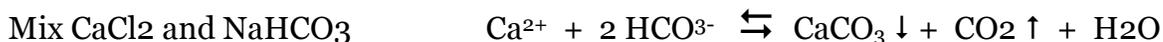
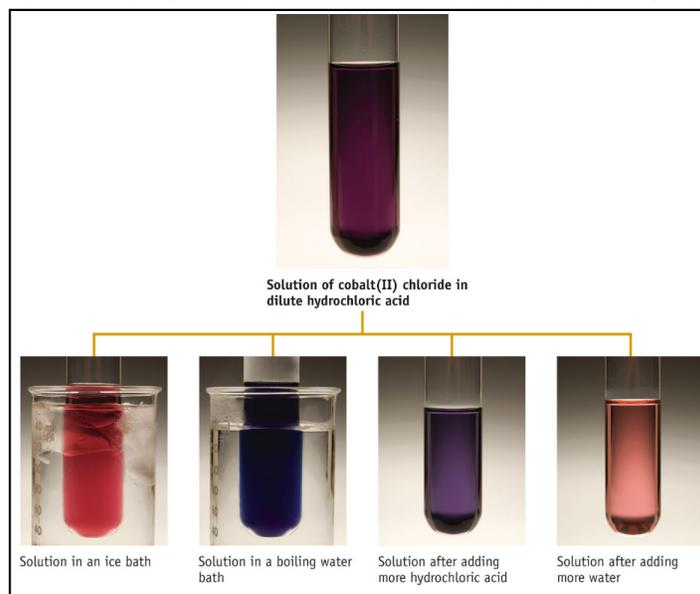


These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Book Material. Additional material that is in the Text Book will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

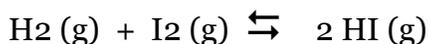
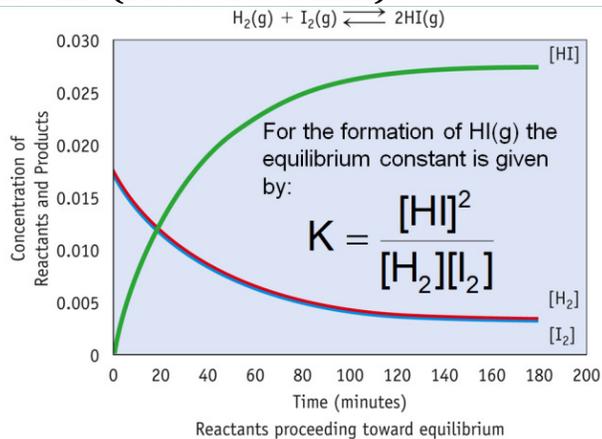
NOTE THESE ARE DRAFT LECTURE NOTES!

Chemical Reactions are Reversible (at least some or most of them!) – Use \rightleftharpoons
They are Dynamic – in constant motion with forward and reverse reactions'



If you add CO_2 , the precipitated CaCO_3 will dissolve, the reaction reverses
At equilibrium, the rate of the forward reaction = the rate of the reverse reaction

16.2 Equilibrium Constant - K (Note: No Units)



$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad K \text{ is constant at a given } T$$

Example: Start with $[H_2] = [I_2] = 0.0175 \text{ mol/L}$ at 425°C and no HI present.

At equilibrium $[H_2] = [I_2] = 0.0037 \text{ mol/L}$ and $[HI] = 0.0276 \text{ mol/L}$.

ICE Table

	H₂ (g)	+	I₂ (g)	\rightleftharpoons	2 HI (g)	
Initial	0.0175		0.0175		0	assume mol/L
Change	-0.0138		-0.0138		+0.0276	
Equilibrium	0.0037		0.0037		0.0276	

$$K = [HI]^2 / [H_2][I_2] = [0.0276]^2 / [0.0037][0.0037] = 56 \quad \text{Note No Units}$$

$2 \text{ NOCl (g)} \rightleftharpoons 2 \text{ NO (g)} + \text{Cl}_2 \text{ (g)}$ 2.00 mol NOCl in 1.00 L flask, at equilibrium NO is 0.66 mol/L
What is K? Watch Stoichiometry

$2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$

	[NOCl]	[NO]	[Cl ₂]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

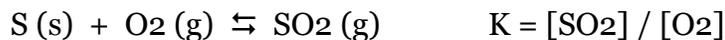
$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$$

For a reaction at Equilibrium $aA + bB \rightleftharpoons cC + dD$

Equilibrium Constant Expression = $K = [C]^c [D]^d / [A]^a [B]^b$

1. Concentrations are at Equilibrium
2. Product is in numerator, reactants in denominator
3. Each concentration is raised to the power of the coefficient
4. The value of K depends on the particular reaction and temp
5. **Values of K are Dimensionless**

Reactions involving Solids – concentration of any solid reactants or products are not included in the equilibrium expression



Reactions in Solutions – for aqueous solutions, the molar concentration of water is not included in the equilibrium expression

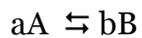


Gases For $PV = nRT$, gas concentration = $n/V = P / RT$, so the Partial Pressure of a gas is related to its concentration and is K_p $H_2 (g) + I_2 (g) \rightleftharpoons 2 HI (g) \quad K_p = P_{HI}^2 / P_{H_2} P_{I_2}$

EXAMPLE 16.1 P 725 Write the equilibrium Expression for:

- a. $N_2 (g) + 3 H_2 (g) \rightleftharpoons 2 NH_3 (g)$
- b. $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$
- c. $CaCO_3 \downarrow \rightleftharpoons CaO \downarrow + CO_2 \uparrow$

Meaning of K



$$K = [B]^b / [A]^a$$

$K > 1$ Product [B] is favored

$K < 1$ Reactant [A] is favored

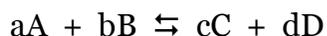
Table 16.1 Selected Equilibrium Constant Values

Reaction	Equilibrium Constant, K (at 25 °C)	Product- or Reactant-Favored at Equilibrium
<i>Combination Reaction of Nonmetals</i>		
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	4.2×10^{52}	$K > 1$; product-favored
$2 H_2(g) + O_2(g) \rightleftharpoons 2 H_2O(g)$	3.2×10^{81}	$K > 1$; product-favored
$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$	3.5×10^8	$K > 1$; product-favored
<i>Ionization of Weak Acids and Bases</i>		
$HCO_2H(aq) + H_2O(\ell) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$ formic acid	1.8×10^{-4}	$K < 1$; reactant-favored
$CH_3CO_2H(aq) + H_2O(\ell) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$ acetic acid	1.8×10^{-5}	$K < 1$; reactant-favored
$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$ carbonic acid	4.2×10^{-7}	$K < 1$; reactant-favored
$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ ammonia	1.8×10^{-5}	$K < 1$; reactant-favored
<i>Dissolution of "Insoluble" Solids</i>		
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	3.8×10^{-9}	$K < 1$; reactant-favored
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}	$K < 1$; reactant-favored

Reaction Quotient Q

K is for reactions at Equilibrium

Q is for reactions NOT at Equilibrium



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

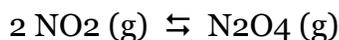
$Q = K$ The system is at Equilibrium then

$Q < K$ Reactants \rightarrow Products to be at equilibrium

$Q > K$ Products \rightarrow Reactants to be at equilibrium

**STUDENTS
WORK THIS
OUT – PROVE IT**

OWL Interactive Example 6.2



$K = 170$ at 298 K

At time t, $NO_2 = 0.015$ M, $N_2O_4 = 0.025$ M.

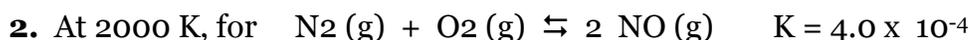
$$Q = [N_2O_4] / [NO_2]^2 = 0.025 \text{ M} / (0.015 \text{ M})^2 = 111.11 = 110$$

$Q = 110$, $K = 170$ so Q is less than K, need to go Reactants to Products

Review Check 16.2



Write the Equilibrium Const Expression



In a flask, $N_2 = 0.50$ M, O_2 is 0.25 M, NO is 4.2×10^{-3} M. Is the system at equilibrium?

16.3 Determining Equilibrium Constant

If the concentration of each component is known at equilibrium, K can be calculated

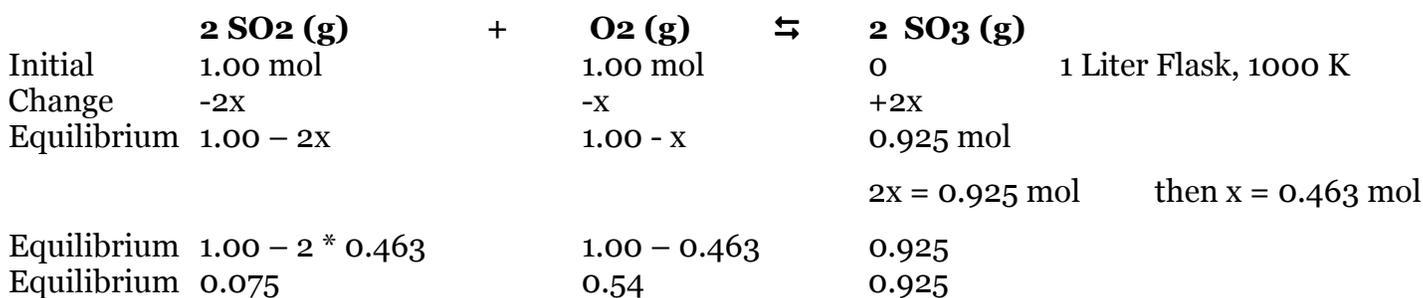
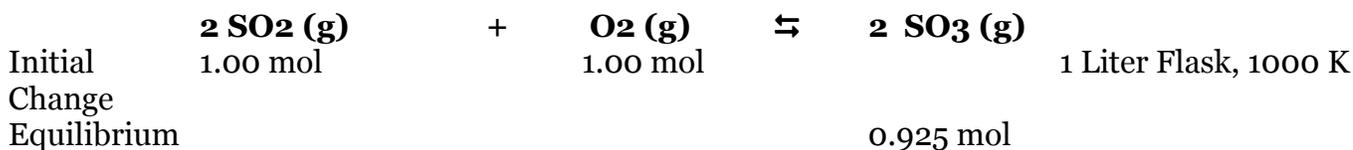


$$3.61 \times 10^{-3} \text{ mol/L} \quad 6.11 \times 10^{-4} \text{ mol/L} \quad 1.01 \times 10^{-2} \text{ mol/L}$$

$$K = [\text{SO}_3]^2 / [\text{SO}_2]^2 [\text{O}_2] = (1.01 \times 10^{-2})^2 / (3.61 \times 10^{-3})^2 (6.11 \times 10^{-4}) = 1.28 \times 10^4$$

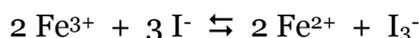
K is large, so, products are favored

Now, put 1.00 mol of SO₂ (g) and 1.00 mol of O₂ (g) in a 1.00 L flask at 1000 K, at equilibrium there is 0.925 mol SO₃ (g). What is K?

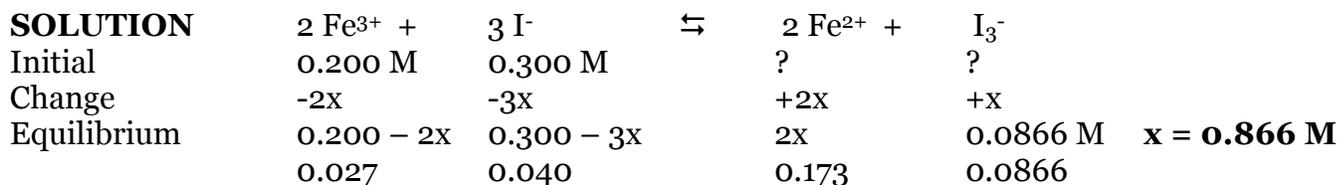
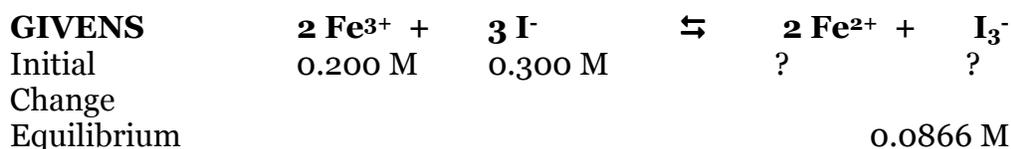


$$K = [\text{SO}_3]^2 / [\text{SO}_2]^2 [\text{O}_2] = (0.925)^2 / (0.075)^2 (0.54) = 2.8 \times 10^2$$

Interactive Example 16.3



Initial Concentration Fe³⁺ = 0.200 M, I⁻ = 0.300 M. At equilibrium I₃⁻ 0.0866 M

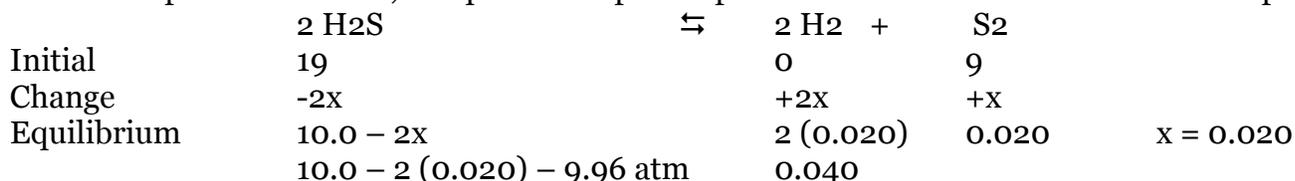


$$K = [\text{Fe}^{2+}]^2 [\text{I}_3^-] / [\text{Fe}^{3+}]^2 [\text{I}^-]^3 = (0.173)^2 (0.0866) / (0.027)^2 (0.040)^3 = 5.6 \times 10^4$$

Example 16.4



Start with 10 atm pressure of H₂S, at equilibrium partial pressure of S₂ is 0.020 atm. What is K_p



$$K_p = (P_{\text{H}_2})^2 P_{\text{S}_2} / (P_{\text{H}_2\text{S}})^2 = (0.040)^2 (0.020) / (9.96)^2 = 3.2 \times 10^{-7}$$

16.4 Using Equilibrium Constants in Calculations $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$
 At 425 °C, 1.00 mol of H_2 and I_2 put in a 0.500 L flask. $K = 55.64$, what is the equilibrium []

	$\text{H}_2(\text{g}) +$	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
Initial	2.00 M	2.00 M		0
Change	-x	-x		+2x
Equilibrium	$2.00 - x$	$2.00 - x$		2x

$$K = 55.64 = [\text{HI}(\text{g})]^2 / [\text{H}_2(\text{g})] [\text{I}_2(\text{g})] = (2x)^2 / (2.00 - x)(2.00 - x) = (2x)^2 / (2.00 - x)^2$$

Take square root of both sides $7.459 = 2x / (2.00 - x)$

$$7.549(2.00 - x) = 2x \quad \rightarrow \quad 14.91 - 7.549x = 2x \quad \rightarrow \quad 14.9 = 9.549x$$

$$x = 1.56 \text{ (book gets 1.58)}$$

$$[\text{H}_2(\text{g})] = [\text{I}_2(\text{g})] = 2.00 - x = 0.44 \text{ M} \quad [\text{HI}(\text{g})] = 2x = 3.12 \text{ M}$$

Using a Quadratic $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ $\text{PCl}_5 = 1.60 \text{ M}, K=1.20$.
 What is [] of products at equilibrium

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g}) +$	$\text{Cl}_2(\text{g})$
Initial	1.60 M		0	0
Change	-x		+x	+x
Equilibrium	$1.60 - x$		x	x

$$K = [\text{PCl}_3] [\text{Cl}_2] / [\text{PCl}_5] = 1.20 = x * x / (1.60 - x)$$

$$x^2 = 1.20(1.60 - x) = 1.92 - 1.20x \quad x^2 + 1.20x - 1.92 = 0$$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solve for X =

Roots are 0.910 and -2.11. So $x = 0.910 \text{ M}$

$$[\text{PCl}_5] = 1.60 - 0.910 = 0.69 \text{ M} \quad [\text{PCl}_3] = [\text{Cl}_2] = x = 0.91 \text{ M}$$

Realistic approximation: $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$
 $K = 5.6 \times 10^{-12}$ at 500 K [K is a small number, Not very much product]

Initial I_2 is 0.45 M, what are equilibrium concentrations?

	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{I}(\text{g})$
Initial	0.45 M		0
Change	-x		+2x
Equilibrium	$0.45 - x$		2x

$$K = 5.6 \times 10^{-12} = [\text{I}(\text{g})]^2 / [\text{I}_2(\text{g})] = (2x)^2 / (0.45 - x)$$

ASSUME: Since K is very very small, the amount of $\text{I}(\text{g})$ is very small and x is very small

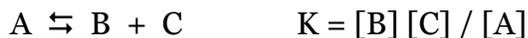
Therefore $(0.45 - x)$ is 0.45 minus a very small number, so we can ignore x in $(0.45 - x)$

$$5.6 \times 10^{-12} = (2x)^2 / 0.45 \quad \rightarrow \quad 2.52 \times 10^{-12} = 4x^2 \quad \rightarrow \quad 6.3 \times 10^{-13} = x^2$$

$$x = 7.9 \times 10^{-7}$$

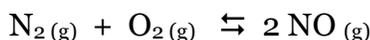
$$[\text{I}(\text{g})] = 0.45 - x = 0.45 - 7.9 \times 10^{-7} = \text{Still equals } 0.45 \text{ M}$$

Now Prove the Assumption



If K is less than 1 and $(100 * K) < [A]$ then you can make the above assumption

INTERACTIVE EXAMPLE 16.6



At 1500 K, $K = 1.0 \times 10^{-5}$ Air is 80% N_2 and 20% O_2 in Moles/L.

What is the equilibrium concentration of all.

	$N_2(g)$	+	$O_2(g)$	\rightleftharpoons	$2 NO(g)$
Initial	0.80		0.20		0
Change	-x		-x		+2x
Equilibrium	$0.80 - x$		$0.20 - x$		2x

$$K = 1.0 \times 10^{-5} = [NO]^2 / [N_2][O_2] = (2x)^2 / (0.80 - x)(0.20 - x)$$

Per guidelines, K is less than 1 and $100 * K = 1.0 \times 10^{-3}$ is less than $[N_2]$ which is 0.80

$$K = 1.0 \times 10^{-5} = (2x)^2 / (0.80)(0.20) \quad 1.6 \times 10^{-6} = 4x^2 \quad x = 6.3 \times 10^{-6}$$

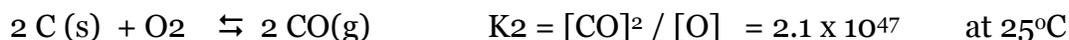
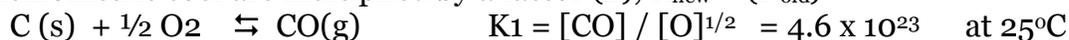
$$[N_2] = 0.80 - 6.3 \times 10^{-6} = 0.80 \text{ M} \quad [O_2] = 0.20 - 6.3 \times 10^{-6} = 0.20 \text{ M}$$

$$[NO] = 2x = 1.3 \times 10^{-3}$$

Students Prove the Assumption and Prove the answer by solving the Quadratic.

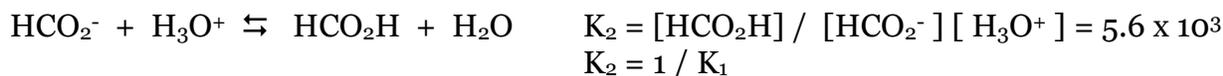
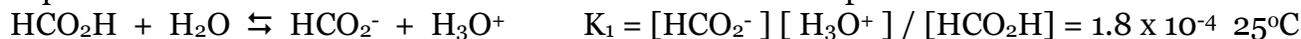
16.5 Balanced Equations and Equilibrium Constants

1. Stoichiometric coef are multiplied by a factor (2), $K_{\text{new}} = (K_{\text{old}})^{\text{factor}}$

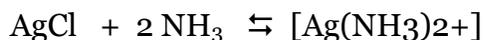
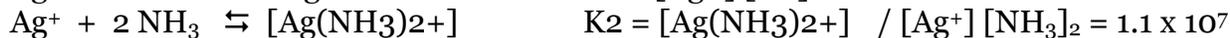


$$K_1 = [CO] / [O]^{1/2} = \{ [CO]^2 / [O] \}^{1/2} = K_2^{1/2}$$

2. The equilibrium constants for a reaction and its reverse are reciprocals of each other



3. If you add two reactions, you multiply the equilibrium constants



$$K_{\text{net}} = K_1 * K_2 = [Ag^+][Cl^-][Ag(NH_3)_2^+] / [Ag^+][NH_3]^2 = [Cl^-][Ag(NH_3)_2^+] / [NH_3]^2$$

$$K_{\text{net}} = K_1 * K_2 = 2.0 \times 10^{-3}$$

Students do Example 16.7

16.6 Disturbing a Chemical Equation

Changes are compensated for by Le Chatelier's Principle

Disturbance Equilibrium	Bring Back to	Effect on Equilibrium	Effect on K
Increase T	Reaction consumes the energy	Shift in Endothermic direction	Changes K
Increase T	Energy is generated by the reaction	Shift in Exothermic direction	Changes K
Add reactant	Reactant is consumed	[Product] is increased	No Change in K
Add product	Product is consumed	[Reactant] is increased	No Change in K
For a gas increase volume or increase pressure	Pressure Decreases	Composition changes to reduce # of gas molecules	No Change in K
Increase volume or decrease pressure	Pressure Increases	Composition changes to increase # of gas molecules	No Change in K

Interactive Example 16.8



1.00 L flask, 0.500 mol/L Butane, 1.25 mol/L isobutene is at equilibrium.

Then 1.50 mol of Butane is added, ? conc of each.

	Butane	\rightleftharpoons	Isobutane
Initial	0.500		1.25
Conc adding Butane	0.500 + 1.50		1.25
Change	0.500 + 1.50 - x		1.25 + x

$$K = 2.5 = [\text{Isobutane}] / [\text{Butane}] = (1.25 + x) / (0.500 + 1.50 - x)$$

$$2.50 (2.00 - x) = 1.25 + x \quad \rightarrow \quad 5.00 - 2.50x = 1.25 + x$$

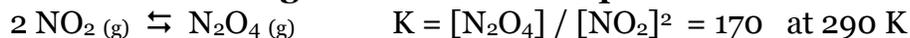
$$5.00 - 1.25 = x + 2.50x \quad \rightarrow \quad 3.75 = 3.50x$$

$$x = 1.07 \text{ mol/L}$$

$$\text{Butane} = 0.500 + 1.50 - x = 0.500 + 1.50 - 1.07 = 1.07 \text{ mol/L}$$

$$\text{Isobutane} = 1.25 + x = 1.25 + 1.07 = 2.32 \text{ mol/L}$$

Effect of Volume Changes on Gas Phase Equilibrium



If we half the volume of the flask -> Both gas concentrations will double

$$\text{Start:} \quad [\text{N}_2\text{O}_4] = 0.0280 \quad [\text{NO}_2] = 0.0128$$

$$\text{Volume Halved} \quad [\text{N}_2\text{O}_4] = 0.0560 \quad [\text{NO}_2] = 0.0256$$

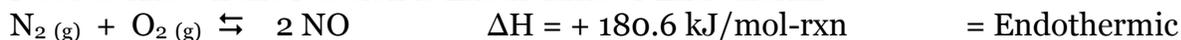
$$Q = [\text{N}_2\text{O}_4] / [\text{NO}_2]^2 = (0.0256)^2 / (0.0560) = 84.5$$

$K = 170$ is greater than $Q = 84.5$. Must increase the amount of Product

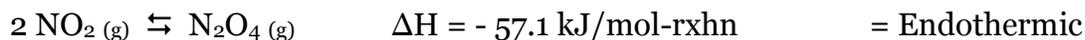
1. For gases, for a volume decrease, there is a change in equilibrium to have a smaller number of gas molecules
2. For a volume increase, there is a change in equilibrium to have a larger number of gas molecules
3. For no change in volume, if there is no change in the number of gas molecules going from reactants to products, there is no effect. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$

Effect of Temperature Changes on Equilibrium Composition

Need to know if the reaction is Exothermic or Endothermic



If we increase HEAT, Q will decrease. Then K is greater than Q, we shift to form Product



If we increase HEAT, Q will increase. Then Q is greater than K, we shift to form Reactant

1. Increase the temperature of a system at equilibrium, the equilibrium will shift in the direction that absorbs energy as heat, in the Endothermic Direction
2. Decrease the temperature of the system, the equilibrium will shift in the direction that releases energy as heat – in the Exothermic direction

3. Changing temperature changes K