Chapter 4
Heat Effects

Heat Effects:

- ***Sensible Heat***: When the transfer of heat produces a change in temperature.
- ***Latent Heat***: When a phase change takes place with out a change in temperature.
- Other heat effects includes heat accompany ***chemical reactions***, and heats associated with ***formation or separation of solutions*** and heat effects of ***mixing process***.

4.1 Sensible Heat Effects

Molar or specific enthalpy, H,

$$H = H(T,P)$$

Then, $dH = (\delta H/\delta T)_P\, dT + (\delta H/\delta p)_T\, dP$

$\underset{C_p \text{ Eq'n}(2.20)}{=}$ $\underset{\text{Zero, under the following conditions:}}{=}$

1- The change occurs @ constant pressure, dP = 0 Or
2- The enthalpy of substance is indep. of pressure.
(exactly for ideal gas, and approximately for low press. gases.)

Then, $dH = C_p\, dT$

and $$\Delta H = \int_{T1}^{T2} C_p\, dT \qquad (4.2)$$

Since $Q = \Delta H$ Rev., Const. Press., nonflow process & st. st. process.

Then $$Q = \Delta H = \int_{T1}^{T2} C_p\, dT \qquad (4.3)$$

Similarly, $U = U(T,P)$

$$\Delta U = \int_{T1}^{T2} C_v\, dT \qquad (4.1)$$

Since $Q = \Delta U$ Rev., Const. Vol., nonflow process & st. st. process.

Then $$Q = \Delta U = \int_{T1}^{T2} C_v\, dT$$

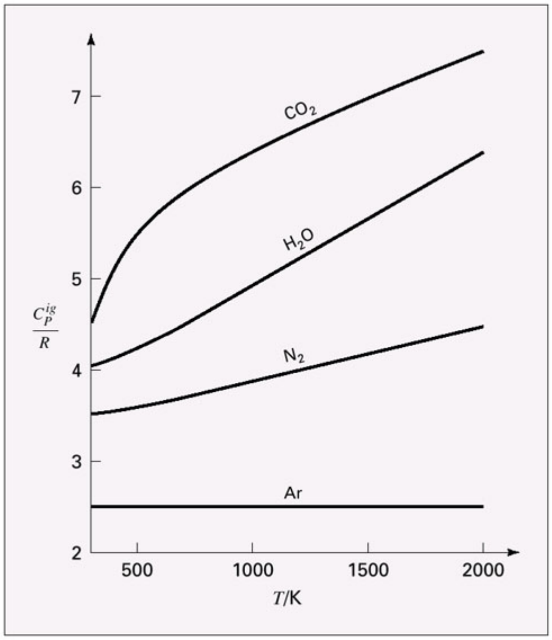
- **Heat Capacities of Gases**

- For gases it's the ideal gas heat capacity (rather than the actual) that is used in evaluation of the thermodynamic properties such as U and H.

- ***Ideal gas*** properties are used because such properties can be evaluated by two steps:
  A. Calculation of ideal gas values from ideal heat capacities.
  B. From PVT data of the difference between real gas and ideal gas values.

- The ideal gas heat capacities are different for different gases and ***function of Temp.*** but indep. of Pressure.

Figure 4.1: Ideal-gas heat capacities of argon, nitrogen, water, and carbon dioxide.



- Can be given an experimental equations:
  $C^{ig}_P = A + BT + C\,T^2 + DT^{-2}$
  Table C-1 gives values of these constants.
- C^{ig}_P/R is dimensionless.
- For ideal gas, $C^{ig}_V/R = C^{ig}_P/R - 1$ (4.5)

- **Heat Capacities of Gas mixtures**
  $C^{ig}_{Pmixture} = y_A C^{ig}_{P_A} + y_B C^{ig}_{P_B} + y_C C^{ig}_{P_C}$ (4.6)
  Where, y is mole fraction.

- **Heat Capacities of solids & liquids**

  $C_P / R = A + BT + C\,T^2 + DT^{-2}$ (4.4)

Table C-2, C-3and Perry's hand book , gives values of these constants.
Read Ex. 4.1 and 4.2

- **Iteration procedure is required to calculate T_2 given T_1 and Q or ΔH.**

- Define a mean heat capacity, C_{P_H}, as

  $$C_{P_H} = \int_{T1}^{T2} C_p\, dT / T_2 - T_1$$

- Substitute to the above eq'n,
  $C_P / R = A + BT + C\,T^2 + DT^{-2}$
  and integrate,

$$\boxed{\bullet\ C_{P_H} / R = A + BT_H + C/3\,(4\,T_H^2 - T_1 T_2) + D / T_1 T_2} \qquad \underline{\mathbf{a}}$$

Where $T_H = T_1 + T_2 / 2$ The arithmetic mean temperature.

- Then, $\int_{T1}^{T2} C_p\, dT = C_{P_H}\,(T_2 - T_1)$

and, $\boxed{\Delta H = C_{P_H}\,(T_2 - T_1)}$ $\underline{\mathbf{b}}$

Consequently, $\boxed{T_2 = \Delta H / C_{P_H} + T_1}$ $\underline{\mathbf{c}}$

Solve by iteration:

- Assume value of T_2.
- Subs. in eq'n **a**, then find C_{P_H}.
- Subs. in eq'n **c**, then find T_2.
- Recalculate C_{P_H}, repeat until convergence is achieved for T_2.

OR, use the book solution using τ

4.2 Latent Heats of Pure Substances

- **Latent heat of**

Fusion	**S → L**
Vaporization	**L → G**
Sublimation	**S → G**

<u>During this process, 2 phases exist.</u>

- Latent heat is function of temp. and related to other system properties by exact thermodynamic equations:

Clapeyron Equation

$$\boxed{\Delta H = T\,\Delta V\, dp^{sat}/dT} \qquad \textit{(4.11)}$$

Where,
ΔH = Latent heat.
ΔV = Volume change accompanying the phase change.
p^{sat} = Vapor pressure.

When applied for vaporization,
dp^{sat}/dT = Slope of vapor pressure vs. temp.
$\Delta V = V^{sat}_{Vap} - V^{sat}_{Liq}$

- Latent heats may also be measured calorimetrically. Experimental values are available at selected temperatures for many substances.

- Correlations, like Calpeyron, are available but no enough data information at the desired temperature are known.

- For this reasons, approximate methods have been developed to estimate latent heat of vaporization. They are serve one of two purpose:
    - To predict the heat of vaporization at the normal boiling point.
    - To estimate the heat of vaporization at any temperature from that known at another single temperature.

- ***Trouton's rule***: Rough estimates of latent heat of vaporization for pure liquids at their normal boiling point.

$$\boxed{\Delta H_n / R\, T_n \sim 10}$$

Experimental values for this ratio are: Ar, 8.0; N_2, 8.7; O_2, 9.1; HCl, 10.4; C_6H_6, 10.5; H_2S, 10.6; and H_2O, 13.1.

- ***Riedel Equation***:.

$$\boxed{\Delta H_n / R\, T_n = 1.092\, (\ln P_c - 1.013) / 0.93 - T_{r_n}} \qquad (4.12)$$

Where, T_n = normal boiling pt.
ΔH_n = molar latent heat of vaporization @ T_n.
P_c = critical pressure, bar.
T_{r_n} = reduced temp. @ T_n.

Error < 5%

- ***Watson Equation***:

$$\boxed{\Delta H_2 / \Delta H_1 = (1 - T_{r_2} / 1 - T_{r_1})^{0.38}} \qquad (4.13)$$

Simple and accurate.

Read Ex. 4.4

4.3 Standard Heat of Reaction

- Chemical reactions are accompanied by the transfer of heat, by temp. changes or by both.

- Enthalpy changes during reaction

$$\Delta H = \Delta H_p - \Delta H_R$$

Or the heat of reaction, when both reactant and products are under the same T, P.

- Standard states:
    - Liquids and solids: The real pure liquid or solid at 1 bar.
    - Gases: The pure substance in the ideal-gas state at 1 bar (10^5 Pa). (used to be 1 atm (101,325 Pa)).

- Property values at standard stae is denoted by (^{o}). For example heat capacity at standard state is: $Cp^o = Cp^{ig}$

- The heat of reaction depends on how the reaction written:

$\frac{1}{2} N_2 + 3/2\ H_2 \rightarrow NH_3$ $\Delta H^o_{298} = -46{,}11$ J

Or

$N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta H^o_{298} = -92{,}22$ J (Double)

4.4 Standard Heat of Formation

- ***A formation reaction is the reaction, which forms one mole of a single compound from its constituent elements.***

  For example,

  $C + \frac{1}{2} O_2 + 2H_2 \rightarrow CH_3OH$

  The formation reaction of Methanol.

  But,

  $H_2O + SO_3 \rightarrow H_2SO_4$

  Not formation reaction.

- The standard heat of formation for compounds are tabulated at 298 K (the standard reference temperature). (ΔH^{o}_{298}).
  Given at <u>table C.4</u>.

- Heat of formation reactions at different temperatures can be calculated from heat capacity data and the known value of the standard heat of formation at 298 K.

- **Standard heat of formation for any elements = 0.**

- Chemical equations and standard heat of reaction resulted may added or subtracted to give the standard heat of the required reaction. (Hess's law).

  Consider,

  $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ @ 25°C

  The formation reactions related to this reaction are as follow:

  $CO_2(g)$: $C(s) + O_2(g) \rightarrow CO_2$ $\Delta H^{o}_{f\,298} = -393{,}509$ J
  $H_2(g)$: is an element. $\Delta H^{o}_{f\,298} = 0$
  $CO(g)$: $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\Delta H^{o}_{f\,298} = -110{,}526$ J
  $H_2O(g)$: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ $\Delta H^{o}_{f\,298} = -241{,}818$ J

  Rewrite these equations so that their sum gives the desired reaction

  $CO_2(g) \rightarrow C(s) + O_2(g)$ $\Delta H^{o}_{f\,298} = +393{,}509$ J
  $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\Delta H^{o}_{f\,298} = -110{,}526$ J
  $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ $\Delta H^{o}_{f\,298} = -241{,}818$ J

  $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ $\Delta H^{o}_{f\,298} = 41{,}166$ J

- Standard heat of formation depend on the compound state (g, L, …).

  H_2 (g) + ½ O_2 (g) → H_2O (g) $\Delta H^o_{f\,298}$ = -241,818 J

However, for

  H_2 (g) + ½ O_2 (g) → H_2O (L) $\Delta H^o_{f\,298}$ = -285,830 J

The difference (44,012 J) is approximately the heat of vaporization of H_2O @ 25°C.

Read Example 4.5

4.5 Standard Heat of Combustion

- **A combustion reaction is defined as a reaction between an element or compound and oxygen to form specified combustion products.**

- Many standard heat of formation cam be determined through combustion reactions.

  Consider the formation of n-butane

  4C (s) + 5H_2 (g) → C_4H_{10} (g)
  This reaction does not proceed as indicated above.
  So, we can't directly measure its heat of formation. However consider the combustion reactions:

4C (s) + 4O_2 (g) → 4CO_2 (g) ΔH^o_{298} = (4)(-393,509) J
5H_2 (g) + 5/2O_2 (g) → 5H_2O (L) ΔH^o_{298} = (5)(-285,830) J
4 CO_2 (g) + 5H_2O (L) → C_4H_{10} (g) + 13/2O_2 (g) ΔH^o_{298} = (4)(2,877,396) J

4C (s) + 5H_2 (g) → C_4H_{10} (g) ΔH^o_{298} = -125,790 J

The result is standard heat of formation of n-butane listed in table C.4.

4.6 Temperature Dependence of ΔH^o

- Standard heat of reaction from standard heat of formation at 298 K can be calculated directly:

$$\Delta H^o = \sum \nu_i \Delta H^o_{fi} \qquad (4.15)$$

For example, $4HCl\ (g) + O_2\ (g) \rightarrow 2H_2O\ (g) + 2\ Cl_2\ (g)$

$$\Delta H^o = 2\ \Delta H^o_{f\,H2O} - 4\ \Delta H^o_{f\,HCl}$$

@ 298 K from table C.4

$$\begin{aligned} \Delta H^o &= 2(-241{,}818) - 4(-92{,}307) \\ &= -\ 114{,}408\ J \end{aligned}$$

- If reaction occurs at temperature other than 298 K,

$$d\ \Delta H^o = \Delta C_p^o\ dT \qquad (4.17)$$

Integrate between 298K and T

$$\Delta H^o = \Delta H^o_{298} + R \int_{298.15}^{T} \Delta C_p^o / R\ \ dT \qquad (4.18)$$

Then, $\boxed{\Delta H^o = \Delta H^o_{298} + \Delta C_{p\ H}^{o} (T - 298.15)}$

Where $\Delta C_{p\ H}^{o}$ can be evaluated similar to $C_{p\ H}^{o}$ (mean heat capacity) as:

$$\boxed{\Delta C_{P\ H}^{o} / R = \Delta A + \Delta B T_H + \Delta C/3\ (4\ T_H^2 - T_1\ T_2) + \Delta D / T_1\ T_2}$$

Where $\Delta A = \sum \nu_I A_i$ and so on ………

<u>Read Example 4.6.</u>

4.7 Heat Effects Of Industrial Reactions

- Industrial reactions are rarely carried out under standard state conditions.
    - Reactants may not present in stoichiometric ratios.
    - Reaction may not go to completion.
    - Final temperature may differ from the initial temperature.
    - Inert species may be present.
    - Several reactions may occur simultaneously.

- Calculations of the heat effects of actual reactions are based on theoretical flame temperature (TFT) calculation.

- TFT: is useful to predict the highest achievable temperature, which is useful to select the material type. Usually highest temperature occurs at adiabatic process.

Example 4.7

Read Examples 4.8 and 4.9