

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
Heat Capacity =		Heat Capacity =

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

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

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

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)

Example problems

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

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.

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

$1 \text{ mol Ba}(\text{NO}_3)_2$
 $1 \text{ mol Na}_2\text{SO}_4$
 $\Delta H = \frac{q}{\text{MOLES USED}}$
 $\Delta H = \frac{33.64 \text{ KJ}}{1 \text{ mol USED}} = -33.64 \text{ KJ/mol}$

EACH REACTANT USED ENTIRE 1.0 MOLES

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.

b) Calculate the molar heat capacity of aluminum.

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: $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}(s)$

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.

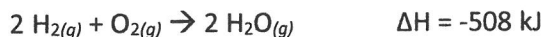
$q = m C_p \Delta t$
 $(100g)(4.17)(.80^\circ\text{C}) = 333.6 \text{ J}$ OR 0.3336 KJ

$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$
 $\frac{0.1 \text{ mol}}{1L} \times 0.05L = 0.005 \text{ mol}$
 of $\text{Ag}^+ + \text{Cl}^-$
 * BOTH USE ALL MOLES *

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

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?

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

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

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:

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

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



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.



a) $2 B_{(s)} + 3/2 O_{2(g)} \longleftrightarrow B_2O_{3(s)} \quad \Delta H = -1273 \text{ kJ}$

b) $B_2O_{6(s)} + 3 O_{2(g)} \longleftrightarrow B_2O_{3(s)} + 3 H_2O_{(g)} \quad \Delta H = -2035 \text{ kJ}$

c) $H_{2(g)} + 1/2 O_{2(g)} \longleftrightarrow H_2O_{(l)} \quad \Delta H = -286 \text{ kJ}$

d) $H_2O_{(l)} \longleftrightarrow H_2O_{(g)} \quad \Delta H = +44 \text{ kJ}$

Handwritten solution for EX 5:

a) $2B + 3/2 O_2 \longleftrightarrow B_2O_3 \quad \Delta H = -1273 \text{ kJ}$

REVERSED FROM ABOVE TO MAKE B_2O_6 PRODUCT!
 \rightarrow b) $B_2O_3 + 3H_2O \rightarrow B_2H_6 + 3O_2 \quad \Delta H = +2035 \text{ kJ}$

\rightarrow c) $3H_2 + 3/2 O_2 \rightarrow 3H_2O \quad \Delta H = 3(-286) \text{ kJ}$

\rightarrow d) $3H_2O \rightarrow 3H_2O \quad \Delta H = 3(44) \text{ kJ}$

$2B + 3H_2 \rightarrow B_2H_6 \quad \Delta H = +36 \text{ kJ (ENDOTHERMIC)}$

EX 6: Given the following data:

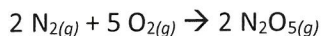
$\xrightarrow{\text{X2 TO MATCH H}_2\text{O BELOW}}$ $H_{2(g)} + 1/2 O_{2(g)} \rightarrow H_2O_{(l)} \quad H = -258.8 \text{ kJ} \times 2 = -517.6 \text{ kJ}$

$\rightarrow N_2O_5_{(g)} + H_2O_{(l)} \rightarrow 2 HNO_3_{(l)} \quad H = -76.6 \text{ kJ} \times 2 = +153.2 \text{ kJ}$

FLIP TO MAKE N_2O_5 PRODUCT & X2 TO MATCH ENDING N_2O_5
 $\rightarrow 1/2 N_{2(g)} + 3/2 O_{2(g)} + 1/2 H_{2(g)} \rightarrow HNO_3_{(l)} \quad H = -174.1 \text{ kJ} \times 4 = -696.4 \text{ kJ}$

\uparrow X4 TO MATCH ENDING N_2

Calculate the enthalpy change for the reaction



$\Delta H = -1060.8 \text{ kJ}$

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:



$\Delta H = ?$

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

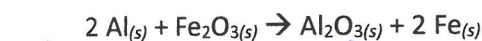
$$[4(34\text{K}) + 6(-286\text{K})] - [4(-46\text{K}) + 7(\emptyset)]$$

$$\Delta H_f = -1397.82\text{K}$$

$\Delta H_f^\circ \text{NH}_3 = -46.11\text{K}$
 $\Delta H_f^\circ \text{O}_2 = \emptyset$ (ELEMENTAL STATE)
 $\Delta H_f^\circ \text{NO}_2 = 33.18\text{K}$
 $\Delta H_f^\circ \text{H}_2\text{O} = -285.83\text{K}$

- ① COFFEE CUP CALORIMETRY
- ② HESS'S LAW
- ③ ΔH_f in formation

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



$\Delta H = -850 \text{ kJ}$

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

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

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$$13.3 \text{ g Al} \left| \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right| \frac{-850 \text{ kJ}}{2 \text{ mol Al}} = -209.4 \text{ kJ}$$

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
- $$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = +6.0 \text{ kJ}$$
- Some reactions, though not spontaneous become spontaneous at higher temperatures.
- $$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad \Delta H = +178.3 \text{ kJ}$$
- (at 1100 K, this reaction becomes spontaneous)

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

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 S 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
- 2) dissolving bromine in hexane
- 3) condensing gaseous bromine to liquid bromine

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:

$$\begin{aligned} \text{CaCO}_3 &= 92.9 \text{ J/mol}\cdot\text{K} \\ \text{CaO} &= 39.8 \text{ J/mol}\cdot\text{K} \\ \text{CO}_2 &= 213.7 \text{ J/mol}\cdot\text{K} \end{aligned}$$



$$\Delta S^{\circ} = (39.8 + 213.6) - 92.9 = +160.5$$

*↑ GAS MOLES (+) ENTROPY

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



a) dissolving one mole of calcium hydroxide in water

$$\begin{aligned} \text{Ca(OH)}_2 &= 83.4 \\ \text{Ca}^{2+} &= 74.8 \\ \text{OH}^{-} &= 34.8 \end{aligned}$$

$$\Delta S^{\circ} = [74.8 + (2 \times 34.8)] - 83.4$$
$$\Delta S^{\circ} = 61$$

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



$$\Delta S^{\circ} = [213.6 + 139.8] - [186.2 + 2(205.0)] = -242.8$$

*LESS GAS FORMED

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

* $T = \text{TEMP}$ (MUST BE IN KELVIN)
 * 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



CaSO_4	$\Delta H = -142.0$
	$\Delta S = 106$
	$\Delta G = -104.0$
Ca^{2+}	$\Delta H = -542.7$
	$\Delta S = 71.9$
	$\Delta G = -552.0$
SO_4^{2-}	$\Delta H = -909.3$
	$\Delta S = 213.7$
	$\Delta G = -745.0$

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

$$\Delta H = [-542.7 + (-909.3)] - [-142] = -1310 \text{ KJ}$$

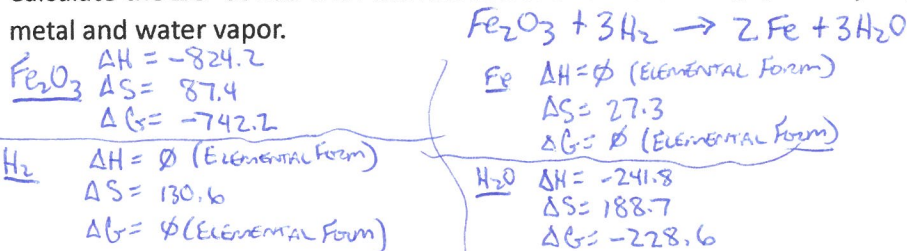
$$\Delta S = [71.9 + 213.7] - (106) = 179.6 \text{ J}$$

$$\Delta G = \Delta H - T \cdot \Delta S \text{ in KJ} \rightarrow (-1310) - (298 \times 0.1796 \text{ KJ}) = -1363.5$$

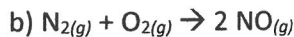
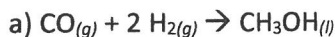
Calculation of ΔG° at other temperatures than standard

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.



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



$$\Delta H^\circ = [(2 \times \text{Fe}) + (3 \times \text{H}_2\text{O})] - [(1 \times \text{Fe}_2\text{O}_3) + (3 \times \text{H}_2)] \rightarrow [(2 \times \emptyset) + (3 \times -241.8)] - [(1 \times -824.2) + (3 \times 0)]$$

$$\Delta H = 98.8$$

$$\Delta S^\circ = [(2 \times 27.3) + (3 \times 188.7)] - [(1 \times 87.4) + (3 \times 130.6)] \rightarrow \Delta S^\circ = 141.5 \text{ KJ}$$

$$\Delta G^\circ = 98.8 - (503 \text{ K} \cdot 0.1415 \text{ KJ}) = +27.63 \text{ KJ} \Rightarrow \text{NOT SPONTANEOUS}$$

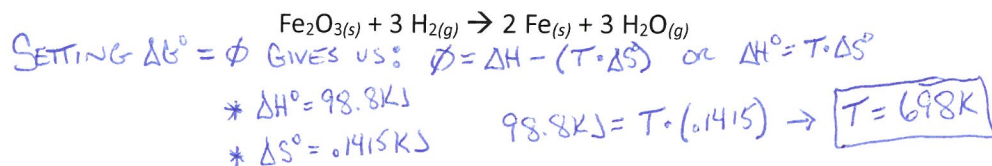
a) $\Delta H_f^\circ = -238.70 - (-110 + 0) = -128.2 \text{ KJ}$
 $\Delta S^\circ = 0.1268 \text{ KJ} - [0.1976 + 2(0.1306)] = -0.332 \text{ KJ}$
 $\Delta G_{335K}^\circ = -128.2 - (355 \text{ K} \cdot -0.332 \text{ KJ}) = -10.3 \text{ KJ} \Rightarrow \text{SPONTANEOUS}$

b) $\Delta H_f^\circ = 2(90.2) - (0.0 + 0.0) = 180.4 \text{ KJ}$
 $\Delta S^\circ = 2(0.2107) - [0.1915 + 0.205] = 0.0249 \text{ KJ}$
 $\Delta G_{335K}^\circ = 180.4 - (355 \text{ K} \cdot 0.0249 \text{ KJ}) = +171.6 \text{ KJ} \Rightarrow \text{NONSPONTANEOUS}$

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:



Temperature for spontaneity:

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

At what temperature does the following reaction occur: $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

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: $\text{Zn}(s) + 2 \text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$ @ 25°C

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

$$\begin{aligned}
 G &= \Delta G^\circ + RT \ln Q \\
 &= -147.1 + [(0.00831)(298\text{K}) \left(\ln \frac{[\text{Zn}^{2+}][P_{\text{H}_2}]}{[\text{H}^+]^2} \right)] \\
 &= -147.1 + [(0.00831)(298\text{K}) \left(\ln \frac{(0.10\text{M})(750\text{mmHg}) \left(\frac{1\text{Atm}}{760\text{mmHg}} \right)}{(1.0 \times 10^{-4})^2} \right)] \\
 &= -147 + 39.9 \text{ kJ} \\
 &= -107.2 \text{ kJ}
 \end{aligned}$$

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

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

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

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

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

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

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

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

$\ln 4$

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

* 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: $\Delta G^\circ = -RT \ln K$ (must be at standard conditions)

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