CHEMISTRY

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Last class..

❑ Thermodynamics and chemical equilibrium

❑ CLA 1 - ??

In this class

❑ Thermodynamics and chemical equilibrium, continuation

Chemical Equilibrium & Thermodynamics

Equilibrium and Thermodynamics

Free Energy and Equilibrium
➢ Relate Equilibrium constant to the energetics (ΔH & ΔS) of a reaction
➢ Equilibrium constant depends on ΔG:
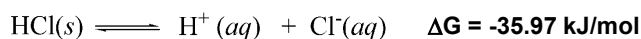
$\Delta G° = $ -RT ln K_{eq}

$$K = e^{-\Delta G^o / RT}$$

where
> **R (gas constant) = 8.314472 J/(K·mol)**
> **T = temperature in kelvins**

➢ The more negative ΔG → larger equilibrium constant
➢ Example : Why HCl is easily ionized ?

$$HCl(s) \rightleftharpoons H^+(aq) + Cl^-(aq) \qquad \Delta G = -35.97 \text{ kJ/mol}$$

$$K = e^{-\Delta G^o / RT} = e^{-(-35.97 \, x10^3 \, J/mol)(8.314472J/(K·mol)(298.15K)} = 2.00 \, x10^6$$

Because K is very large, HCl is very soluble in water and nearly completely ionized
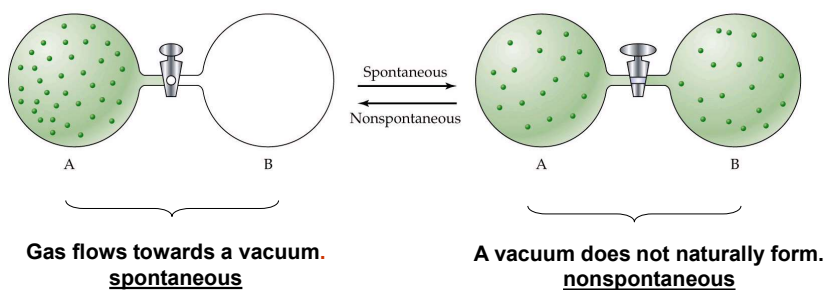
Chemical Equilibrium

Equilibrium and Thermodynamics

Free Energy and Equilibrium
- If ΔG^o is negative or K >1 the reaction is spontaneous
  - **Reaction occurs by just combining the reactants**

- If ΔG^o is positive or K < 1, the reaction is <u>not</u> spontaneous
  - **Reaction requires external energy or process to proceed**

Spontaneous

Nonspontaneous

A   B   A   B

Gas flows towards a vacuum.
<u>**spontaneous**</u>

A vacuum does not naturally form.
<u>**nonspontaneous**</u>

Criteria, reaction

❑ When a reaction is **<u>favored by both enthalpy ($\Delta H_o < 0$) and entropy ($\Delta S_o > 0$)</u>**, there is no need to calculate the value of ΔG_o to decide whether the reaction should proceed.

❑ The same can be said for reactions favored by neither enthalpy **<u>($\Delta H_o > 0$) nor entropy ($\Delta S_o < 0$).</u>**

❑ Free **<u>energy calculations become important for reactions favored by only one of these factors</u>**.

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VARIATION OF ΔG IN RELATION WITH Δ H & Δ S

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K$$

Enthalpy Change	Entropy Change	Spontaneous Reaction?
Exothermic (ΔH < 0)	Increase (ΔS > 0)	Yes, ΔG < 0
Exothermic (ΔH < 0)	Decrease (ΔS < 0)	Only at low temps, if |T ΔS| < |ΔH|
Endothermic (ΔH > 0)	Increase (ΔS > 0)	Only at high temps, if |TΔS| >|ΔH|
Endothermic (ΔH > 0)	Decrease (ΔS < 0)	No, ΔG > 0

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▶ If ΔH is positive and ΔS is negative, ΔG will always be positive regardless of temperature. For example: $3O_2(g) \longrightarrow 2O_3(g)$; $\Delta H° = 285.4$ kJ mol^{-1}, $\Delta S° = -137.5$ J mol^{-1}.

▶ If ΔH is negative and ΔS is positive, ΔG will always be negative regardless of temperature. For example: $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$; $\Delta H° = -196.5$ kJ mol^{-1}, $\Delta S° = 166.8$ J mol^{-1}.

▶ If both ΔH and ΔS are both negative, then ΔG will be negative at low temperatures and become positive at high temperatures. The temperature at which ΔG crosses over from negative to positive depends upon the relative magnitude of ΔH and ΔS. For example: $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$; $\Delta H° = -177.0$ kJ mol^{-1}, $\Delta S° = -285.11$ J mol^{-1}.

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Chemical Equilibrium

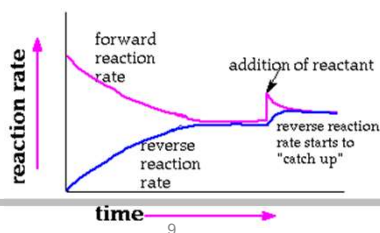## SRM

Le Châtelier's Principle

1.) What Happens When a System at Equilibrium is Perturbed?
   - Change concentration, temperature, pressure or add other chemicals

Equilibrium is re-established
**Reaction accommodates the change in products, reactants, temperature, pressure, etc.
Rates of forward and reverse reactions re-equilibrate.**

Chemical Equilibrium

SRM

Le Châtelier's Principle

Effect of Temperature on Equilibrium

Combine Gibbs free energy and Equilibrium Equations:

$$K = e^{-\Delta G^{\circ}/RT} = e^{-(\Delta H^{\circ} - T\Delta S)/RT}$$

$$= e^{-\left(\Delta H^{\circ}/RT + \Delta S/R\right)}$$

$$= e^{-\Delta H^{\circ}/RT} \cdot e^{\Delta S^{\circ}/R}$$

Only Enthalpy term is temperature dependent:

$$K(T) \propto e^{-\Delta H^{\circ}/RT}$$

Thermodynamics & equilibrium

❑ **Calculating Enthalpy Changes and Entropy Changes from the Change in K_{eq} with Temperature**

$$\Delta G^o = - RT \ln K_{eq}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$- RT \ln K_{eq} = \Delta H^o - T\Delta S^o$$

$$\ln K_{eq} = - \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

A graph of **lnK (y-axis) vs. 1/T (x-axis) has a slope related to the standard enthalpy change and a y-intercept related to the standard entropy change** for the equilibrium. Once the values of ΔH^o and ΔS^o are both known, it is a relatively trivial process to find ΔG^o using the following expression.

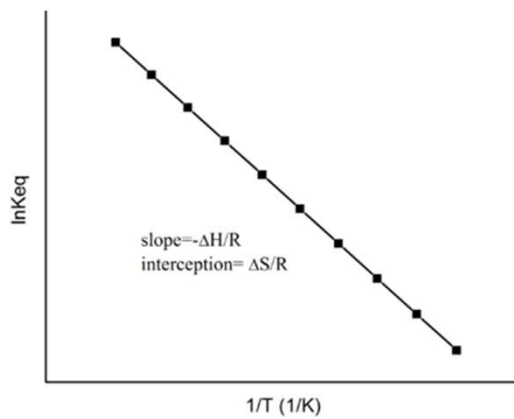**Calculating Enthalpy Changes and Entropy Changes from the Change in K_{sp} with Temperature**

❑ To determine H^o and S^o, plot $\ln K_{eq}$ vs 1/T. The resulting straight line will have a slope equal to $-H^o/R$ and an intercept equal to S^o/R.
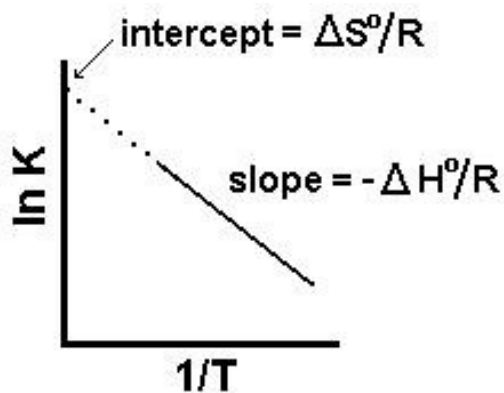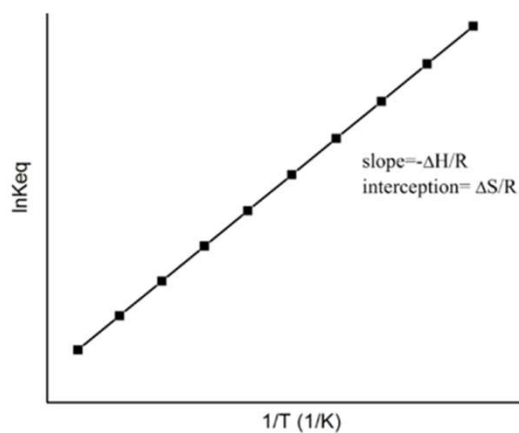
❑ For an endothermic reaction, ΔH > 0 (and the gas constant R > 0), so slope is less than 0. Thus, for an endothermic reaction, the van't Hoff plot should always have a negative slope.

❑ For an exothermic reaction, ΔH < 0 . Thus, for an exothermic reaction, the van't Hoff plot should always have a positive slope.

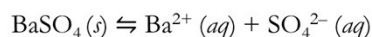## Solubility Equilibrium (K_{sp})

❑ In saturated solutions dynamic equilibrium exists between undissolved solids and ionic species in solutions

❑ Solids continue to dissolve and ion-pairs continue to form solids.

❑ The rate of dissolution process is equal to the rate of precipitation.

$$BaSO_4\,(s) \leftrightharpoons Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq)$$

The solubility-product expression for $BaSO_4$, $K_{sp} = [Ba^{2+}]\,[SO_4{}^{2-}]$

- The equilibrium constant indicates how soluble the solid is in water and is referred to as the **solubility-product constant** (or simply the **solubility product**). It is denoted K_{sp}, where sp stands for solubility product.
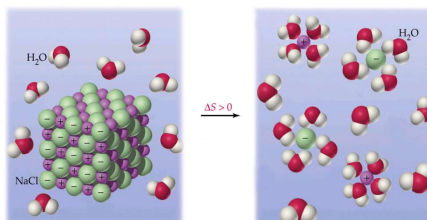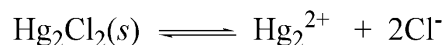
Solubility Equilibrium

Solubility Product

1.) Equilibrium constant for the reaction which a solid salt dissolves to give its constituent ions in solution

➢ Solid omitted from equilibrium constant because it is in a standard state
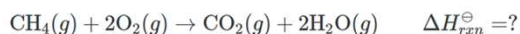

➢ Example:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2{}^{2+} + 2Cl^-$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.2 \times 10^{-18}$$

CALCULATION OF ENTHALPY

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^{\ominus}_{rxn} = ?$$

In order to calculate the standard enthalpy of reaction, we need to look up the standard enthalpies of formation for each of the reactants and products involved in the reaction. These are typically found in an appendix or in various tables online. For this reaction, the data we need is:

$$\Delta H^{\ominus}_f\{CH_4(g)\} = -75 \text{ kJ/mol}$$

$$\Delta H^{\ominus}_f\{O_2(g)\} = 0 \text{ kJ/mol}$$

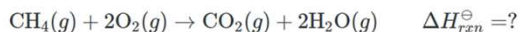$$\Delta H^{\ominus}_f\{CO_2(g)\} = -394 \text{ kJ/mol}$$

$$\Delta H^{\ominus}_f\{H_2O(g)\} = -284 \text{ kJ/mol}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^{\ominus}_{rxn} = ?$$

Note that because it exists in its standard state, the standard enthalpy of formation for oxygen gas is 0 *kJ/mol*. Next, we sum up our standard enthalpies of formation. Keep in mind that because the units are in kJ/mol, we need to multiply by the stoichiometric coefficients in the balanced reaction equation.

$$\sum \Delta H^{\ominus}_f\{products\} = \Delta H^{\ominus}_f\{CO_2(g)\} + \Delta H^{\ominus}_f\{H_2O(g)\}$$
$$= (1)(-394) + (2)(-284) = -962 \text{ kJ/mol}$$

$$\sum \Delta H^{\ominus}_f\{reactants\} = \Delta H^{\ominus}_f\{CH_4(g)\} + \Delta H^{\ominus}_f\{O_2(g)\}$$
$$= (1)(-75) + (2)(0) = -75 \text{ kJ/mol}$$

Now, we can find the standard enthalpy of reaction:

$$\Delta H^{\ominus}_{rxn} = \sum \Delta H^{\ominus}_f\{products\} - \sum \Delta H^{\ominus}_f\{reactants\}$$
$$= (-962) - (-75) = -887 \text{ kJ/mol}$$

ΔHº is +ve when reaction is endothermic
ΔHº is −ve when reaction is exothermic

CALCULATION OF ENTROPY

The standard entropy (ΔS^o) of a substance is the value of entropy of the substance at 298 K and 1 atm.

$$CH_4(g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$$

From the Table of Thermodynamic Data, the Standard entropies of the substances involved in the above reaction are:

substances	ΔS (J/K.mol)
$CH_4(g)$	186
$O_2(g)$	205
$CO_2(g)$	214
$H_2O(l)$	70

The entropy change of the reaction can be calculated as:

$\Delta S^o_{reaction} = \Sigma n_p S(\text{products}) - \Sigma n_r S(\text{reactants})$

$\Delta S^o = [214 + 70 * 2] - [186 + 205 * 2] = -242$ J/K
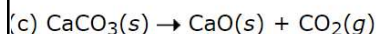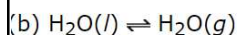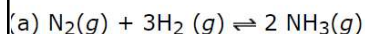
Thermodynamic Laws: Outcomes

❑ **The Zeroth Law** deals with thermal equilibrium and provides a means for measuring temperatures.

❑ **The First Law** deals with the conservation of energy and introduces the concept of internal energy.

❑ **The Second Law** of thermodynamics provides with the guidelines on the conversion of internal energy of matter into work. It also introduces the concept of entropy.

❑ **The Third Law** of thermodynamics defines the absolute zero of entropy. The entropy of a pure crystalline substance at absolute zero temperature is zero.

Problems

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Which of the following processes will lead to an increase in the entropy of the system?

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

(b) $H_2O(l) \rightleftharpoons H_2O(g)$

(c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(d) $NH_4NO_3(s) + H_2O(l) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

2. A sample of gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work (in joules) done by the gas if it expands (a) against a vacuum and (b) against a constant external pressure of 1.2 bar.

Solution – Problem 1

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A) Because the total number of molecules decreases in this reaction, the system becomes more ordered. The entropy of the system therefore **decreases.**

(b) Gases are more disordered than the corresponding liquids, so the entropy of the **system increases**.

(c) Reactions in which a compound decomposes into two products lead to an **increase in entropy** because the system becomes more disordered. The increase in entropy in this reaction is even larger because the starting material is a solid and one of the products is a gas.

(d) The NH_4^+ and NO_3^- ions are free to move in a random fashion through the aqueous solution, whereas these ions are locked into position in the crystal. As a result, the entropy of the system **increases in this reaction**.

Solution – Problem 2

(a) Because the external pressure of a vacuum is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0 \text{ bar})(4.0 \text{ L}) = 0$$

(b) The external, opposing pressure is 1.2 bar, so

$$w = -P\Delta V = -(1.2 \text{ bar})(4.0 \text{ L}) = -4.8 \text{ L bar}$$

To convert the answer to joules, we write

$$w = -4.8 \text{ L bar} \times \frac{100 \text{ J}}{1 \text{ L bar}} = -4.8 \times 10^2 \text{ J}$$

Problem - 3

3. Using standard thermodynamic values, calculate the enthalpy of the reaction of the **combustion of butane gas with oxygen gas to form carbon dioxide and liquid water**.

ΔH_f $H_2O(l)$ = -285.83 kJ/mol
ΔH_f $CO_2(g)$ = -393.51 kJ/mol
ΔH_f $C_4H_{10}(g)$ = -61.87 kJ/mol

Solution – Problem 3

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❑ Chemical Equation:
  $2C_4H_{10}(g) + 13\ O_2(g) => 8\ CO_2(g) + 10\ H_2O(l) + heat$

$\Delta H_{rxn} = [8*(-285.83\ kJ) + 10\ (-393.51\ kJ)] - [(13*0\ kJ) + 2(-61.87\ kJ)] =$
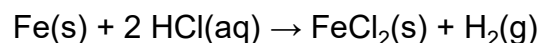
- 6093.41 kJ/mol

Problem 4

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❑ Using standard thermodynamic data, calculate the equilibrium constant at 298.15 K for the reaction shown below. Predict whether this reaction is feasible at this temperature and what does K value tells about the reaction?

$Fe(s) + 2\ HCl(aq) \rightarrow FeCl_2(s) + H_2(g)$

$\Delta G^0_f\ (FeCl_2) = -302.3\ kJ/mol$

$\Delta G^0_f\ (HCl) = -131.2\ kJ/mol$

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Solution – Problem 4

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Fe(s) + 2 HCl(aq) → FeCl₂(s) + H₂(g)
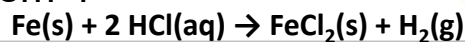
$$\Delta G^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$$
$$= (1 \text{ mol})(\Delta G_f^\circ[\text{FeCl}_2(s)]) - (2 \text{ mol})(\Delta G_f^\circ[\text{HCl(aq)}])$$
$$= (1 \text{ mol})(-302.3 \text{ kJ/mol}) - (2 \text{ mol})(-131.2 \text{ kJ/mol})$$
$$= -39.9 \text{ kJ}$$

$$\Delta G^\circ = -RT\ln K$$
$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-39.9\,\text{kJ/mol})}{(8.3145 \times 10^{-3}\text{ kJ/K}\cdot\text{mol})(298.15\text{ K})} = 16.1$$
$$K = e^{16.1} = 9.78 \times 10^6$$

The large negative ΔG° and K value tells us that the position of equilibrium for this reaction lies very far toward products.

Problem - 5

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Used the below information to determine if $NH_4NO_{3(s)}$ will dissolve in water at room temperature.

Compound	ΔH_f^o	ΔS_f^o
$NH_4NO_{3(s)}$	-365.56	151.08
$NH_{4(aq)}^+$	-132.51	113.4
$NO_{3(aq)}^-$	205.0	146.4

Solution - 5

$$NH_4NO_3(s) \xrightarrow{H_2O} NH_4(aq)^+ + NO_3(aq)^-$$
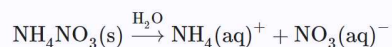
This would normally only require calculating ΔG^o and evaluating its sign. However, the ΔG^o values, they must be calculated manually from calculated ΔH^o and ΔS^o values for the reaction.

- *Calculate ΔH^o :*

$$\Delta H^o = \sum n\Delta H^o_{f_{products}} - \sum m\Delta H^o_{f_{reactants}}$$

$$\Delta H^o = \left[(1 \; mol \; NH_3)\left(-132.51 \; \frac{kJ}{mol}\right) + (1 \; mol \; NO_3^-)\left(-205.0 \; \frac{kJ}{mol}\right)\right]$$

$$- \left[(1 \; mol \; NH_4NO_3)\left(-365.56 \; \frac{kJ}{mol}\right)\right]$$

$$\Delta H^o = -337.51 \; kJ + 365.56 \; kJ = 28.05 \; kJ$$

$$\Delta S^o = \sum n\Delta S^o_{f_{products}} - \sum S\Delta H^o_{f_{reactants}}$$

$$\Delta S^o = \left[(1 \; mol \; NH_3)\left(113.4 \; \frac{J}{mol \; K}\right) + (1 \; mol \; NO_3^-)\left(146.6 \; \frac{J}{mol \; K}\right)\right]$$

$$- \left[(1 \; mol \; NH_4NO_3)\left(151.08 \; \frac{J}{mol \; K}\right)\right]$$

$$\Delta S^o = 259.8 \; J/K - 151.08 \; J/K = 108.7 \; J/K$$

$$T_K = 25\,^oC + 273.15K = 298.15\ K$$

$$\Delta S^o = 108.7\ \cancel{J}/K \left(\frac{1\ kJ}{1000\ \cancel{J}}\right) = 0.1087\ kJ/K$$

$$\Delta H^o = 28.05\ kJ$$

Plug in ΔH^o, ΔS^o and T into Equation 1.7

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G^o = 28.05\ kJ - (298.15\ \cancel{K})(0.1087\ kJ/\cancel{K})$$

$$\Delta G^o = 28.05\ kJ - 32.41\ kJ$$

$$\Delta G^o = -4.4\ kJ$$

This reaction is spontaneous at room temperature since ΔG° is negative. Therefore NH$_4$NO$_3$(s) will dissolve in water at room temperature.

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.