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11:39 AM

Chapter 17
Equilibrium: The extent of Chemical Reactions

Homework:12,16,18,19,25,29,31,35,36,41,4548,53,55,63,64,65,67,71,74, 81,98,107

Describing Chemical Equilibrium

Chemical equilibrium occurs when the forward rate of a reaction is equal to the reverse rate of the reaction. Consider the following equilibrium reaction :

$aA + bB \leftrightarrow cC + dD$

The forward rate is given by:

$rate_f = k_f[A]^a[B]^b$

and the reverse rate is given by:

$rate_r = k_r[C]^c[D]^d$

Setting these two rates equal you get:

$k_f[A]^a[B]^b = k_r[C]^c[D]^d$

Solving for the ratio of the constants you get:

$k_f/k_r = [C]^c[D]^d/[A]^a[B]^b$

$K = [C]^c[D]^d/[A]^a[B]^b$ or simply $K= [Products]^x/[reactants]^y$

where the ratio k_f/k_r is called the equilibrium constant and can be given any of several names:

- K_a Equilibrium constant for an acid
- K_b Equilibrium constant for a base
- K_{eq} Equilibrium constant for a general reaction equation
- K_{sp} Solubility product (Note: does not include reactant concentration)
- $K_{diss.}$ Dissociation Equilibrium constant

Just to name a few. But don't despair!! They are conceptually the same thing that is:

$K_{whatever} = [Products]^x/[reactants]^y$

where x and y are the coefficients of the reactants and products in the balanced chemical equation.

Problem:

For the reaction $H_2 + I_2 \leftrightarrow 2HI$, the equilibrium concentrations at 490°C are .0862M H_2 , .263 M I_2 and 1.02 M HI.

a) What is the equilibrium constant for the reaction.

b) If 1 mole of H_2 and 1 mole of I_2 are introduced into a 1-liter container at 490°C, what are the concentrations of each substance at equilibrium

Problem:

Consider the Haber process: $N_2 + 3H_2 \leftrightarrow 2NH_3$, show graph of changing

concentrations of each species assuming stoichiometric amounts.

Write the equilibrium constant for the reaction.
Equilibrium constants are sometimes expressed in terms of pressure for gaseous reactions. The relation between K_p and K_c can be derived from the ideal gas equation if we assume that the gases in the reaction behave ideally.
$PV = nRT \implies P = (n/V)RT = MRT$ therefore: $K_p = K_c(RT)^{\Delta n}$
where: Δn = moles gaseous products - moles gaseous reactants
Problem: At 20°C the equilibrium constant for the formation of ammonia is $2.37 \times 10^{-3}\ M^{-2}$.
a) If 1.00 moles of NH_3 is placed in a 1 liter container, what are the final concentrations of each substance.
b) What is the final pressure?
c) What is the final pressure of each constituent?
d) What is the K_p.

LeChâtelier's Principle:

If a stress is placed upon a system in equilibrium, the system will shift in such a way as to reduce the stress.
Problem:
Consider the reaction: $H_2 + I_2 \leftrightarrow 2HI$ at 490°C. See previous problem for K_c. At equilibrium $[H_2] = .5M$, $[I_2] = .2M$
a) What is the [HI]?
b) If the concentration of H_2 is instantly increased to 1 M, in which direction will the reaction shift?
c) After the increase in $[H_2]$ to 1 M, what are the final concentrations of each substance?
d) Suppose that in the above equilibrium, the concentration of I_2 is reduced; in which direction will the reaction shift?
e) Suppose that in the above equilibrium, the concentration of HI is reduced; in which direction will the reaction shift?
f) In which direction will the reaction shift if the pressure is increased?
g) What will happen if a nickel catalyst is added to the reaction vessel?

Problem:
Consider the equilibrium reaction: $3H_2 + N_2 \leftrightarrow 2\ NH_3 + \text{heat}$
a) In which direction will the reaction shift if the pressure is increased?
b) If the system at equilibrium is heated, in which direction will the reaction shift?

Heterogeneous Equilibrium

Equilibrium reactions can involve a system that is not homogeneous i.e.

where one or more of the reactants and /or products are in different phases. Consider the reaction:

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

What is the equilibrium expression for the above reaction.

Problem:

At 20°C what is the equilibrium constant (K_c) for the vaporization of water.

Effect of Temperature on Equilibrium Constant: The van't Hoff Equation

Just as temperature affects the rate of a chemical reaction, temperature also affects the position of an equilibrium and hence the equilibrium constant. The van't Hoff equation describes how the equilibrium constant varies with temperature.

$\ln(K_2/K_1) = (-\Delta H^o_{rxn}/R) \times (1/T_2 - 1/T_1)$

Exothermic	Endothermic	Isothermic
K decreases with increasing temperature. Reaction shifts left.	K increases with increasing temperature Reaction shifts right.	K remains constant with increasing temperature. No shift.

Problem:

What can the van't Hoff equation be used to find?

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