Gas Equilibrium

At a constant volume and temperature, pressure can be substituted for M in a RICE table!

- This is because pressure is directly proportional to moles, and moles are directly proportional to M

Example: The noble gas krypton reacts with chlorine gas in a rigid, sealed container at constant temperature. Initially, the partial pressure of krypton is 0.85 atm and the partial pressure of Cl_2 is 1.35 atm. When the reaction goes to completion, the partial pressure of the remaining krypton is 0.40 atm. What is formula of the compound produced?

$$Kr_{(g)} + Cl_{2(g)} \rightarrow Kr_xCl_y$$

$Kr_{(g)}$	$Cl_{2(g)}$
0.85	1.35
− 0.45	−1.35
0.40	∅

$\Rightarrow$ 0.45 mol Kr : 1.35 mol Cl_2

1 Kr : 3 Cl_2

$\Rightarrow$ 1 Kr : 6 Cl $\Rightarrow$ $KrCl_6$

The Equilibrium Constant, K (the Law of Mass Action): relates the concentrations of reactants and products at equilibrium at a given temperature.

K_c & K_p – Not the same!

For the general reaction: $aA + bB \leftrightharpoons cC + dD$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{(P_{products})^{coefficient}}{(P_{reactants})^{coefficient}}$$ where P is the partial pressure of the gas

Le Châtelier's Principle

If a "stress" (change) is applied to a system at equilibrium,

processes will occur to counteract (undo) that change.

Examples of Counteracting

1. Heat:
   a. If you add heat to a system, it will shift in a way that it tends to use up the added heat.
   b. If you remove heat from a system, it will shift in a way that it tends to produce heat.
2. Adding or removing a reagent:
   a. If you remove a reagent, the reaction shifts to replace it. *(NOT solids and liquids!)*
   b. If you add a reagent, the reaction shifts to get rid of it. *(NOT solids and liquids!)*
3. Pressure/ Volume: **Depends on number of** moles **of gas!**
   a. ↑ pressure (or ↓ volume) favors a shift to the side with the fewest # of moles of gas.
   b. ↓ pressure (or ↑ volume) favors a shift to the side with the greatest # of moles of gas.
4. Catalysts: NO effect on K; just gets to equilibrium faster (Kinetics moment)!

REMEMBER – nothing but a change in temperature will change the VALUE of K

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Let's practice!

1. Consider the following reaction: $2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O\ (l)$ Write the equilibrium expression, K_p, for this equation. At equilibrium, the partial pressure of hydrogen gas is 0.9968 atm and the partial pressure of oxygen gas is 1.105 atm. Calculate K_p. Does this reaction favor reactants, products, or neither? Explain.

$$K_p = \frac{1}{(P_{H_2})^2 (P_{O_2})} = \frac{1}{(0.9968)^2 (1.105)} = \boxed{0.9108}$$

Favors reactants a bit, since $K_p < 1$, but 0.9 is close to 1 and so the amount of reactants is just a little bit more than products.

2. $2\ Cl_2O_5(g) \rightleftharpoons 2\ Cl_2(g) + 5\ O_2(g)$

If the mole fractions in this system at equilibrium are Cl_2: 0.243, O_2: 0.274, Cl_2O_5: 0.483, and the total pressure of the system is 3.00 atm, what is K_p?

$P_{Cl_2} = (3\text{ atm})(0.243) = 0.729\text{ atm}$

$P_{O_2} = (3\text{ atm})(0.274) = 0.822\text{ atm}$

$P_{Cl_2O_5} = (3\text{ atm})(0.483) = 1.45\text{ atm}$

$$K_p = \frac{(P_{Cl_2})^2 (P_{O_2})^5}{(P_{Cl_2O_5})^2} = \frac{(0.729)^2 (0.822)^5}{(1.45)^2} = \boxed{0.0949}$$

3. Consider the following reaction at equilibrium: $2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$ + heat $\quad \Delta H = -391.2$ kJ/mol

(same, ↓ or ↑?)

Disturbance	After equilibrium is re-established, what will be the effect on each of the following?			$K_p = (P_{O_2})^3$ Why?
	n_{O_2}	P_{O_2}	K_P	
↑V of container	↑	same	same	shift right, ↑ n_{O_2} until P_{O_2} is same as initial
☆ ↓V of container	↓	same	same	shift left, ↓ n_{O_2} (↓ " " ")
Add inert gas	same	same	same	no effect!
☆ Add more KCl	same	same	same	adding a solid has no effect on equil. (not part of K_p)
↑Temperature	↓	↓	↓	shift left, ↓ n_{O_2} = ↓ P_{O_2} = ↓ K_p
☆ ↓Temperature	↑	↑	↑	shift right, ↑ n_{O_2} = ↑ P_{O_2} = ↑ K_p
☆ Add more O_2	↓	same	same	shift left, ↓ n_{O_2} until n_{O_2} and P_{O_2} are the same as initial

Free Response Practice

1. $NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$ $\Delta H° = +93$ kiloJoules

The equilibrium above is established by placing solid NH_4HS in an evacuated container at 25ºC. At equilibrium, some solid NH_4HS remains in the container. Predict and explain each of the following.

a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container.
b) The effect on the equilibrium partial pressure of NH_3 gas when additional solid H_2S is introduced into the container. (Hint: $H_2S(s)$ readily sublimes into $H_2S(g)$.)
c) The effect on the mass of solid NH_4HS present and the value of the equilibrium constant when the volume of the container is decreased.
d) The effect on the mass of solid NH_4HS present and the value of the equilibrium constant when the temperature is increased.

a.) No effect on P_{NH_3}! Adding/removing solids has no effect on the equilibrium position (solids aren't included in K_p).

b.) P_{NH_3} decreases! Adding $H_2S_{(s)}$ is really adding $H_2S_{(g)}$, since the solid sublimes. The added $H_2S_{(g)}$ shifts equilibrium left to use up $H_2S_{(g)}$ + re-establish equilibrium, which will use up some $NH_{3(g)}$, decreasing P_{NH_3}.

c.) mass of $NH_4HS_{(s)}$ increases, K remains the same, b/c ↓V of the container ↑P, causing the rxn to shift left towards fewer moles of gas to re-establish equilibrium, producing more $NH_4HS_{(s)}$. The leftward shift decreases P_{NH_3} and P_{H_2S} back to their initial values, leaving K unchanged (nothing can change the value of K except changing temp!)

d.) mass of $NH_4HS_{(s)}$ decreases, K increases - b/c the rxn is endothermic (heat is a reactant), ↑T shifts the rxn right to use up the added heat, which will also use up some $NH_4HS_{(s)}$. As the rxn shifts right more products are produced, increasing both P_{NH_3} and P_{H_2S}. Since $K_p = (P_{NH_3})(P_{H_2S})$, the value of K will increase.