Equilibrium Calculations Continued

Heterogeneous Equilibrium

Solid ammonium hydrogen sulfide, NH_4HS, dissociates appreciably even at room temperature forming ammonia, NH_3, and hydrogen sulfide, H_2S, gases. What is the total pressure at equilibrium if solid NH_4HS is placed in an evacuated container and allowed to reach equilibrium? $K_P = 0.108$ at 25ºC.

	$NH_4HS(s)$	⇔	$NH_3(g)$	+	$H_2S(g)$
I	X		0		0
C			+x		+x
E			x		x

$K_P = P_{NH3} * P_{H2S}$
$0.108 = x * x$
$x^2 = 0.108$
$x = 0.329$ atm

$P_{TOTAL} = P_{NH3} + P_{H2S} = 0.329 \text{ atm} + 0.329 \text{ atm} = 0.658 \text{ atm}$

Check:
$K_P = P_{NH3} * P_{H2S} = (0.329 \text{ atm})(0.329 \text{ atm}) = 0.108 \text{ atm}^2$ √

Predicting Direction using the reaction quotient, Q_C

For the reaction:
$H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$ $K_C = 57.0$ at 700 K

If a flask contains 0.10M H_2, 0.20M I_2, and 0.40M HI, is the system at equilibrium? If not, in which direction with the reaction proceed?

Set up the reaction quotient and calculate the value at the conditions provided.
If the value of $\mathbf{Q_C = K_C}$, then the system is **at equilibrium**.
If the value of $\mathbf{Q_C > K_C}$, the ratio of products to reactants is too high so the system must react so that **R <- P** in order to attain equilibrium.
If the value of $\mathbf{Q_C < K_C}$, the ratio of products to reactants is too low so the system must react so that **R -> P** in order to attain equilibrium.

$$Q_C = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(0.40M)^2}{(0.10M)(0.20M)} = 8.0$$

Since 8.0 < 57.0, the system is no at equilibrium and there are too few products so reaction will proceed towards products (R-> P).

Example:

At 700K, the K_C for the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ is 0.291. Determine the equilibrium concentrations if 2.00×10^{-2}M N_2, 1.00M H_2, and 3.00×10^{-1}M NH_3 are initial present in the container.

	$N_2(g)$	+	$3H_2(g)$	$\Leftrightarrow$	$2NH_3(g)$
I	0.0200M		1.00M		0.300M
C	?		?		?
E					

Since both reactant and product concentrations are initially present, which way will the reaction proceed in order to attain equilibrium?

Use the reaction quotient to determine the direction.

$$Q_C = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(0.300M)^2}{(0.0200M)(1.00M)^3} = 4.5M^{-2}$$

Since $4.5 > 0.291$ then $Q_C > K$ and the reaction will proceed toward the reactants side to attain equilibrium.

	$N_2(g)$	+	$3H_2(g)$	$\Leftrightarrow$	$2NH_3(g)$
I	0.0200M		1.00M		0.300M
C	+x		+3x		–2x
E	0.200+x		1.00+3x		0.300–2x

$$K_C = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(0.300 - 2x)^2}{(0.0200 + x)(1.00M + 3x)^3} = 0.291$$

$$0 = \frac{(0.300 - 2x)^2}{(0.0200 + x)(1.00M + 3x)^3} - 0.291$$

$Y = \text{Screen}$

$$Y_1 = \frac{(0.300 - 2x)^2}{(0.0200 + x)(1.00M + 3x)^3} - 0.291$$

$Y_2 = 0$

Solve for the intersect point (which is the same as solving for root of the equation. The window range must be Xmin=0 to Xmax=0.15. Why?

Answer:
x = 0.0561M

Equilibrium Values:
$[NH_3]$ = 0.300 –2x = 0.300M – 2(0.0561M) = 0.188M
$[N_2]$ = 0.0200+x = 0.0200M + 0.0561M = 0.0761M
$[H_2]$ = 1.00+3x = 1.00M + 3(0.0561M) = 1.17M

Check:

$$K_C = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(0.188M)^2}{(0.761M)(1.17M)^3} = 0.290M^{-2}$$

LeChatelier's Principle

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in the direction that relieves the stress.

Example:
Isopropyl alcohol, $(CH_3)_2CHOH$, decomposes in the gas phase at 400°C releasing acetone, $(CH_3)_2CO$, and hydrogen. The enthalpy of the reaction is 57.3 kJ per mole isopropyl alcohol.

Reaction: $(CH_3)_2CHOH(g) \Leftrightarrow (CH_3)_2CO(g) + H_2(g)$

Does the amount of acetone product **increase**, **decrease**, or **remain constant** when the following changes occur?

(A) increase in temperature	Favors endothermic reaction which is toward products.
(B) increase in volume	When volume increases, pressure decreases –favoring side with more particles (toward products).
(C) argon gas added	Pressure increases but no change in concentration of reactant or product occurs – no effect.
(D) H_2 added	With addition of product (increase concentration), reaction shifts toward reactants.
(E) Catalyst added	No change since both forward and reverse reactions are affected equally.