

UNIT 11 – CHAPTER 6 STUDENT NOTES: THERMOCHEMISTRY

Calorimetry – Science of measuring heat

Terms

- **Heat Capacity** = heat absorbed/change in temperature

EX 1:	H ₂ O	C ₂ H ₅ OH
	Add 10 kJ of heat	Add 10 kJ of heat
	10 – 15°C	10 – 22°C

$$\text{Heat Capacity} = \frac{10 \text{ kJ}}{10 - 15} = \boxed{2 \frac{\text{kJ}}{^\circ\text{C}}}$$

$$\text{Heat Capacity} = \frac{10}{10 - 22} = \boxed{.83 \frac{\text{kJ}}{^\circ\text{C}}}$$

Specific Heat Capacity = heat capacity/gram

$$\text{H}_2\text{O} = 4.18 \text{ J/g} \cdot ^\circ\text{C}$$

Molar Heat Capacity = heat capacity/mole

$$\text{H}_2\text{O} = 75.2 \text{ J/mol} \cdot ^\circ\text{C}$$

ENTHALPY CHANGE: $\Delta H = \frac{q}{\text{MOLES CONSUMED}}$

$$\text{H}_2\text{O} = 18.0 \text{ cal/mol} \cdot ^\circ\text{C}$$

Heat capacities of common substances

H ₂ O = 4.18 J/g·°C	Aluminum = .897 J/g·°C
Iron = .412 J/g·°C	Carbon dioxide = .839 J/g·°C
Steel = .466 J/g·°C	Lead = .129 J/g·°C

Terms

- **Work** – Work = Force X Distance; Pressure X Δ Volume
- **Heat** – $q = m \cdot C_p \cdot \Delta t$ (Joules)
- **Internal Energy** – Sum of work and heat $E = q + w$ (-) work done by a gas – expansion
(+) work done to a gas - compression

Coffee-cup calorimetry – uses a simple polystyrene cup to measure heat exchange

EX 2: When 1.00 grams of calcium chloride is added to 50.0 grams of water in a coffee-cup calorimeter, it dissolves and the temperature rises from 25.00°C to 28.51°C. Assuming that all the heat given off by the reaction is transferred to the water, calculate the heat for this reaction. (Heat of solution)

$$q = M \cdot C \cdot \Delta t$$

$$q = (50 \text{ g}) (4.18) (3.51)$$

$$\boxed{q = 733.6 \text{ J}}$$

Example problems

1) Consider the following reaction: $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightleftharpoons 2 \text{NaNO}_3(\text{aq}) + \text{BaSO}_4(\text{s})$

Calculate the enthalpy change if 1.00 liter of each reactant at a concentration of 1.00 M is reacted to form the precipitate and the temperature of the solution goes from 25.0°C to 28.1°C and the density of the solution is 1.3 g/mL.

$$C_p = 4.18$$
$$1\text{L} + 1\text{L} = 2\text{L TOTAL} \quad \frac{1000\text{mL}}{1\text{L}} \times \frac{1.3\text{g}}{1\text{mL}} = 2600\text{g}$$
$$q = m C_p \Delta t$$
$$q = (2600\text{g})(4.18)(3.10^\circ\text{C}) = 33,643.6\text{J} \text{ or } \boxed{33.64\text{KJ}}$$

$$\begin{array}{l} 1\text{mol Ba}(\text{NO}_3)_2 \\ 1\text{mol Na}_2\text{SO}_4 \end{array} \quad \begin{array}{l} \text{EACH REACTANT} \\ \text{USED ENTIRE} \\ 1.0\text{MOLES} \end{array}$$
$$\Delta H = \frac{q}{\text{MOLES USED}}$$
$$\Delta H = \frac{33.64\text{KJ}}{1\text{mol USED}} = \boxed{-33.64\text{KJ/mol}}$$

2) The specific heat capacity of aluminum is 0.900 J/g · °C.

a) Calculate the energy needed to raise the temperature of an 850-gram block of aluminum from 22.8°C to 94.6°C. $q = m C_p \Delta t \rightarrow (850)(0.900)(71.8) = \boxed{54,927\text{J} \text{ or } 54.93\text{KJ}}$

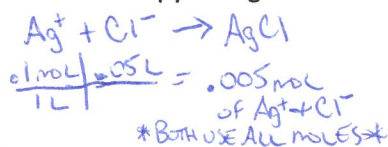
b) Calculate the molar heat capacity of aluminum.

$$M_{\text{H}_2} = \frac{0.900}{\frac{1}{27}} = \boxed{24.3 \frac{\text{J}}{\text{mol} \cdot ^\circ\text{C}}}$$

3) In a coffee-cup calorimeter, 50.0 mL of 0.100 M AgNO_3 and 50.0 mL of 0.100 M HCl are mixed to yield the following reaction: $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s})$

The two solutions were initially at 22.6°C and the final temperature is 23.4°C. Calculate the heat that accompanies this reaction. Assume that the combined solution has a mass of 100.0 grams and has a specific heat capacity of 4.17 J/g · °C. Calculate the enthalpy change for the reaction in kJ/mol.

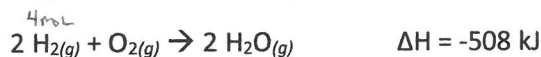
$$q = m C_p \Delta t$$
$$(100\text{g})(4.17)(.80^\circ\text{C}) = 333.6\text{J} \text{ or } \boxed{0.3336\text{KJ}}$$



$$\Delta H = \frac{0.3336\text{KJ}}{0.005\text{mol}}$$
$$\Delta H = \boxed{-66.72\text{KJ/mol}}$$

Thermochemical equation – a chemical equation that shows the enthalpy relation between products and reactants

EX 3: Consider the following thermochemical equation:



a) How much heat is evolved when 4 moles of H_2 are ignited?

$$\frac{4\text{mol H}_2}{2\text{mol H}_2} \times \frac{508\text{KJ}}{1} = \boxed{1,016\text{KJ} \text{ EMITTED}}$$

b) How much heat is evolved when 20.0 grams of H_2O is produced?

$$\frac{20.0\text{g H}_2\text{O}}{18\text{g H}_2\text{O}} \times \frac{1\text{mol H}_2\text{O}}{2\text{mol H}_2\text{O}} \times \frac{508\text{KJ}}{1} = \boxed{282.2\text{KJ}}$$

c) How much heat is evolved when 10.0 grams of H_2 and 20.0 grams of O_2 react?

$$\frac{10.0\text{g H}_2}{2\text{g H}_2} \times \frac{1\text{mol H}_2}{2\text{mol H}_2} \times \frac{508\text{KJ}}{1} = 1,270\text{KJ}$$

$$\frac{20.0\text{g O}_2}{32\text{g O}_2} \times \frac{1\text{mol O}_2}{2\text{mol O}_2} \times \frac{508\text{KJ}}{1} = \boxed{317.5\text{KJ}}$$

Hess's Law – The change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

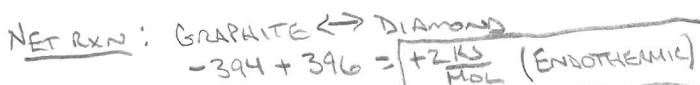
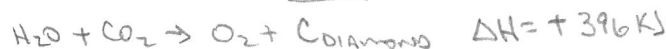
EX 4: Calculate the heat change for the conversion of graphite to diamond using the following information:

$$H_{\text{combustion (graphite)}} = -394 \text{ kJ/mole}$$

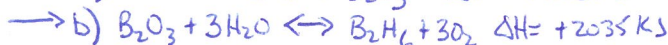
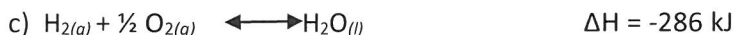
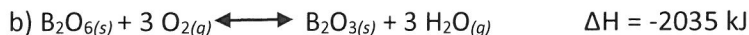
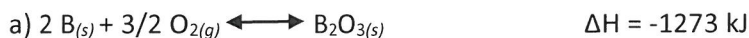
$$H_{\text{combustion (diamond)}} = -396 \text{ kJ/mole}$$



* THEN REVERSE TO CREATE DIAMOND PRODUCT *



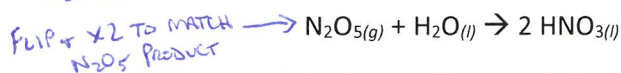
EX 5: Diborane (B_2H_6) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program. Calculate the H_{reaction} for the synthesis of diborane.



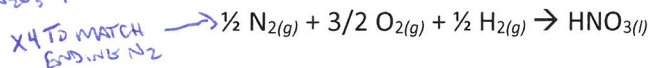
EX 6: Given the following data:



$$H = -258.8 \text{ KJ} \rightarrow 2(+258.8 \text{ KJ}) = +517.6 \text{ KJ}$$



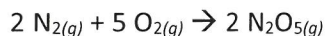
$$H = -76.6 \text{ KJ} \rightarrow 2(+76.6 \text{ KJ}) = +153.2 \text{ KJ}$$



$$H = -174.1 \text{ KJ} \rightarrow 4(-174.1 \text{ KJ}) = -696.4 \text{ KJ}$$

Calculate the enthalpy change for the reaction

$$\Delta H = -25.6 \text{ KJ}$$



Standard Enthalpies of Formation – of a compound is equal to the enthalpy change when one mole of the compound is formed at a constant pressure of 1.0 atm and a fixed temperature, 25°C, from the elements in their states at that pressure and temperature.

- Most enthalpies of formation are negative numbers, meaning that the compound forms from its elements & is exothermic
- Elements in their standard states have a standard enthalpy of formation equal to zero.

In standard enthalpies of formation calculations, keep in mind:

- 1) When a reaction is reversed, the magnitude of all Heats remains the same, but its sign changes.
- 2) When the balanced equation for a reaction is multiplied by an integer, the value of H for that reaction must be multiplied by the same integer.
- 3) Elements in their standard states are not included in the Heat calculated, that is standard heat for an element in its standard state is **zero**.

EX 7: Calculate the enthalpy change for the following reaction:



$\Delta H = ?$

$$\Delta H_f^\circ = \sum H_{fp} - \sum H_{fr}$$

$$[4(34\text{KJ}) + 6(-286\text{KJ})] - [4(-46\text{KJ}) + 7(\emptyset)]$$

$$\Delta H_f^\circ = -1397.82\text{KJ}$$

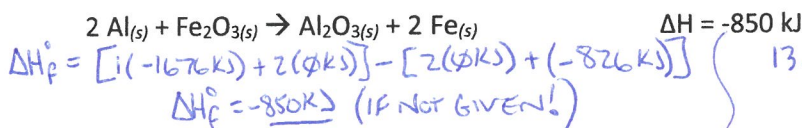
$$\Delta H_f^\circ \text{NH}_3 = -46.11\text{KJ}$$

$$\Delta H_f^\circ \text{O}_2 = \emptyset \text{ (ELEMENTAL STATE)}$$

$$\Delta H_f^\circ \text{NO}_2 = 33.18\text{KJ}$$

$$\Delta H_f^\circ \text{H}_2\text{O} = -285.83\text{KJ}$$

EX 8: How much heat is released by 13.3 grams of Al in the equation:



$$\Delta H_f^\circ = [1(-1676\text{KJ}) + 2(\emptyset\text{KJ})] - [2(\emptyset\text{KJ}) + (-826\text{KJ})]$$

$$\Delta H_f^\circ = -850\text{KJ} \text{ (IF NOT GIVEN!)}$$

THERMOCHEMISTRY – Chapter 17

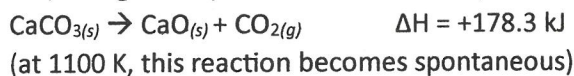
$$\frac{13.3\text{g Al}}{27.0\text{g Al}} \times \frac{1\text{mol Al}}{2\text{mol Al}} \times \frac{-850\text{KJ}}{2\text{mol Al}} = -209.4\text{KJ}$$

END SECTION 2

Chemical reactions are driven by two factors:

Energy Factor – Many spontaneous reactions proceeded with a decrease of energy

- Almost all exothermic reactions are spontaneous
- Most phase changes are endothermic, yet spontaneous
- Some reactions, though not spontaneous become spontaneous at higher temperatures.



Randomness Factor – Nature tends to move spontaneously from a state of lower probability to higher probability.

- Nature tends to move spontaneously from a more ordered to more random state.
- Entropy (S) is the measure of the randomness factor.

$$S = S_{\text{final}}^\circ - S_{\text{initial}}^\circ$$

-S = nonspontaneous; +S = spontaneous

UNIT 12
SECTION 1

Factors that influence entropy

- A liquid has a higher entropy than a solid from which it is formed.
- A gas has a higher entropy than the liquid from which it is formed.
- Increasing the temperature of a substance increases its entropy (especially in phase changes).

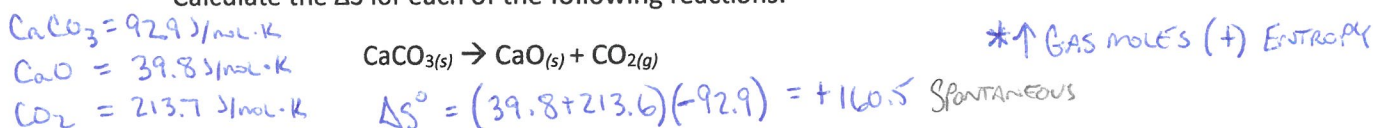
Predict whether the ΔS is positive or negative for each of the following processes.

- 1) taking dry ice from the freezer where the temperature is -80°C and allowing it to warm to room temperature $+$ (Solid $\rightarrow$ Gas = MOST ORGANIZED TO MORE RANDOM)
- 2) dissolving bromine in hexane $+$ (MOST ORGANIZED TO MORE RANDOM)
- 3) condensing gaseous bromine to liquid bromine $-$ (GOING FROM MORE RANDOM TO LESS RANDOM)

Calculating ΔS° for a reaction

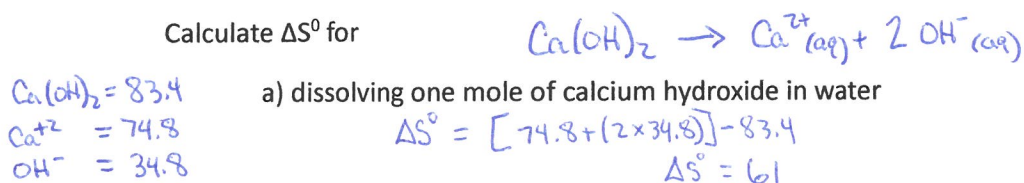
$$\Delta S^{\circ} = \sum S^{\circ}_{\text{products}} - \sum S^{\circ}_{\text{reactants}}$$

Calculate the ΔS for each of the following reactions:

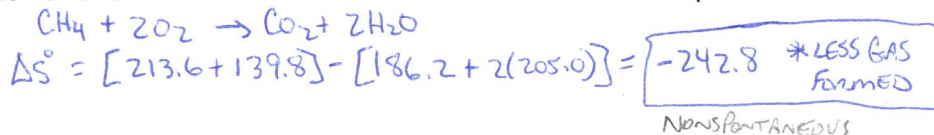


A reaction that results in an increase in the number of moles of a gas is accompanied by an increase in entropy; if the gas molecules decrease, entropy is a negative number

Calculate ΔS° for



b) the combustion of one mole of methane to form carbon dioxide and liquid water



Free Energy (ΔG)

Two quantities affect reaction spontaneity: enthalpy (ΔH) and entropy (ΔS).

Gibbs Free Energy (ΔG) – represents that portion of the total energy change that is available (i.e., free) to do useful work.

(+) energy must be supplied

(-) energy is released for work

Gibbs-Helmholtz Equation: $\Delta G = \Delta H - T \cdot \Delta S$

Sign determines spontaneity: $\Delta G (-)$ reaction is spontaneous

$\Delta G (+)$ reaction will not take place

$\Delta G = 0$ system is at equilibrium

TEMP MUST BE KELVIN!

*WHEN FINDING ΔG , ΔS
MUST BE CONVERTED TO KJ*

Two factors tend to make ΔG negative:

1) A negative value of ΔH

2) A positive value of ΔS (many physical changes, the entropy increase is the major or driving force i.e., melting ice)

Standard Free Energy Change

Standard conditions – gases at 1 atmosphere and solutions 1.0 M and 25°C

For the reaction: $\text{CaSO}_4(s) \rightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)$

Calculate a) ΔH° b) ΔS° c) ΔG° at 25°C

$$\Delta H: [-543 + (-909.3)] - [-1433] = -19.3 \text{ kJ}$$

$$\Delta S: [-55 + 20] - [107] = -142 \text{ J}$$

$$\Delta G = \Delta H - T\Delta S \text{ in kJ} \rightarrow (-19.3) - (298 \cdot 0.142 \text{ kJ}) = -61.6$$

Calculation of ΔG° at other temperatures than standard

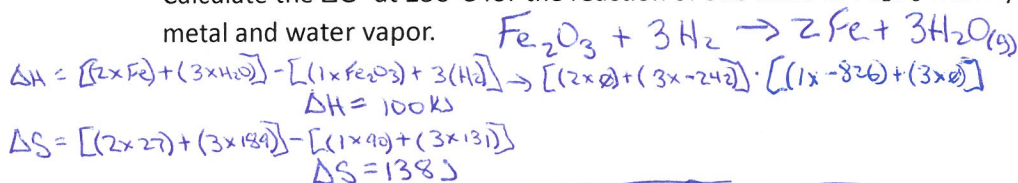
$$\begin{array}{l} \text{CaSO}_4 \quad \Delta H = -1433 \\ \Delta S = 107 \\ \Delta G = -1320 \end{array}$$

$$\begin{array}{l} \text{Ca}^{2+} \quad \Delta H = -543 \\ \Delta S = -55 \\ \Delta G = -553 \end{array}$$

$$\begin{array}{l} \text{SO}_4^{2-} \quad \Delta H = -909.3 \\ \Delta S = 20 \\ \Delta G = -445 \end{array}$$

To a good degree of approximation, the temperature variation for ΔH° and ΔS° can be neglected. This means that to apply the Gibbs-Helmholtz equation to temperatures other than 25°C, you need only change the value of the temperature.

Calculate the ΔG° at 230°C for the reaction of one mole of Fe_2O_3 with hydrogen. The products are iron metal and water vapor.



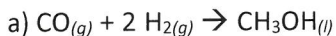
$$\begin{array}{l} \text{Fe}_2\text{O}_3 \quad \Delta H = -826 \\ \Delta S = 90 \\ \Delta G = -740 \end{array}$$

$$\begin{array}{l} \text{H}_2 \quad \Delta H = 0 \text{ (ELEMENTAL FORM)} \\ \Delta S = 131 \\ \Delta G = 0 \end{array}$$

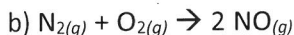
$$\begin{array}{l} \text{Fe} \quad \Delta H = 0 \\ \Delta S = 27 \\ \Delta G = 0 \end{array} \quad \begin{array}{l} \text{H}_2\text{O}(g) \quad \Delta H = -242 \\ \Delta S = 189 \\ \Delta G = -229 \end{array}$$

$$\Delta G = 100 - (503 \text{ K} \cdot 0.138 \text{ kJ}) = 30.6 \therefore \text{NOT SPONTANEOUS}$$

Calculate the ΔG° at 335 K for each reaction below and tell if it is spontaneous or nonspontaneous.



$$\begin{array}{l} \text{CH}_3\text{OH}(l) \quad \Delta H = -239 \\ \Delta G = -166 \\ \Delta S = 127 \end{array} \quad \begin{array}{l} \text{CO}(g) \quad \Delta H = -110.5 \\ \Delta G = -137 \\ \Delta S = 198 \end{array} \quad \begin{array}{l} \text{H}_2(g) \quad \Delta H = 0 \\ \Delta S = 131 \\ \Delta G = 0 \end{array}$$



$$\begin{array}{l} \text{NO}(g) \quad \Delta H = 90 \\ \Delta G = 87 \\ \Delta S = 211 \end{array} \quad \begin{array}{l} \text{N}_2 \quad \Delta H = 0 \\ \Delta G = 0 \\ \Delta S = 192 \end{array} \quad \begin{array}{l} \text{O}_2 \quad \Delta H = 0 \\ \Delta G = 0 \\ \Delta S = 205 \end{array}$$

$$\text{a) } \Delta H_f^\circ = [-239] - [(1 \times -110.5) + (2 \times 0)] = -128.5 \text{ kJ}$$

$$\Delta S_f^\circ = [127] - [(1 \times 198) + (2 \times 131)] = -333 \text{ J}$$

$$\Delta G_{335\text{K}} = -128 - (335 \text{ K} \cdot -0.333 \text{ kJ}) = -16.4 \therefore \text{SPONTANEOUS}$$

$$\text{b) } \Delta H_f^\circ = [2(90)] - [(1 \times 0) + (1 \times 0)] = 180 \text{ kJ}$$

$$\Delta S_f^\circ = [2(211)] - [(1 \times 192) + (1 \times 205)] = 25 \text{ J}$$

$$\Delta G_{335\text{K}} = 180 - (335 \text{ K} \cdot 0.025 \text{ kJ}) = 171.6 \therefore \text{NONSPONTANEOUS}$$

Effect of temperature on spontaneity

	ΔH°	ΔS°	$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$	
I	(-)	(+)	always (-)	Spontaneous at all temps reverse rxn always nonspontaneous
II	(+)	(-)	always (+)	Nonspontaneous at all temperatures
III	(+)	(+)	(+) at low T, (-) at high T	*If ΔH° and ΔS° have opposite signs, it is impossible to reverse the direction of spontaneity by a change in temperature. Both terms ΔH° and $T \cdot \Delta S^\circ$ reinforce each other
IV	(-)	(-)	(-) at low T, (+) at high T	

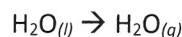
At what temperature does ΔG° become zero for the reaction:

$\Delta H = [(2 \times 0) + (3 \times -242)] - [(1 \times -826) + (3 \times 0)]$
 $\Delta H = -600 \text{ kJ}$
 $\Delta S = [(2 \times 27) + (3 \times 189)] - [(1 \times 90) + (3 \times 131)]$
 $\Delta S = 138 \text{ J/K}$
 $\text{Fe}_2\text{O}_3(s) + 3 \text{H}_2(g) \rightarrow 2 \text{Fe}(s) + 3 \text{H}_2\text{O}(g)$
 SETTING $\Delta G^\circ = 0$ GIVES US: $0 = \Delta H - (T \cdot \Delta S)$ OR $\Delta H = T \cdot \Delta S$
 $* \Delta H^\circ = 98.8 \text{ kJ}$
 $* \Delta S^\circ = 0.1415 \text{ kJ/K}$
 $98.8 \text{ kJ} = T \cdot (0.1415) \rightarrow T = 698 \text{ K}$
 $100 \text{ kJ} = T \cdot (0.138 \text{ kJ/K})$
 $T = 724.6 \text{ K}$

Temperature for spontaneity:

$$T = \Delta H^\circ / \Delta S^\circ$$

At what temperature does the following reaction occur:



Effect of pressure and temperature

$$G = \Delta G^\circ + RT \ln Q$$

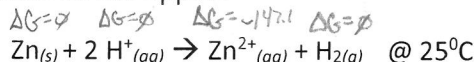
T = degrees Kelvin

$$R = 8.31 \times 10^{-3} \text{ kJ/K}$$

Q rules

- 1) gases enter as their partial pressures in atmospheres
- 2) aqueous solutions enter as their molar concentrations
- 3) pure liquids and solids do not appear

Consider the reaction:



$$\Delta H \text{ Zn}^{2+} = -153.39$$

$$\Delta S \text{ Zn}^{2+} = -112.1$$

Calculate

a) G° $\Delta G^\circ = [(1 \times -147.1) + (1 \times 0.0)] - [(1 \times 0.0) + (1 \times 0.0)] = -147.1 \text{ kJ/mol}$

b) G when $P_{\text{H}_2} = 750 \text{ mm Hg}$, $[\text{Zn}^{2+}] = 0.10 \text{ M}$, $[\text{H}^+] = 1.0 \times 10^{-4} \text{ M}$

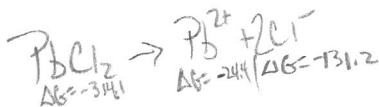
$$G = \Delta G^\circ + RT \ln Q$$

$$= -147.1 + [(0.00831)(298 \text{ K}) \ln \frac{[\text{Zn}^{2+}][P_{\text{H}_2}]}{[\text{H}^+]^2}]$$

$$= -147.1 + [(0.00831)(298 \text{ K}) \ln \frac{(0.10)(750 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}})}{(1.0 \times 10^{-4})^2}]$$

$$= -147 + 39.9 \text{ kJ}$$

$$= -107.2 \text{ kJ}$$



Show by calculation whether dissolving lead (II) chloride is spontaneous when:

a) $[\text{Pb}^{2+}] = 1.0 \text{ M}$, $[\text{Cl}^-] = 2.0 \text{ M}$

b) $[\text{Pb}^{2+}] = 1.0 \times 10^{-5} \text{ M}$, $[\text{Cl}^-] = 2.0 \times 10^{-5} \text{ M}$

$$\Delta G^\circ = +27.3 \text{ KJ} - [(1.00831)(298)(\ln(1.0 \times 10^{-5})^1 \cdot (2.0 \times 10^{-5})^2)]$$

$\ln(4 \times 10^{-15})$

$$\Delta G = -54.8 \text{ KJ} \quad * \text{SPONTANEOUS}$$

$$\Delta G^\circ = [-24.4 + (2 \times -131.2)] - [-314.1] = +27.3 \text{ KJ}$$

$$\Delta G = +27.3 \text{ KJ} - [(1.00831)(298)(\ln(1.0)^1 \cdot (2.0)^2)]$$

$\ln 4$

$$\Delta G = +30.71 \text{ KJ}$$

* NONSPONTANEOUS
* NO SOLUBILITY

Free energy change and the equilibrium constant, K

For spontaneity: ΔG° must be negative (-)

K must be greater than 1

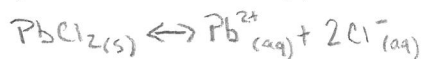
ΔE° must be (+)

ΔG° and K are related:

$$\Delta G^\circ = -RT \ln K \quad (\text{must be at standard conditions})$$

$\swarrow 8.314 \quad \searrow 298$

Using ΔG°_f tables in appendix 1, calculate the solubility product constant, K_{sp} , for PbCl_2 at 25°C .



$$\Delta G^\circ_{\text{RXN}} = \sum \Delta G^\circ_{\text{PRODUCTS}} - \sum \Delta G^\circ_{\text{REACTANTS}}$$

$$\Delta G^\circ_{\text{RXN}} = [\Delta G^\circ_f(\text{Pb}^{2+}) + 2\Delta G^\circ_f(\text{Cl}^-)] - [\Delta G^\circ_f(\text{PbCl}_2)]$$

$$\Delta G^\circ_{\text{RXN}} = [(-24.4) + (2 \times -131.2)] - [-314.2]$$

$$\Delta G^\circ_{\text{RXN}} = 27.4 \text{ KJ} = 27,400 \text{ J/mol}$$

$$27,400 = (-8.314)(298) \ln K$$

$$-11.06 = \ln K \rightarrow e^x = -11.06$$

$$K = 1.6 \times 10^{-5}$$