED

EXAMPLE: K_c IS LARGE

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

AT 25°C $K_c = 4.1 \times 10^8$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

← NUMERATOR IS 4.1×10^8 LARGER THAN DENOMINATOR

IF $[N_2] = 0.01\,M$

$[H_2] = 0.01\,M$

SUBSTITUTE INTO EQUILIBRIUM EXPRESSION

$$4.1 \times 10^8 = \frac{x^2}{0.01 \times 0.01^3} = \frac{x^2}{1 \times 10^{-8}}$$

$$[NH_3]^2 = 4.1$$

$[NH_3] = 2\,M$; 200 TIMES GREATER THAN 0.01 M

EXAMPLE: K_c IS SMALL

$$N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$$

AT 25°C $K_c = 4.6 \times 10^{-31}$

IF $[N_2] = 1\,M$

$[O_2] = 1\,M$

DO PROBLEM 14.44

SUBSTITUTE INTO EQUILIBRIUM EXPRESSION

$$4.6 \times 10^{-31} = \frac{[NO]^2}{1 \times 1}$$

$[NO]^2 = 4.6 \times 10^{-31}$ $[NO] = 6.8 \times 10^{-16}$