

**Ch. Thermochemistry (Thermodynamics)**

-is the study of energy.

I. Energy is the capacity to do work or produce heat.

Law of Conservation of Energy

Energy cannot be created or destroyed, just transferred.

1<sup>st</sup> Law of Thermodynamics

The energy in the universe is constant.

State Functions

-depend only on the current state of the system. P, V, T, energy

Heat

Heat flows from hot to cold: high KE, high velocity particles collide with cold/slower particles, making them speed up, increasing their KE.

Exothermic

Heat energy flows out of a system into its surroundings.  
(hot pack) \*\*burning paper

Endothermic

Heat energy flows into a system from its surroundings.  
(cold pack) \*\*ice cube melting

$\Delta E = q + w$        $\Delta E =$  change in internal energy of a system (joules)  
q = heat, w = work

$w = -P\Delta V$       P = pressure  
                          $\Delta V = V_f - V_i$  (change in volume)  
                         \*\* **1 L·atm = 101.3 J**

Ex. 1) A system gives off 196 kJ of heat to its surroundings and the surroundings do  $4.20 \times 10^5$  J of work on the system. Find  $\Delta E$  of the system.

$$\frac{4.20 \times 10^5 \text{ J}}{1 \times 10^3 \text{ J}} \left| \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \right. = 420 \text{ kJ}$$

$$\Delta E = q + w = -196 \text{ kJ} + 420 \text{ kJ} = \mathbf{224 \text{ kJ}}$$

(-) q, since heat is lost,

(+) w, since work gained by system (work done on it)

Ex. 2) A balloon is being inflated. The volume of the balloon changes from 400 L to 750 L by the addition of  $2.40 \times 10^6$  J of heat. Assume the balloon expands against a constant pressure of 1.00 atm. Find  $\Delta E$  of the balloon.

$$\Delta E = q + w \quad w = -P\Delta V \quad \Delta V = V_f - V_i$$

$$w = -(1.00 \text{ atm})(750 \text{ L} - 400 \text{ L})$$

$$w = -350 \text{ L}\cdot\text{atm}$$

$$w = \frac{-350 \text{ L}\cdot\text{atm}}{1 \text{ L}\cdot\text{atm}} \left| \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right. = -3.54 \times 10^4 \text{ J}$$

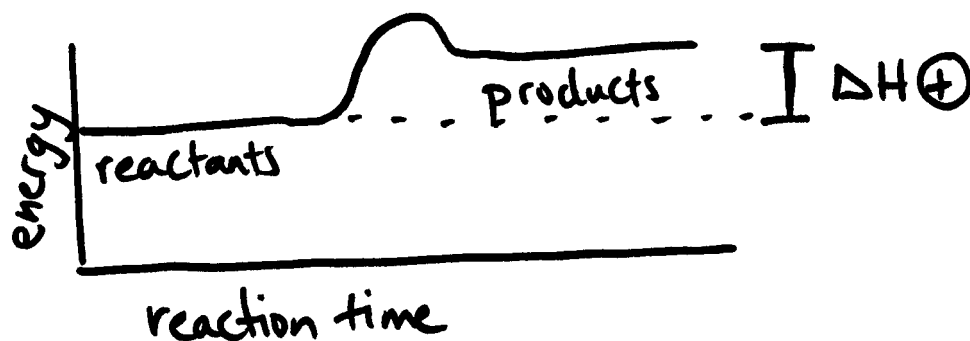
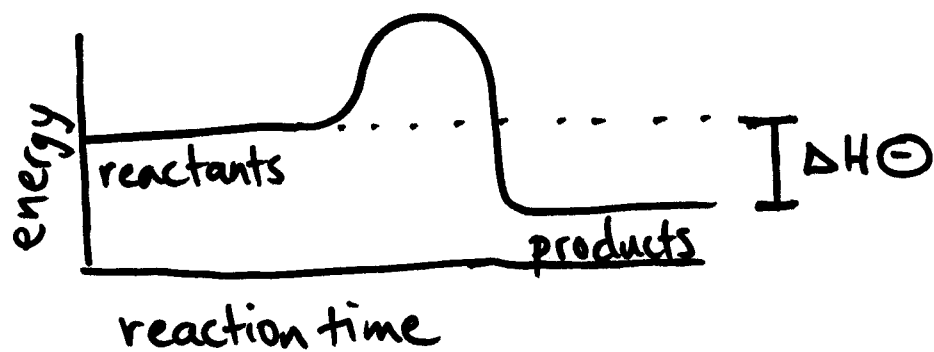
$$\Delta E = q + w = 2.40 \times 10^6 \text{ J} - 3.54 \times 10^4 \text{ J}$$

$$\Delta E = 2.36 \times 10^6 \text{ J}$$

## II. Enthalpy (H)

-is the heat energy.

$q = H$  at constant P



We can measure the difference in heat for the formation of compounds from their elements. See Textbook for  $\Delta H_f^\circ$  values ( $^\circ$  for standard state,  $_f$  for formation) cr = crystalline solid



### #38 Notes III. Calorimetry

-is the science of measuring heat.

$$\Delta E = q + w \quad w = -P\Delta V$$
$$q = sm\Delta T \quad \text{where } s = \text{specific heat capacity,}$$
$$m = \text{mass, and } \Delta T = T_f - T_i$$

#### Specific heat capacity (s)

-is the energy required to raise the temperature one degree Celsius for one gram of the substance.

$$s \text{ for H}_2\text{O} = 4.184 \text{ J/(g}\cdot\text{°C)} = 1 \text{ calorie, } s \text{ for Fe} = 0.45 \text{ J/(g}\cdot\text{°C)}$$

#### Molar heat capacity

-is the same except for 1 mol of the substance.  $\text{J}/(\text{mol}\cdot\text{°C})$

\*\*so the “q” equation would have mols for “m”, instead of mass

Ex. 1a) How much heat is required to raise 8.77 g  $\text{CCl}_4$  from  $37.1 \text{ °C}$  to  $56.4 \text{ °C}$ ?

$$s \text{ for CCl}_4 = 0.856 \text{ J/(g}\cdot\text{°C)}$$

$$q = sm\Delta T = (0.856 \text{ J/(g}\cdot\text{°C)}) (8.77 \text{ g}) (56.4 \text{ °C} - 37.1 \text{ °C})$$
$$= (0.856 \text{ J/(g}\cdot\text{°C)}) (8.77 \text{ g}) (19.3 \text{ °C}) = \mathbf{1.45 \times 10^2 \text{ J}}$$

Ex. 1b) Calculate the molar heat capacity.

$$\frac{0.856 \text{ J}}{\text{g}\cdot\text{°C}} \left| \frac{154.13115 \text{ g CCl}_4}{1 \text{ mol CCl}_4} \right. = \mathbf{132 \text{ J/(mol}\cdot\text{°C)}}$$

Ex.1c) Calculate the heat of raising 24.1 mol  $\text{CCl}_4$  from  $25 \text{ °C}$  to  $325 \text{ °C}$ .

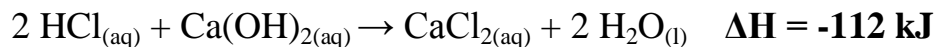
$$q = sm\Delta T = (132 \text{ J/(mol}\cdot\text{°C)}) (24.1 \text{ mol}) (325 \text{ °C} - 25 \text{ °C})$$
$$= (132 \text{ J/(mol}\cdot\text{°C)}) (24.1 \text{ mol}) (300 \text{ °C}) = \mathbf{9.5 \times 10^5 \text{ J}}$$

Ex. 2) A 25.0 g sample of metal was heated to  $90.0 \text{ °C}$  and added to  $50.0 \text{ cm}^3$  of water at  $20.0 \text{ °C}$ . What is the specific heat of the metal, if the final temperature was  $22.0 \text{ °C}$ ?

<u>Metal</u>	<u>Water</u>	D = m/v
Loses heat	Gains heat	$(1.0 \text{ g/cm}^3) = \frac{m}{(50.0 \text{ cm}^3)}$
$-q =$	$+q$	$50.0 \text{ g} = m$
$-sm\Delta T =$	$+sm\Delta T$	

$$\begin{aligned}
 -s (25.0 \text{ g}) (22.0 \text{ }^\circ\text{C} - 90.0 \text{ }^\circ\text{C}) &= (4.184 \text{ J/(g}\cdot\text{ }^\circ\text{C)}) (50.0 \text{ g}) (22.0 \text{ }^\circ\text{C} - 20.0 \text{ }^\circ\text{C}) \\
 -s (25.0 \text{ g}) (-68 \text{ }^\circ\text{C}) &= (4.184 \text{ J/(g}\cdot\text{ }^\circ\text{C)}) (50.0 \text{ g}) (2.0 \text{ }^\circ\text{C}) \\
 s (1700) &= (418.4) \\
 \mathbf{s = 0.246 \text{ J/(g}\cdot\text{ }^\circ\text{C)}}
 \end{aligned}$$

Ex. 3) Calculate the final temperature of the mixture when 300.0 ml of 1.00 M HCl is mixed with 350.0 ml of 0.750 M Ca(OH)<sub>2</sub>. (T<sub>i</sub> = 25 °C, final mass of mixture = 650.0 g, s = 4.18 J/(g·°C))



↑  
for the whole reaction, i.e. for **1 mol CaCl<sub>2</sub>**, for 2 H<sub>2</sub>O etc.

Find limiting reagent:

$$\begin{aligned}
 &\text{HCl} \\
 M &= \text{mol/L} \\
 1.00 \text{ M HCl} &= \frac{\text{mol}}{0.300 \text{ L}} \\
 0.300 &= \text{mol HCl}
 \end{aligned}$$

$$\begin{aligned}
 &\text{Ca(OH)}_2 \\
 M &= \text{mol/L} \\
 0.750 \text{ M Ca(OH)}_2 &= \frac{\text{mol}}{0.350 \text{ L}} \\
 0.263 &= \text{mol Ca(OH)}_2
 \end{aligned}$$

$$\frac{0.300 \text{ mol HCl}}{2 \text{ mol HCl}} \left| \frac{1 \text{ mol CaCl}_2}{1 \text{ mol CaCl}_2} = 0.150 \text{ mol CaCl}_2 \leftarrow \text{limiting reagent}$$

$$\frac{0.263 \text{ mol Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} \left| \frac{1 \text{ mol CaCl}_2}{1 \text{ mol Ca(OH)}_2} = 0.263 \text{ mol CaCl}_2$$

$$\frac{0.150 \text{ mol CaCl}_2}{1 \text{ mol CaCl}_2} \left| \frac{-112 \text{ kJ}}{1 \text{ mol CaCl}_2} = -16.8 \text{ kJ heat produced}$$

$$\Delta E = q + w, \text{ no work, so } \Delta E = q = sm\Delta T$$

\*\*since heat is produced, T<sub>f</sub> should be larger than T<sub>i</sub>

So change heat to positive

$$\frac{16.8 \text{ kJ}}{1 \text{ kJ}} \left| \frac{1 \times 10^3 \text{ J}}{1 \text{ kJ}} = (4.18 \text{ J/(g}\cdot\text{ }^\circ\text{C)}) (650.0 \text{ g}) (T_f - 25 \text{ }^\circ\text{C})$$

$$\begin{aligned}
 6.18 &= T_f - 25 \text{ }^\circ\text{C} \\
 \mathbf{31 \text{ }^\circ\text{C} = T_f}
 \end{aligned}$$





$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

(+)  $\Delta S_{\text{universe}}$  is spontaneous, since it gains entropy,  
 $\Delta S_{\text{surroundings}}$  is usually *determined by heat flow to/from the system.*

For example: Melting Ice

For the system: the ice gains heat ( $\Delta H = (+)$ ),  
the ice goes from solid to liquid (it gains entropy,  $\Delta S = (+)$ )

For the surroundings: it loses heat to the ice ( $\Delta H = (-)$ ),  
so it loses entropy as well ( $\Delta S = (-)$ )

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

(+) to be spontaneous.       $\uparrow$        $\uparrow$   
   (+)      (-)      Which is stronger? Will the ice melt?

This is determined by temperature.

When the surroundings is  $> 0^\circ\text{C}$ , the ice melts. ( $\Delta S_{\text{system}}$  is stronger.  $\Delta S_{\text{universe}}$  be (+).)

When the surroundings is  $< 0^\circ\text{C}$ , the ice doesn't melt.

( $\Delta S_{\text{surroundings}}$  is stronger.  $\Delta S_{\text{universe}}$  be (-).)

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T} \quad \text{but} \quad \Delta S_{\text{system}} = \frac{+\Delta H_{\text{system}}}{T} \quad T \text{ is in Kelvin}$$

Ex. 1) The melting point of iron is  $1535^\circ\text{C}$  and the enthalpy of fusion is  $13.8 \text{ kJ/mol}$ .  
What is the entropy of fusion ( $\Delta S_{\text{system}}$ )? What is the  $\Delta S_{\text{surroundings}}$ ?

$$\Delta S_{\text{system}} = \frac{13.8 \text{ kJ/mol}}{1808 \text{ K}} = \frac{7.63 \times 10^{-3} \text{ kJ}}{\text{mol}\cdot\text{K}} \left| \frac{1 \times 10^3 \text{ J}}{1 \text{ kJ}} \right| = \mathbf{7.63 \text{ J/mol}\cdot\text{K}}$$

So,  $\Delta S_{\text{surroundings}} = \mathbf{-7.63 \text{ J/mol}\cdot\text{K}}$



### #41 Notes III. 3<sup>rd</sup> Law of Thermodynamics

The entropy of a perfect crystal at 0 Kelvin is ZERO.

(Absolute Zero temperature = no vibrations, no random movement, no Kinetic Energy)

### IV. Gibb's Free Energy (G)

-is the chemical potential energy.

$\Delta G (-)$  = spontaneous

$\Delta G (+)$  = nonspontaneous

$$\Delta G = \Delta H - T\Delta S \quad \Delta G \text{ in kJ/mol, } \Delta H \text{ in kJ/mol, } T \text{ in Kelvin,}$$
$$\Delta S \text{ in J/(mol}\cdot\text{K) **so change to kJ/(mol}\cdot\text{K)}$$

Ex.1) Will a reaction be spontaneous at 25 °C, if  $\Delta H = 542 \text{ kJ/mol}$  and  $\Delta S = -14 \text{ J/(mol}\cdot\text{K)}$ ?

$$\frac{-14 \text{ J}}{\text{mol}\cdot\text{K}} \left| \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \right. = -0.014 \text{ kJ/(mol}\cdot\text{K)}$$

$$\Delta G = \Delta H - T\Delta S = (542 \text{ kJ/mol}) - [(298 \text{ K}) (-0.014 \text{ kJ/(mol}\cdot\text{K)})]$$

$$\Delta G = 542 \text{ kJ/mol} + 4.172 \text{ kJ/mol} = \mathbf{546 \text{ kJ/mol (+) so nonspontaneous}}$$

$$\Delta G_{\text{reaction}} = \sum n \Delta G_{\text{products(final)}} - \sum n \Delta G_{\text{reactants(initial)}}$$

$$\Delta S_{\text{reaction}} = \sum n \Delta S_{\text{products(final)}} - \sum n \Delta S_{\text{reactants(initial)}}$$

Ex. 2a) Calculate  $\Delta G_{\text{reaction}}$  for:  $2 \text{ HF}_{(g)} \rightarrow \text{H}_{2(g)} + \text{F}_{2(g)}$

$$\Delta G_{\text{reaction}} = \sum n \Delta G_{\text{products(final)}} - \sum n \Delta G_{\text{reactants(initial)}}$$

$$\Delta G_{\text{reaction}} = [(1 \text{ mol H}_2) (0 \text{ kJ/mol}) + (1 \text{ mol F}_2) (0 \text{ kJ/mol})]$$
$$- [(2 \text{ mol HF}) (-273.2 \text{ kJ/mol})]$$

$$\Delta G_{\text{reaction}} = 0 + 0 + 546.4 \text{ kJ} = \mathbf{+546.4 \text{ kJ nonspontaneous}}$$

Ex. 2b) Calculate  $\Delta S_{\text{reaction}}$

$$\Delta S_{\text{reaction}} = \sum n \Delta S_{\text{products(final)}} - \sum n \Delta S_{\text{reactants(initial)}}$$

$$\Delta S_{\text{reaction}} = [(1 \text{ mol H}_2) (130.684 \text{ J/(mol}\cdot\text{K)}) + (1 \text{ mol F}_2) (202.78 \text{ J/(mol}\cdot\text{K)})]$$
$$- [(2 \text{ mol HF}) (173.779 \text{ J/(mol}\cdot\text{K)})]$$

$$\Delta S_{\text{reaction}} = 130.684 \text{ J/K} + 202.78 \text{ J/K} - 347.558 \text{ J/K} = \mathbf{-14.094 \text{ J/K decreasing}}$$

**\*End of Notes\*** (Assignments #42-43 are Review Assignments. There are no notes for these assignments.)