5.111 Lecture Summary #19 **Friday, October 24, 2014**

Reading for Today: Sections 10.9-10.13 (Sections 9.9-9.13 in 4th ed.)
Reading for Lecture #20: Sections 9.8 - 9.13 (8.8-8.13 same in 4th ed.) on solubility; Sections 11.1 – 11.2, 11.4-11.6 (10.1-10.2, 10.4-10.6 in 4th ed.) on acids and bases.

Topics: I. External effects on K (Le Châtelier's Principle) continued
II. Temperature dependence of K
III. Applications of Le Le Châtelier's Principle
IV. Sig figs for logs

I. EXTERNAL EFFECTS ON K (LE CHÂTELIER'S PRINCIPLE) CONTINUED

A. CHANGING THE VOLUME OF A GASEOUS SYSTEM

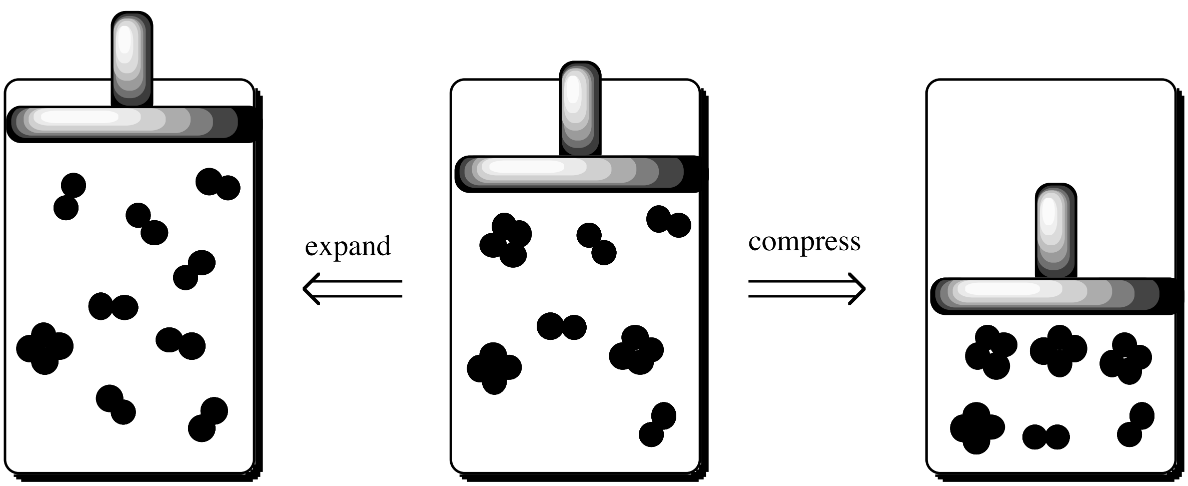
A decrease in the volume of a gaseous system causes an ___________________ in the total pressure.

IDEAL GAS LAW ______________________ where P is pressure, V is Volume,

T is temperature , n is ___________________ , R is the ideal gas constant.

Le Châtelier's principle predicts that the system would respond, if possible, in such a way as to **reduce** the total pressure.

Example $2P_2$ **(g)** $\rightleftharpoons$ P_4 **(g)**



i) A **decrease** in volume shifts the reaction to the right (toward product).

This change occurs because for every 2 molecules of P_2 consumed only 1 molecule of P_4 is formed.

A shift to the right **reduces** the total pressure, partially compensating for the external stress of the volume change.

Now consider in terms of Q and K.
Suppose the volume is decreased by a factor of 2 at constant temperature.
This change will increase the partial pressure of P_2 by 2 and of P_4 by 2, initially.

$$Q = \frac{P_{P_4}}{(P_{P_2})^2} = \frac{2}{2^2} = \frac{1}{2}$$

Q decreases by a factor of 2, and Q < K. ΔG is ____________________.

Reaction proceeds in forward direction (toward products) until Q=K again.

ii) An **increase** in volume shifts the reaction to the left (**toward reactants**).

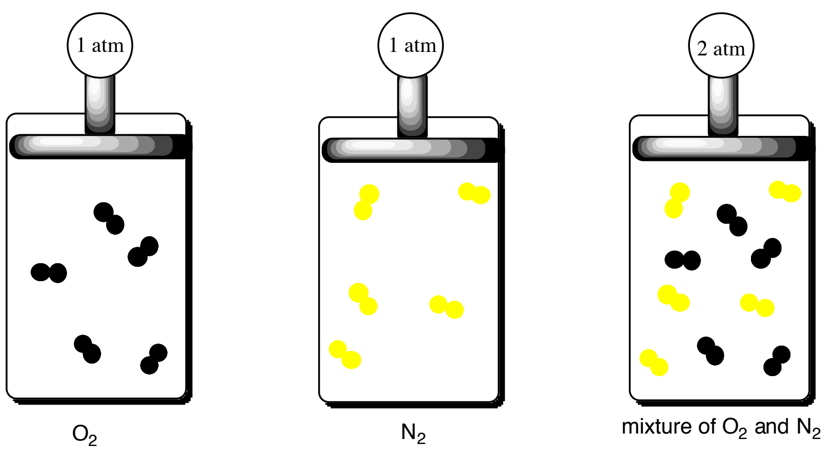
For every one molecule of P_4 that is consumed, _______ molecules of P_2 are formed.
Thus a shift of the reaction toward reactants, increases the total pressure.

B. ADDING INERT GAS

Case 1) For $2P_2\ (g) \rightleftharpoons P_4$, what happens if an inert gas is added to the container increasing the total pressure at constant temperature?

Answer: ____ Why?
Q depends on the partial pressure of P_2 and P_4 gases and the partial pressures do not change here.

Review Partial Pressure: The partial pressure is the pressure that each gas would exert if it alone were present in the container.



$$P_A = n_A \frac{RT}{V}$$

$$P_{tot} = P_A + P_B + P_C + etc = (n_A + n_B + n_C + etc) \frac{RT}{V} = n_{tot} \frac{RT}{V}$$

When the total pressure increases due to the addition of an inert gas, the partial pressure of each gas is unchanged. When the partial pressure is the same, Q doesn't change. When Q doesn't change, there is no shift.

Case 2) For $2P_2\ (g) \rightleftharpoons P_4\ (g)$, what happens if an inert gas is added to the container but the total pressure and temperature are kept constant?

Answer: the reaction ____

For the pressure to be kept constant, the ____________________ of the container must have increased. And when ____________________ **increases**, partial pressures **decrease**, causing this reaction to ________________________.

C. CHANGING THE TEMPERATURE

Raising the temperature of an equilibrium mixture by adding heat causes the reaction to shift such that some of the heat is **absorbed**.

Le Châtelier's principle is consistent with this observation.

Raising the temperature of an exothermic reaction favors the formation of ____________ .

Reactants $\xrightarrow{\text{Heat produced}}$ Products (exothermic direction)

Reactants $\xleftarrow{\text{Heat absorbed}}$ Products (endothermic direction)

Raising the temperature of an endothermic reaction favors the formation of **products.**

Reactants $\xrightarrow{\text{Heat absorbed}}$ **Products** (endothermic direction)

Reactants $\xleftarrow{\text{Heat produced}}$ Products (exothermic direction)

Here ΔH is the predictive tool

Example $2SO_2\ (g) + O_2 \rightleftharpoons 2SO_3\ (g)$ $\Delta H° = -197.78$ kJ/mol

If heat is added, which direction will the reaction go?

II. TEMPERATURE DEPENDENCE OF K

K can change with **temperature** and **reaction rates** can change with **temperature**.

$\Delta G° = -RT \ln K = \Delta H° - T\,\Delta S°$ or $\ln K = -\Delta H°/RT + \Delta S°/R$

Since it is reasonable to assume that $\Delta H°$ and $\Delta S°$ are approximately independent of temperature over the range of temperatures of interest, K changes with a change in T.

Consider a reaction carried out at Temperatures T_1 and T_2:

$\ln K_2 = -\Delta H°/RT_2 + \Delta S°/R$ and $\ln K_1 = -\Delta H°/RT_1 + \Delta S°/R$

Subtracting the second equation from the first gives:

$$\ln \left[\frac{K_2}{K_1} \right] = -\frac{\Delta H°}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$ Van't Hoff Equation

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If $\Delta H° < 0$

$T_2 > T_1$ then (-)(-)(-) = (-) $K_1 > K_2$

$T_2 < T_1$ then (-)(-)(+) = (+) $K_1 < K_2$

If $\Delta H° > 0$

$T_2 > T_1$ then (-)(+)(-) = $K_1 \quad K_2$

$T_2 < T_1$ then (-)(+)(+) = $K_1 \quad K_2$

III. APPLICATIONS OF LE CHÂTELIER'S PRINCIPLE

A. MAXIMIZING THE YIELD OF A REACTION

The Harber-Bosch Process.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ exothermic reaction

1.6 x 10^{10} kg of ammonia produced by this process per year in US

low temperature favors products, good   but low temperature slows rate, bad

Compromise temperature used is 500°C.

What are other ways to drive the reaction toward products?

All living things need nitrogen, and there is lots of N_2 in the air, but it is hard to split N_2. Thus, we use the environmentally unfriendly Harber-Bosch Process, but bacteria can catalyze the same reaction using an enzyme called nitrogenase.

B. LE CHÂTELIER AND HEMOGLOBIN

The combination of oxygen with hemoglobin (Hb), which carries oxygen through the blood, can be represented by

$Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)$

where HbO_2 is oxyhemoglobin (oxygen bound to hemoglobin)

At an altitude of 3 km the partial pressure of oxygen is only about 0.14 atm, compared to 0.2 atm at sea level.

According to Le Châtelier's principle, the equilibrium would be shifted to the left. This change causes hypoxia.

How can the body compensate?

$Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)$

IV. SIG FIG RULES FOR LOGS AND EXPONENTIALS (PAGE A5 IN BOOK)

log $(7.310 \times 10^{3}) = 3.8639$ (4 sig figs in mantissa)
log $(7.310 \times 10^{23}) = 23.8639$ (4 sig figs in mantissa)
The characteristic (left of decimal point) is determined solely by the location of the decimal point in the number and not by the number's precision, it is not included when counting sig figs. The mantissa (right of decimal point) should be written with as many sig figs as the original number.

$10^{0.389} = 2.45$ (3 sig figs in answer)
$10^{12.389} = 2.45 \times 10^{12}$(3 sig figs in answer)

There are no simple rules for assessing significant figures for natural logarithms. One should convert ln to log and then use log rules, but for the purposes of this course, just use log sig fig rules for ln too.

Let's try an example