Unit#7 AP Chem Topic#8 Equilibrium

Student Edition

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General Equilibrium

Equilibrium Topic#8

Formula Page

EQUILIBRIUM

$$K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$K_b = \frac{[\mathrm{OH}^-][\mathrm{HB}^+]}{[\mathrm{B}]}$$

$$K_w = [OH^-][H^+] = 1.0 \times 10^{-14} @ 25^{\circ}C$$

= $K_a \times K_b$

$$pH = -\log[H^+], \; pOH = -\log[OH^-]$$

$$14 = pH + pOH$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pOH = pK_b + log \frac{[HB^+]}{[B]}$$

$$pK_a = -\log K_a, pK_b = -\log K_b$$

$$K_p = K_c (RT)^{\Delta n},$$

where Δn = moles product gas – moles reactant gas

Equilibrium Constants

K_a (weak acid)

K_b (weak base)

 $K_{\rm w}$ (water)

 K_p (partial pressures; gases)

*K*_c (molar concentrations)

*K*_{sp} (solubility product; insoluble ionic compounds)

 $HA(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + A^{-}(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

 $B(aq) + H_2O(l) \rightleftharpoons BH^*(aq) + OH(aq)$

 $K_b = \frac{[BH^+][OH^-]}{[B]}$

Half Titration Point

$$[A^{-}] = [HA]$$

$$pH = pK_a$$
or
$$[HB^{+}] = [B]$$

$$pOH = pK_b$$

ICE Tables

Elimination of $\pm x$ Ionization Rule (< 5% ionization)

Electrochemistry

$$K = 10^{(nE/0.0592)}$$

$$E_{cell}^0 = \frac{0.0592}{n} \log K$$

Thermochemistry

$$K = e^{(-\Delta G/2.48)}$$

$$\Delta G = -RT \ln K$$

$$K_{\text{eq}} = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b}$$

Equilibrium Topic#8

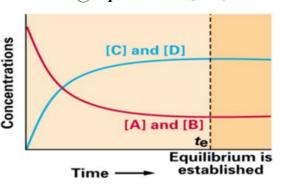
Equilibrium Intro

Generalities of Equilibrium

- State where the rate of the forward reaction is equal to the rate of the reverse reaction.
- Concentration of all species remains constant (constant *T*).
- Reactions are reversible, yet some have great obstacles going in one direction.
 - High E_a , gas release, solid formed (precipitation), etc.
- Dynamic equilibrium reaction going forward and in reverse.
- Take a look at the reaction of carbon monoxide and steam in a closed vessel:
 - Does the reaction favor reactants or products?
 - What can you say about the relative energies of reactants and products?
 - What can be you say about the reaction rate? Why?
 - What can you say about the degree of organization?

$$A + B \rightleftharpoons C + D$$

(a) equilibrium $k_{\rm f} = k_{\rm r}$



Is $K_{eq} > 1$ or < 1 for the above graph?

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Equilibrium Constant/Expression

Significance of K

K > 1	favors product formation at equilibrium (1.0x10 ⁴)
K >> 1	almost entirely products at equilibrium $(1.0x10^{23})$
K < 1	favors reactants at equilibrium (1.0×10^{-4})

 $K \ll 1$ almost entirely reactants at equilibrium $(1.00x10^{-23})$

Equilibrium Expression

• Law of Mass Action

$$K_{\text{eq}} = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b}$$

- General reaction equation: $aA + bB \leftrightarrow cC + dD$
- K_c aqueous concentrations/gases in a vessel of known volume
- \bullet K_p gases, partial pressures
- $K_{\rm w}$ water = 1.0×10^{-14}
- $K_{\rm sp}$ ionic compounds (solubility product)
- K_a acids
- K_b bases
- When writing an equilibrium expression from a balanced equation, only aqueous and gaseous substances are written in the expression.
 - For example, $CaCO_3(s) + 2H^+(aq) \leftrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$ the equilibrium expression is $K = \underline{[Ca^{2+}][CO_2]}$ $\underline{[H^+]^2}$

Equilibrium	l
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Self-Ionization of Water

The process of water's self-ionization is an endothermic process. Energy can be written as a reactant in the chemical equation.

Does the self-ionization increase / decrease when water is heated?

Equilibrium	ì
Tonic#8	

Equilibrium Expression

Sample WS#1 - Equilibrium Expression

1. Write the equilibrium expression for the following reaction: $4NH_3(g) + 7O_2(g) \leftrightarrow 4NO_2(g) + 6H_2O(g)$

$$K_{c} = \frac{[NO_{2}]^{4} [H_{2}O]^{6}}{[NH_{3}]^{4} [O_{2}]^{7}}$$

* When given in Mor moles and volume.

$$K_{p} = \frac{(P_{NO_{2}})^{4} (P_{H_{2}O})^{4}}{(P_{NH_{3}})^{4} (P_{O_{2}})^{7}} \times When species are given in pressure units (KPa, artm, mmHa, torr, etc.)$$

	Equilibrium
Equilibrium Constant	Topic#8

Effect on Changing the balanced Equation of an Equilibrium Equation.

- Multiplying the coefficients by a factor, n, raises K to the power of the factor, n, K^n
- Reversing the equation take the reciprocal of K, 1/K.
- Adding equations multiply *K* values.

Affecting K Practice Problems

2. The following equilibrium concentrations were observed for the Haber process at 127°C.

$$\begin{aligned} N_2(g) + 3H_2(g) &\longleftrightarrow 2NH_3(g) \\ [NH_3] = 3.1x10^{-2} \text{ mol/L}, \ [N_2] = 8.5x10^{-1} \text{ mol/L}, \ \text{and} \ [H_2] = 3.1x10^{-3} \text{ mol/L} \end{aligned}$$

a) Calculate the value of K at 127°C for this reaction.
$$K_{C} = \frac{[NH_{3}]^{\frac{3}{2}}}{[N_{2}][H_{2}]^{\frac{3}{2}}} = \frac{(3.1 \times 10^{-2})^{\frac{3}{2}}}{(8.5 \times 10^{-2})(3.1 \times 10^{-3})^{2}} = \frac{3.8 \times 10^{-4}}{3.8 \times 10^{-4}}$$
*product driven equilibrium

b) Calculate the value of the equilibrium constant at 127°C for the reaction: $2NH_3(g) \Leftrightarrow N_2(g) + 3H_2(g)$

$$K_r = \frac{1}{K_f} = \frac{1}{(3.8 \times 10^4)} = [2.6 \times 10^{-5}]$$

c) Calculate the value of the equilibrium constant at 127° C for the reaction: $1/2N_2(g) + 3/2H_2(g) \Leftrightarrow NH_3(g)$

$$K' = (K)^{\frac{1}{2}} = (3.8 \times 10^{4})^{\frac{1}{2}} = [1.9 \times 10^{2}]$$
(Ans: 3.8x10⁴, 2.6x10⁻⁵, and 1.9x10²)

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Equilibrium Topic#8

3. The following results were collected for two experiments involving the reaction at 600°C between sulfur dioxide and oxygen to form gaseous sulfur trioxide. Show that the equilibrium constant is the same in both cases. $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$

Experiment 1		Experiment 2		
Initial	Equilibrium	Initial	Equilibrium	
$[SO_2]_0 = 2.00M$	$[SO_2] = 1.50M$	$[SO_2]_0 = 0.500M$	$[SO_2] = 0.590M$	
$[O_2]_0 = 1.50M$	$[O_2] = 1.25M$	r -1.	$[O_2] = 0.0450M$	
$[SO_3]_0 = 3.00M$	$[SO_3] = 3.50M$	$[SO_3]_0 = 0.350M$	$[SO_3] = 0.260M$	

Experiment # 1
$$K_{c} = \frac{[SO_{3}]^{2}}{[SO_{2}]^{2}[O_{2}]}$$

$$K_{c} = \frac{(3.5)^{2}}{(1.5)^{2}(1.25)} = 4.36$$

$$K_c = \frac{(0.26)^2}{(0.59)^2(0.045)} = 4.32$$

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Equilibrium of Gases

- K_p uses partial pressures of gases in a sealed vessel while K_c is for concentration.
- $K_p = K_c(RT)^{\Delta_n}$ where Δn is the change in moles of gaseous species between reactants and products.
 - $\blacksquare \Delta n = \text{total moles of gas produced} \text{total moles of gas reacting}$
 - $\blacksquare R$ ideal gas law constant (0.0821)
 - $\blacksquare T$ in Kelvin
- $K_c = K_p$ when there is no net change in gaseous moles.

Calculating Values of Kp

4. The reaction for the formation of nitrosyl chloride, $2NO(g) + Cl_2(g) \leftrightarrow 2NOCl(g)$, was studied at 25° C. The pressures at equilibrium were found to be $P_{NOCl} = 1.2$ atm, $P_{NO} = 5.0 \times 10^{-2}$ atm, and $P_{Cl2} = 3.0 \times 10^{-1}$ atm. Calculate the value of K_p for this reaction at 25° C.

$$\frac{GvN}{P_{NOCI}^{2} \cdot 1.2atm} = \frac{NTK}{(P_{NOCI})^{2}} - \frac{1.9 \times 10^{-1}}{(P_{NO})^{2} \cdot (P_{CI_{2}})} - \frac{1.9 \times 10^{-1}}{(P_{NO})^{2} \cdot (P_{CI_{2}})}$$

$$\frac{GvN}{(P_{NOCI})^{2} \cdot 1.2atm} = \frac{NTK}{(P_{NOCI})^{2}} - \frac{1.9 \times 10^{-1}}{(P_{NO})^{2} \cdot (P_{CI_{2}})} - \frac{1.9 \times 10^{-1}}{(P_{NOCI})^{2} \cdot (P_{CI_{2}})}$$

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Equilibrium of Gases

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 - $\blacksquare \Delta n = \text{total moles of gas produced} \text{total moles of gas reacting}$
 - $\blacksquare R$ ideal gas law constant (0.0821)
 - $\blacksquare T$ in Kelvin
- $K_c = K_p$ when there is no net change in gaseous moles.
- 5. Using the value of K_p obtained in Sample 4, calculate the value of K_c at 25°C for the reaction $2NO(g) + Cl_2(g) \leftrightarrow 2NOCl(g)$

$$\Delta_{n} = 2 - (a+1)$$

$$= -1$$

$$K_{c} = \frac{1.9 \times 10^{3}}{(0.0821)(295)}^{-1} = 4.6 \times 10^{4}$$

$$K_{c} = \frac{K_{p}}{(RT)^{4n}}$$

	Equilibrium
Equilibrium of Gases	Topic#8

- 6. Write the expressions K and K_p for the following processes:
 - a. The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.
 - b. Deep blue solid copper (II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper (II) sulfate.

(a)
$$PCI_{5}(s) \Rightarrow PCI_{3}(L) + CI_{2}(g) \quad K_{c} = [CI_{2}] \stackrel{!}{\downarrow} K_{p} = (P_{cI_{2}})$$

(b) $CuSO_{4} \cdot 5H_{2}O(s) \Rightarrow CuSO_{4}(s) + 5H_{2}O(g)$
 $K_{c} = [H_{2}O]^{5} \stackrel{!}{\downarrow} K_{p} = (P_{H_{2}O})^{5}$

	Equilibrium	
Equilibrium Review	 Topic#8	

Can you...

- 1. ...write an equilibrium constant expression?
- 2. ...tell how K is changed if the stoichiometric coefficients are changed on an equation?
- 3. ...tell how to find *K* for a summary equation?
- 4. ...tell how K depends on the way equilibrium concentrations are expressed and how to convert K in terms of K_c vs. K_p ?
- 5. ...explain what *K* is telling you about a reaction?

Equilibriu
Topic#8

Reaction Quotient

The Reaction Quotient (Q)

- Used to determine whether a system is at equilibrium or not.
- Compare Q to K to determine if the reaction is at equilibrium or will shift left or right.
- For the reaction, $aA + bB \leftrightarrow cC + dD$

$$\label{eq:Qc} \begin{split} \mathcal{Q}_c \ = \underbrace{[C]^c[D]^d}_{[A]^a[B]^b} \end{split}$$

- Q = K then system is at equilibrium
- Q < K then system will shift right (increase amount of products (numerator))
- Q > K the system will shift left (increase amount of reactants (denominator))

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Reaction Quotient

Using Q (Reaction Quotient) to Determine if Reaction is at Equilibrium

7. For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0x10⁻². Predict the direction in which the system will shift to reach equilibrium in each of the following cases.

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$
a. $[NH_3]_0 = 1.0x10^{-3}M$, $[N_2]_0 = 1.0x10^{-5}M$, and $[H_2]_0 = 2.0x10^{-3}M$
b. $[NH_3]_0 = 2.00x10^{-4}M$, $[N_2]_0 = 1.50x10^{-5}M$, and $[H_2]_0 = 3.54x10^{-1}M$

- $[NH_3]_0 = 1.0x10^{-4}M$, $[N_2]_0 = 5.0M$, and $[H_2]_0 = 1.0x10^{-2}M$ (Ans: shifts left, no shift, shifts right) c.
- $H_{3}]_{0} = 2.00 \times 10^{-1} M, \quad I_{2}]_{0} = 5.0 M, \text{ and } [H_{2}]_{0} = 1.0 \times 10^{-2} M$ $A = \begin{bmatrix} 1.0 \times 10^{-4} M, & [N_{2}]_{0} = 5.0 M, & [H_{2}]_{0} = 1.0 \times 10^{-2} M \end{bmatrix}$ $A = \begin{bmatrix} 1.0 \times 10^{-2} & (1 \times 11^{-3})^{2} & (1 \times 1$

Equilibrium Topic#8

General Steps in Solving Equilibrium Problems

- 1. Set up a RICE table
 - R balanced reaction of reacting species
 - I initial concentration of species
 - C- determine the change ocurring in terms of x
 - E express the equilibrium concentrations in terms of x
- 2. Set up equilibrium expression and set it equal to a value (if given).
- 3. If given a K value, use it to solve for x.
- 4. If K value is VERY Small (less than 1.0×10^{-4}) then you can eliminate the change to the initial concentration. Hints: (a) Look for very small K values, "x" may be negligible.
 - (b) If "x" is large enough, then you must subtract it from the initial concentration. Your math will be simplified if the problem is a perfect square. If not, you must use the quadratic formula.
 - (c) If none of the initial concentrations are zero, then Q must be calculated first to determine direction of the shift before RICE table.

Reaction
$$\begin{array}{cccc} \text{Reaction} & \text{2HI}(g) \leftrightarrow \text{H}_2(g) + \text{I}_2(g) \\ \text{Initial} & 0.50 & 0 & 0 \\ \text{Change} & -2x & +x & +x \\ \text{Equilibrium} & 0.50\text{-}2x & 0\text{+}x & 0\text{+}x \\ \end{array}$$

$$K_{c} = \underbrace{[H_{2}][I_{2}]}_{[HI]^{2}} = \underbrace{(\mathbf{x})(\mathbf{x})}_{(0.5-2\mathbf{x})^{2}} = \underbrace{(\mathbf{x})^{2}}_{(0.5-2\mathbf{x})^{2}}$$

*If K << 1, then the -2x can be relegated to zero. What this means is the change is sooo small that it does not affect the initial [HI].

Ice Tables - Equilibrium

2HI(9) -

Equilibrium
Topic#8

Calculating Equilibrium Pressures Practice Problems

8. Dinitrogen tetroxide, in its liquid state, was used as one of the fuels on the lunar lander for the NASA Apollo missions. In its gas phase it decomposes to gaseous nitrogen: $N_2O_4(g) \leftrightarrow 2NO_2(g)$. Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71atm. Calculate the equilibrium pressure of $NO_2(g)$. (Ans: 0.600atm)

$$K_{\rho} = 0.133 \qquad N_{2}O_{4}(s) \Rightarrow 2NO_{2}(s) \qquad P_{NO_{2}} = 0.600 \text{ atm}$$

$$P_{N_{2}O_{4}} = 2.71 \text{ atm} \qquad K_{\rho} = \frac{(P_{NO_{2}})^{2}}{(P_{N_{2}O_{4}})}$$

$$K_{\rho} = 0.133 = \frac{(P_{NO_{2}})^{2}}{(P_{N_{2}O_{4}})}$$

$$(0.133)(2.71) = (P_{NO_{2}})^{2}$$

$$P_{N_{3}} = \sqrt{(0.133)(2.71)} = 0.600 \text{ atm}$$

Equilibrium	l
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9. At a certain temperature a 1.00L flask initially contained 0.298mol $PCl_3(g)$ and 8.70x10⁻³ mol $PCl_5(g)$. After the system had reached equilibrium, $2.00x10^{-3}$ mol $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction: $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$. Calculate the equilibrium concentrations of all species and the value of K.

(Ans:
$$[Cl_2] = 2.00 \times 10^{-3} M$$
, $[PCl_3] = 0.300 M$, $[PCl_5] = 6.70 \times 10^{-3} M$, and $K = 8.96 \times 10^{-2} M$)

[PCl₃]₀ = $\frac{0.298 \text{ M}}{1 \text{ L}}$ = $\frac{0.298 \text{ M}}{1 \text{ L}}$ = $\frac{8.76 \times 10^{-3} \text{ M}}{1 \text{ L}}$ = $\frac{8.70 \times 10^{-3} \text{ A}}{1 \text{ L}}$ = $\frac{2.00 \times 10^{-3} \text{ M}}{1 \text{ L}}$ = $\frac{2.00 \times$

Equilibrium
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10. Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700K, the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000mol of each component is mixed in a 1.000L flask. (Ans: $[CO] = [H_2O] = 0.613M$ and $[CO_2] = [H_2] = 1.387M$)

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11. Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15x10² at a certain temperature. In a particular experiment, 3.000mol of each component was added to a 1.500L flask. Calculate the equilibrium concentrations of all species.

(Ans:
$$[H_2] = [F_2] = 0.472M$$
 and $[HF] = 5.056M$)

 $K_c = 1.15 \times 10^2$
 $[HF] = \frac{3.0}{1.5} = \frac{2.000M}{2.000M}$
 $R = \frac{1}{1.5} = \frac{2.000M}{2.000M}$
 $R = \frac{1.15}{1.5} = \frac{0.471}{0.471}$
 $R = \frac{1.15}{1.5} = \frac{0.471}{0.47$

	Equilibrium	
Equilibrium RICE Tables	Topic#8	

12. (OYO) Assume gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant 1.00×10^2 . Suppose HI at 5.000×10^{-1} atm, H₂ at 1.000×10^{-2} atm, and I₂ at 5.000×10^{-3} atm are mixed in a 5.000L flask. Calculate the equilibrium pressure of all species. (Ans: $P_{\rm H1} = 4.29 \times 10^{-1}$ atm, $P_{\rm H2} = 4.55 \times 10^{-2}$ atm, and $P_{\rm I2} = 4.05 \times 10^{-2}$ atm)

	Equilibrium	
LeChatelier's Principle	 Topic#8	

Le Chatielier's Principle

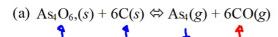
- A system at equilibrium when stressed will compensate for the stress and return to equilibrium.
- Stresses include addition/removal of heat (change in *T*), change in pressure (changed by changing volume), change in concentration of a reactant or product.
 - an addition of a species/heat will force the reaction to shift away from the stress in an effort to re-establish equilibrium.
 - a removal of a species/heat will force the reaction to shift towards the stress in an effort to reestablish equilibrium.
 - a decrease in volume will force the reaction to shift towards the side with the least total gaseous moles in an effort to re-establish equilibrium.
 - an increase in volume will force the reaction to shift towards the side with the most total gaseous moles in an effort to re-establish equilibrium.
 - the value of K_{eq} can ONLY be changed by a change in temperature. Each value of K is dependent on the temperature of the reaction.

Equilibrium

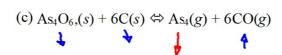
LeChatelier's Principle

Topic#8 (Topic)

- 13. Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid As_4O_6 , which is then reduced using carbon. $As_4O_6(s) + 6C(s) \Leftrightarrow As_4(g) + 6CO(g)$ Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions. K= [Asy][co]"
 - (a) Addition of carbon monoxide
 - (b) Addition or removal of carbon or tetraarsenic hexoxide (As₄O₆)
 - (c) Removal of gaseous arsenic (As₄)



(b) $A_{S_4}O_{6,s}(s) + 6C(s) \Leftrightarrow A_{S_4}(g) + 6CO(g)$



Equilibrium

LeChatelier's Principle

Topic#8 (Topic)

- 14. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.
 - (a) The preparation of liquid phosphorus trichloride by the reaction: $P_4(s) + 6Cl_2(g) \Leftrightarrow 4PCl_3(l)$
 - (b) The preparation of gaseous phosphorus pentachloride according to the equation:

 $PCl_3(g) + Cl_2(g) \Leftrightarrow PCl_5(g)$

(c) The reaction of phosphorus trichloride with ammonia: $PCl_3(g) + 3NH_3(g) \Leftrightarrow P(NH_2)_3(g) + 3HCl(g)$

15. For each of the following reactions, predict how the value of *K* changes as the temperature is increased.

(a)
$$\mathbb{N} + N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$$

$$\Delta H = 181 \text{ kJ}$$

(b)
$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g) + 198$$

$$\Delta H = -198 \text{kJ}$$

	Equilibriun	ı _			
LeChatelier's Principle	Topic#8	key:	unchanged	increases	decreases

16. (OYO) For the reaction, $2SC_2(g) + O_2(g) \Leftrightarrow 2SO_3(g) + \text{heat}$, identify the direction the reaction will shift to alleviate the stress. Determine whether each of the species in the reaction will increase/decrease in concentration.

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g) + heat$$

	shift	$[SO_2]$	$[O_2]$	$[SO_3]$	K
a. Addition of O ₂ .					
b. Addition of SO ₃ .					
c. Decrease in temperature.					
d. Increase in temperature.					
e. Decrease in volume of container.					
f. Increase in the volume of the container.					
g. Addition of SO ₂ .					
h. Removal of SO ₃ .					
i. Removal of O ₂ .					
j. Addition of CO ₂					

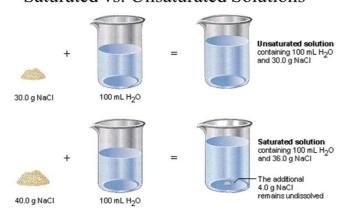
Solubility
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Solubility Equilibrium K_{sp}

Equilibrium Intro

Solubility Topic#8

Saturated vs. Unsaturated Solutions



Unsaturated Solution

 $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ *below saturation point, all of the solute dissoves,

Saturated Solution

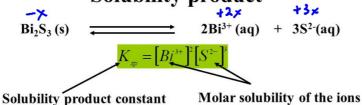
no equilibrium

 $NaCl(s) \Leftrightarrow Na^+(aq) + Cl^-(aq)$

*an equilibrium has been established between the ions and solid

Formulas Solubility
Topic#8

Solubility product



Remember that we are dealing with molar solubilities and not concentration.

For a **saturated solution**, molar solubility is equal to molar concentration.

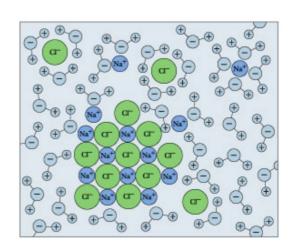
*For every 1M of $Bi_2S_3(s)$ that dissolves 2M of $Bi^{3+}(aq)$ and 3M of $S^{2-}(aq)$ are created.

 $K_{7p} = (2x)^{2}(3x)^{3}$ $(4x^{2})(27x^{3})$ $10x^{3}$ $\mu = (x)(x) = x^{2}$ $K = (2x)^{2}(x) = 4x^{3}$ $K = (3x)^{3}(x) = 27x^{4}$ $K(3x)^{2}(2x)^{3} = 108x^{5}$

Solubility Topic#8

Types of Solutions

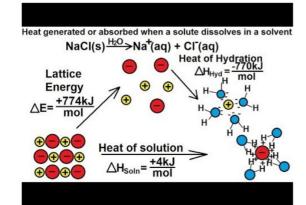
- Even though we determine a compound to be insoluble, it does have a solubility, but it is very low.
- Solubility is defined as "greater than 3 grams per 100mL of water."
- A solution must be saturated to do solubility equilibrium problems.
 - A **saturated** solution must have some of the solute at the bottom of the container.
 - An **unsaturated** solution has no solute on the bottom of the container.
 - A supersaturated solution has more solute per 100mL of water than it should at the specified temperature. This type of solution also has no solute at the bottom. Process: heat solvent (water) and create a saturated solution at this high temperature. Poor of supernatent (water above solid) and then cool slowly. The new cooled solution is supersaturated.



Animation of Dissolution

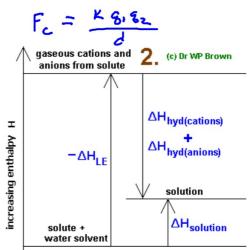
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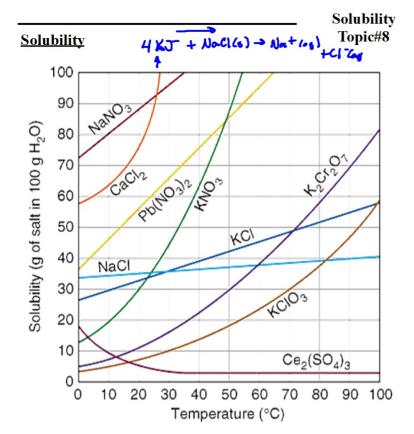
Solubility

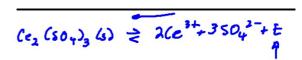


	Lattice Energy	Hydration Energy	Solubility in Water
Compound	(kJ/mol)	(kJ/mol)	g/100 mL
LiC1	834	-884	63.7 (0°C)
NaC1	774	-760	35.7 (0°C)
KC1	7D1	-685	34.7 (20 ℃)
RbC1	680	-664	77 (0°C)
CsC1	657	-640	162 (0°€)
LiF	1032	-1005	0.3 (18°C)
KF	813	-819	92.3 (18 ℃)
KI	632	-617	127 (0°C)
RbF	776	-792	130.6 (18°C)
SrCl ₂	2110	-2161	53.8
AgC1	916	-851	8.9 x 10-5

Solubility Topic#8







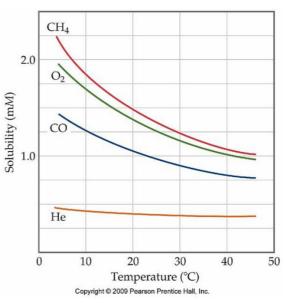


TABLE 11.2 Some Enthalpies and Entropies of Solution in Water at 25°C

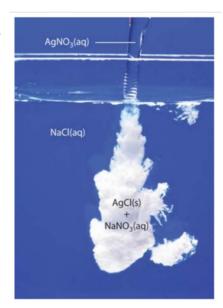
Solubility Topic#8

Solubility

- Slightly soluble salts create a dynamic equilibrium in a saturated solution.
 - For Example: a solution of AgNC₃ and NaCl are mixed creating AgCl (generally, all silver (I) compounds are insoluble).
 - solid AgCl is formed, no ions initially present
 - as the salt disolves, cations (Ag⁺) and anions (Cl⁻) are created
 - [Ag⁺] and [Cl⁻] increase until equilibrium is established (a saturated solution)
 - $K_{\rm sp}$ is the product of the ions in solution.
 - For a saturated solution of AgCl the net ionic equation is $AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq)$
 - $K_{\rm sp} = [{\rm cation}]^n [{\rm anion}]^m$ where n and m are the coefficients of the ions in solution (net ionic equation)

$$K_{\rm sp} = [{\rm Ag^+}][{\rm Cl}^-] = 1.8 \times 10^{-10} \text{ (very low indeed!)}$$

- AgCl(s) is not appear in solubility equilibrium expression.



Solubility	Solubility Topic#8	
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Solubility Rules

- (1) nitrate salts are ALL soluble
- (2) alkali metal and ammonium salts are ALL soluble
- (3) chlorides, bromides, and iodides salts are mostly soluble (Dirty 3: Ag1+, Pb2+, and Hg22+)
- (4) sulfate salts are mostly soluble (Except BaSO₄, CaSO₄, PbSO₄, and Hg₂SO₄)
- (5) hydroxides are mostly insoluble (Except: NH₄OH, LiOH, NaOH, KOH, RbOH, CsOH, Ca(OI₂, Sr(OH)₂, and Ba(OH)₂)
- (6) sulfides (S²⁻), carbonates (CO₃²⁻), chromates (CrO₄²⁻), and phosphates (PO₄³⁻) are insoluble

Equilibrium Sample WS#2 - Solubility Equilibrium Solubility Practice Problems

1. Determine the solubility of each of the following compounds who	en placed in water. Write a yes or no and the number
of the rule you used to come to your conclusion.	

a. KBr d. sodium acetate
b. PbCO₃ e. silver (I) iodide

c. zinc (II) hydroxide f. cadmium (II) sulfide

Solubility
Topic#8

Solubility Expression (K_{sp})

Solubility Expression (K_{sp}) Practice Problems

- 2. Write the $K_{\rm sp}$ expression for the each of the following solubility equations:
 - a. $CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^{-}(aq)$
 - b. $Ag_2CrO_4(s) \leftrightarrow 2Ag^{1+}(aq) + CrO_4^{2-}(aq)$
 - c. $CaC_2O_4(s) \leftrightarrow Ca^{2+}(aq) + C_2O_4^{2-}(aq)$

(C.)
$$K_{5p} = \left[\left(\frac{2\pi}{a^{2}} \right) \left[\left(\frac{1}{2} O_{4}^{2} \right) \right] \right]$$

Solubility
Topic#8

Solubility Expression (K_{sp})

Determining K_{sp} from Experimental Measurements.

- Use RICE table to determine the amount of each ion after equilibrium has been established.
- Substitute concentrations and solve for $K_{\rm sp}$.

K_{sp} Value Practice Problems

3. Calculate the $K_{\rm sp}$ of lead (II) chloride if the lead concentration is $1.62 \times 10^2 M$. (Ans: 1.70×10^5)

Equation:
$$Pb(l_{2} l_{3}) = Pb^{2}(q_{1}) + 2(1-(q_{1}))$$

Change: $-x$ $+x$ $+2x$
 $[Pb^{2+}] = x = 1.62 \times 10^{-2} M$ $Ksp = [Pb^{2+}][C1-]^{2}$
 $[C1] = 2x = 2(1.62 \times 10^{-2})$
 $= 0.0324M$ $Ksp = (1.62 \times 10^{-2})(0.0324)^{3}$
 $= [1.7 \times 10^{-5}]$

	Solubility	
Solubility Expression (K _{sp})	Topic#8	

Determining K_{sp} from Experimental Measurements.

- Use RICE table to determine the amount of each ion after equilibrium has been established.
- Substitute concentrations and solve for K_{sp} .
- 4. (OYO) Calculate the $K_{\rm sp}$ value for bismuth (III) sulfide, which has a solubility of $1.0 \times 10^{-15} \text{mol/L}$ at 25° C. (Ans: 1.1×10^{-73})

Solubility
Topic#8

Solubility Expression (K_{sp})

Estimating Salt Solubility from $K_{\rm sp}$.

- Set up x as the amount of salt that dissolves.
- Use -x and +x in RICE table to solve the amounts of the cations and anions in solution.
- 5. The $K_{\rm sp}$ value for copper (II) iodate, Cu(IC₃)₂, is 1.4x10⁻⁷ at 25°C. Calculate its solubility at 25°C.

Equation:
$$Cu(IO_8)_2(s) \ge Cu^{2s}(a_2) + 2IO_3(a_2)$$
 (Ans: 3.3x10⁻³ mol/L)
+x +2x
+x +2x
Ksp = $[Cu^{2s}][IO_3^{-1}]^2 = 1.4 \times 10^{-7}$
(x) $(2x)^2 = 1.4 \times 10^{-7}$
4 $x^3 = 1.4 \times 10^{-7}$
 $x = \sqrt[3]{\frac{1.4 \times 10^{-7}}{4}} = \sqrt[3.3 \times 10^{-3} \text{ M}$
 $x = \sqrt[3]{\frac{1.4 \times 10^{-7}}{4}} = \sqrt[3.3 \times 10^{-3} \text{ M}$
 $x = \sqrt[3]{\frac{1.4 \times 10^{-7}}{4}} = \sqrt[3.3 \times 10^{-3} \text{ M}$

	Solubility	
Solubility Expression (K _{sp})	Topic#8	

Estimating Salt Solubility from K_{sp} .

- Set up x as the amount of salt that dissolves.
- Use -x and +x in RICE table to solve the amounts of the cations and anions in solution.
- 6. (OYO) The K_{sp} value for cobalt (II) phosphate, $Co_3(PO_4)_2$, is 1.4×10^{-37} at 25°C. Calculate its solubility at this temperature. At equilibrium, what are the concentrations of each ion? (Ans: $1.7 \times 10^{-8} M$, $[Co^{2+}] = 5.0 \times 10^{-8} M$, and $[PO_4^{3-}] = 3.3 \times 10^{-8} M$)

Solubility
Topic#8

Solubility Expression (K_{sp})

Estimating Salt Solubility from K_{sp}.

- Set up x as the amount of salt that dissolves.
- Use -x and +x in RICE table to solve the amounts of the cations and anions in solution.
- 7. Order the following salts based on their relative solubilities: CuS $(K_{sp} = 8.5 \times 10^{-45})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$, and Bi₂S₃ $(K_{sp} = 8.1 \times 10^{-73})$ (Ans: (most) Bi₂S₃ > Ag₂S > CuS (least))

 | Order the following salts based on their relative solubilities: CuS $(K_{sp} = 8.5 \times 10^{-45})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$, and Bi₂S₃ $(K_{sp} = 8.1 \times 10^{-73})$ (Ans: (most) Bi₂S₃ > Ag₂S > CuS (least))

 | Order the following salts based on their relative solubilities: CuS $(K_{sp} = 8.5 \times 10^{-49})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$, and Bi₂S₃ $(K_{sp} = 1.6 \times 10^{-49})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$, and Bi₂S₃ $(K_{sp} = 1.6 \times 10^{-49})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$, and Bi₂S₃ $(K_{sp} = 1.6 \times 10^{-49})$, Ag₂S $(K_{sp} = 1.6 \times 10^{-49})$

Solubility

Solubility Expression (K_{sp}) and Common Ion

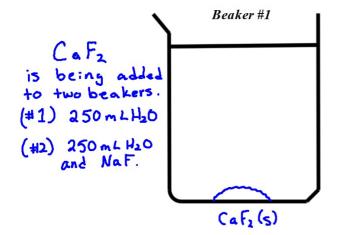
Topic#8

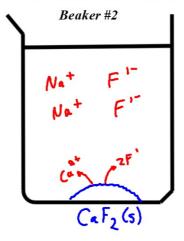
Ksp = [Car][F]2

- Common Ion using K_{sp} . • The solvent already has ions in it. One of which is a common ion with the insoluble solid.
- Set up x as the amount of salt that dissolves.

(aF2(5) = (a2++2)

- The initial amount for at least one of the ions has a value other than zero
- Use -x and +x in RICE table to solve the amounts of the cations and anions in solution.





Since beaker (2) has F' ions already in solution, the amount of CaFz that will dissolve decreases. So, [(a2) in beaker (2) will be lower than [Ca2] in beaker (1). This is called the Common ion effect.

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Solubility Expression (K_{sp}) and Common Ion

Topic#8

Common Ion using K_{sp}.

- The solvent already has ions in it. One of which is a common ion with the insoluble solid.
- Set up x as the amount of salt that dissolves.
- The initial amount for at least one of the ions has a value other than zero
- Use -x and +x in RICE table to solve the amounts of the cations and anions in solution.

Common Ion Practice Problems

8. The $K_{\rm sp}$ for silver carbonate is 8.4 x 10⁻¹². The concentration of carbonate ions in a saturated solution is 1.28 x 10⁻⁴ M. What is the concentration of silver ions? (Ans: Ans: 2.56x10⁻⁴ M)

Equation:
$$A_{2}(O_{3}(s) = 2A_{9}^{1}(O_{1}) + CO_{3}^{2}(O_{2})$$

 $[CO_{3}^{2}] = x = 1.28 \times 10^{-4} \text{ M}$
 $[A_{9}^{+}] = 2x = 2(1.28 \times 10^{-4}) = 2.56 \times 10^{-4} \text{ M}$

Solubility Topic#8

Solubility Expression (K_{sp}) and Common Ion

[Ca P2] = 6.3 ×10 M

9. Calculate the solubility of solid CaF_2 ($Ksp = 4.0x10^{-11}$) in a 0.025M NaF solution. (Ans: $6.4x10^8$)

$$K_{3p} : 4.0 \times 10^{-11} \qquad R: CaF_{2}(s) \Rightarrow Ca^{2+}(aq) + 2F^{2}(aq) \qquad [CaF_{2}] = 6.8 \times 10^{-8} \text{M}$$

$$[NaF] = [F'] = 0.025M \qquad T: \qquad 0.025$$

$$C: - \times \qquad + \times \qquad + 2 \times \qquad 2 \times + 0.025 \qquad 0.01500000$$

$$Solve: \qquad K_{5p} = [Ca^{2+}][F^{-}]^{2}$$

$$4.0 \times 10^{-11} = (\times)(2 \times + 0.025)^{2}$$

$$X = \frac{4.0 \times 10^{-11}}{(0.025)^{2}} = 6.4 \times 10^{-8} \text{M}$$

* Since the ksp < 1.0x10.4, we can eliminate the (2x) because the addition of (2x) to 0.625 will be negligible and will be eliminated through sig figs.

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Solubility Expression (K _{sp}) and Common Ion	Solubility Topic#8		
10. (OYO) The $K_{\rm sp}$ for Ca(OH) ₂ is known to be 4	.68x10 ⁻⁶ . What is th	e solubility of Ca(OH	I) ₂ in 0.0860 M

(Ans: 1.58x10⁻⁴M)

Ba(OH)₂?

Solubility	
Tonic#8	

Precipitation Reactions

With some knowledge of the reaction quotient (Q), we can decide

- $Q < K_{sp}$, the system is not at equilibrium (*uns*aturated)
- $Q = K_{sp}$, the system is at equilibrium (saturated)
- $Q > K_{sp}$, the system is not at equilibrium (*super*saturated)

Precipitates form when the solution is supersaturated!!!!

K_{sp} vs. Q Practice Problems 11. A solution is prepared by adding 750.0mL of $4.00 \times 10^3 M$ Ce(NO₃)₃ to 300.0mL of $2.00 \times 10^{-2} M$ KIO₃ Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution? (Ans: yes; $Q > K_{sp}$) 750 mL x 4.00 x103 M (e3+ R: (e(IO3)36) = (e(i)+310, (e1)
= 3.0 mml (e3+)
-x +x +3x
300 mLx 2.00 x0-2 M IO3 - Q = ((e3+)(IO3-)3 = 6 mmd JO; SOLVE: VT = 750+300 = 1050 mL

Solubility 25 mmol F - 3.0mmd = 22 mml F [F] = 22 mml = 0.0551 **Precipitation Reactions** 12. A solution is prepared by mixing 150.0mL of $1.00 \times 10^{2} M \,\mathrm{Mg}(\mathrm{NO}_3)_2$ and 250.0mL of $1.00 \times 10^{-1} M \,\mathrm{NaF}$. Calculate the concentrations of Mg²⁺ and F⁻ at equilibrium with solid MgF₂. $(K_{\rm sp} = 6.4 \times 10^{-9})$. (Ans: $[{\rm Mg^{2+}}] = 2.1 \times 10^{-6} M$ and $[{\rm F^-}] = 5.50 \times 10^{-2} M$) 150.0 ML X 1.00×10-2 Mg2+ [Mg = 2.1x10-6 M = 1.5 mmd Mgs Mg F2 (8) ≥ Mg2+(42)+2F-(42) 250.0 mL x 1.88 x 10 - MF [F]: 0.055 M = 25 mmol F Ksp = [Mg =] [F] number 25mml $6.4 \times 10^{-9} = (x)(0.055)^{2}$ $X = \frac{6.4 \times 10^{-9}}{(0.055)^{2}} = 0.1 \times 10^{-6} = [M_{3}^{2+}]$ [F] = 0.055 + 2 (21×10-6) = 0.055 0042

Solubility
Topic#8

Precipitation Reactions

Selective precipitation involves a solution containing to ions. The process involves adding an ion into solution that makes an insoluble ionic compound with BOTH of the ions in solution. The Ksp's of these insoluble ionic compounds will be magnitudes in difference, so we can predict which will precipitate out first and the concentration of the added ion at the point of precipitation.

13. A solution contains $1.0 \times 10^{-4} M$ Cu⁺ and $2.0 \times 10^{-3} M$ Pb²⁺. If a source of I⁻ is added gradually to this solution, will PbI₂ ($K_{\rm sp} = 1.4 \times 10^{-8}$) or CuI ($K_{\rm sp} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I⁻ necessary to begin precipitation of each salt.