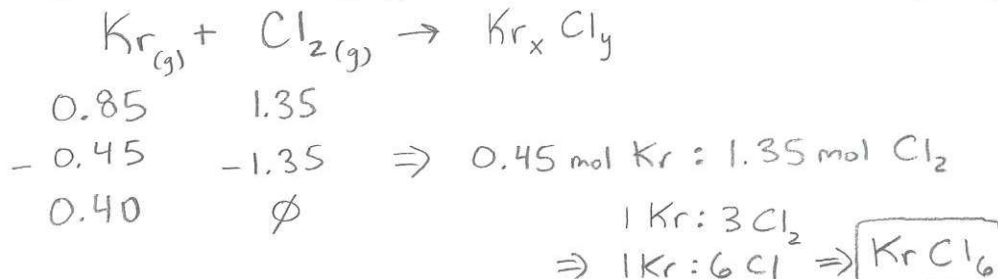


21 22
Gas Equilibrium

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 Cl₂ 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?



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: $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = \frac{(P_{\text{products}})^{\text{coefficient}}}{(P_{\text{reactants}})^{\text{coefficient}}}$$
 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:

- If you add heat to a system, it will shift in a way that it tends to use up the added heat.
- 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:

- If you remove a reagent, the reaction shifts to replace it. (**NOT solids and liquids!**)
- 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!**

- ↑ pressure (or ↓ volume) favors a shift to the side with the fewest # of moles of gas.
- ↓ 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

Let's practice!

1. Consider the following reaction: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$ 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.

$$K_p = \frac{1}{(P_{\text{H}_2})^2 (P_{\text{O}_2})} = \frac{1}{(0.9968)^2 (1.105)} = \boxed{0.9108}$$

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. $2 \text{Cl}_2\text{O}_5(\text{g}) \rightleftharpoons 2 \text{Cl}_2(\text{g}) + 5 \text{O}_2(\text{g})$

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 ?

$$P_{\text{Cl}_2} = (3 \text{ atm})(0.243) = 0.729 \text{ atm}$$

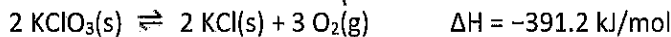
$$P_{\text{O}_2} = (3 \text{ atm})(0.274) = 0.822 \text{ atm}$$

$$P_{\text{Cl}_2\text{O}_5} = (3 \text{ atm})(0.483) = 1.45 \text{ atm}$$

$$K_p = \frac{(P_{\text{Cl}_2})^2 (P_{\text{O}_2})^5}{(P_{\text{Cl}_2\text{O}_5})^2} = \frac{(0.729)^2 (0.822)^5}{(1.45)^2} = \boxed{0.0949}$$

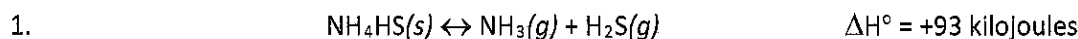
same, ↓ or ↑?

3. Consider the following reaction at equilibrium:



Disturbance	After equilibrium is re-established what will be the effect on each of the following?			$K_p = (P_{\text{O}_2})^3$ 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, ↓ $n_{\text{O}_2} = \downarrow P_{\text{O}_2} = \downarrow K_p$
↓Temperature	↑	↑	↑	shift right, ↑ $n_{\text{O}_2} = \uparrow P_{\text{O}_2} = \uparrow K_p$
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



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

- The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container.
- The effect on the equilibrium partial pressure of NH_3 gas when additional solid H_2S is introduced into the container. (Hint: $\text{H}_2\text{S}(s)$ readily sublimates into $\text{H}_2\text{S}(g)$.)
- 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.
- 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 $\text{H}_2\text{S}(s)$ is really adding $\text{H}_2\text{S}(g)$, since the solid sublimates. The added $\text{H}_2\text{S}(g)$ shifts equilibrium left to use up $\text{H}_2\text{S}(g)$ + re-establish equilibrium, which will use up some $\text{NH}_3(g)$, decreasing P_{NH_3} .

c.) mass of $\text{NH}_4\text{HS}(s)$ increases, K remains the same, b/c $\downarrow V$ of the container $\uparrow P$, causing the rxn to shift left towards fewer moles of gas to re-establish equilibrium, producing more $\text{NH}_4\text{HS}(s)$. The leftward shift decreases P_{NH_3} and $P_{\text{H}_2\text{S}}$ back to their initial values, leaving K unchanged (nothing can change the value of K except changing temp!)

d.) mass of $\text{NH}_4\text{HS}(s)$ decreases, K increases - b/c the rxn is endothermic (heat is a reactant), $\uparrow T$ shifts the rxn right to use up the added heat, which will also use up some $\text{NH}_4\text{HS}(s)$. As the rxn shifts right more products are produced, increasing both P_{NH_3} and $P_{\text{H}_2\text{S}}$. Since $K_p = (P_{\text{NH}_3})(P_{\text{H}_2\text{S}})$, the value of K will increase.