

Chapter 8. Balances on Nonreactive Processes

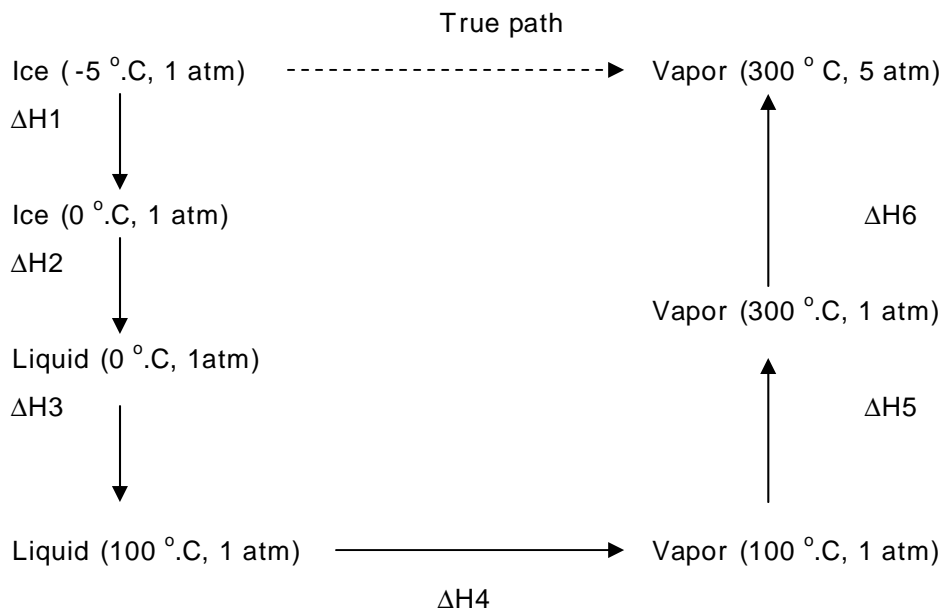
* Topics

- Method of evaluating ΔH and ΔU
- Solving energy balances

8.1 State properties and hypothetical process paths

- * State property - **depends only on the initial and final condition, not on the path**
- * Advantage of using state property
 - Hypothetical process path can be used for the calculation of true process.

Example) Ice, -5 degree C, 1 atm \rightarrow Vapor 300 deg. C, 5 atm



$$\Delta \hat{H} = \sum_{i=1}^6 \hat{H}_i$$

8.2 Changes in P at const. T

* Solid and Liquid

- U is nearly independent of P
- $\Delta U \approx 0, \Delta H \approx V\Delta P$

* Gases

- U and H are nearly independent of P for ideal gases.
- $\Delta U \approx 0, \Delta H \approx 0$ for low pressure (nearly ideal gas)

* For real gases ,

- Tabulated H data
- Thermodynamic relation (from EOS or other methods)

8.3 Changes in T

8.3a Sensible Heat and Heat Capacities

* Sensible Heat () – Heat required to raise temperature of a substance from 1st law of thermodynamics,

$$Q = \Delta U \quad \text{for closed system}$$
$$Q = \Delta H \quad \text{for open system}$$

* Heat capacity at constant volume

$$C_v = \left\{ \lim_{\Delta T \rightarrow 0} \frac{d\hat{U}}{dT} \right\} = \frac{d\hat{U}}{dT} = \left(\frac{\partial U}{\partial T} \right)_v$$

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$

- Ideal gas : exact
- Solid or liquid : good approximation
- Real gas : valid only if V is constant

* Heat capacity at constant pressure

$$C_p = \left\{ \lim_{\Delta T \rightarrow 0} \frac{d\hat{H}}{dT} \right\} = \frac{d\hat{H}}{dT} = \left(\frac{\partial \hat{H}}{\partial T} \right)_p$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

- Ideal gas : exact
- Real gas : valid only if P is constant

$$\Delta H = \int_{T_1}^{T_2} C_p dT + \hat{V}\Delta P$$

- Solid or liquid : good approximation

8.3b Heat Capacity Formulas and Mean Heat Capacities

* Data for heat capacities

$$C_p = a + bT + cT^2 + dT^3$$

values of a,b,c,d are tabulated

- Perry's Handbook
- "Properties of Gases and Liquid "

* Simple Relationship

For liquids and solids , $C_p \approx C_v$

For ideal gases , $C_p = C_v + R$

* Mean Heat Capacity

$$\bar{C}_p = \frac{\hat{H}_2 - \hat{H}_1}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C_p(T) dT}{T_2 - T_1}$$

$$\Delta\hat{H} = \bar{C}_p \Delta T$$

Integration is replaced by simple multiplication

$$\Delta\hat{H}(T_2 \rightarrow T_1) = (\bar{C}_p)_{T_2} (T_2 - T_{ref}) - (\bar{C}_p)_{T_1} (T_1 - T_{ref})$$

(this equation is valid because H is state property)

8.3c Estimation of Heat Capacities

- Estimation Techniques when there are no data for Cp

* Kopp's Rule

- Group Contribution method

* Other sources

- Perry's Handbook

- Properties of Gases and Liquids

* Enthalpy change of mixtures

Rule 1 : assume additivity

$$C_{pm} = \sum y_i C_{pi}(T)$$

$$\Delta H_m = \int_{T_1}^{T_2} C_{pm} dT$$

Rule 2 : For dilute solution, neglect enthalpy change of the solute.

8.3 d Energy Balance for Single -Phase Systems

- Input -Output enthalpy table : Sometimes efficient for complex systems.

8.4 Phase Change Operation

- Heat duties of phase changes are substantial.

- Latent Heats

Latent Heat of Vaporization $\Delta\bar{H}_v$: Liquid-Vapor Transition

Latent Heat of Fusion $\Delta\bar{H}_f$: Solid-Liquid Transition

Latent Heat of Sublimation $\Delta\bar{H}_s$: Solid-Vapor Transition

- Principles can be also extended to solid-solid phase changes.

8.4a Latent Heats

- Latent Heat : heat required for a given phase change at fixed T (or P).

for pure component, F = 1.

Specifying T or P is enough

- Standard heat phase change : Latent heat at 1 atm. (Appendix B.1)

- For closed systems ,

$$Q = m\Delta\bar{U}$$

For liquids and solids, $\Delta\bar{U}_m \approx \Delta\bar{H}_m$

For gases, $\Delta\bar{U}_m = \Delta\bar{H}_m - \Delta(PV) \approx \Delta\bar{H}_m - RT$

8.4b Estimation and Correlation of Latent Heats

- See Perry's Handbook or "Properties of Gases and Liquids"

- Trouton's Rule : Accuracy (+ - 30 %)

$$\Delta\hat{H}_v = 0.088T_b(K), \text{ Nonpolar liquids}$$

$$\Delta\hat{H}_v = 0.109T_b(K), \text{ Water, low m.w. alcohols}$$

- Chen's Equation : Accuracy (+ - 2 %)

$$\Delta\hat{H}_v(kJ/mol) = \frac{T_b [0.0331(T_b/T_c) - 0.0327 + 0.0297 \log_{10} P_c]}{1.07 - (T_b/T_c)}$$

- Estimation Equation of Heat of Fusion

$$\Delta\hat{H}_m(kJ/mol) = 0.0092T_m(K), \text{ Metallic elements}$$

$$\Delta\hat{H}_m(kJ/mol) = 0.025T_m(K), \text{ Inorganic compounds}$$

$$\Delta\hat{H}_m(kJ/mol) = 0.050T_m(K), \text{ Organic compounds}$$

- Estimation of heat of vaporization from vapor pressure data

$$\frac{d(\ln p^*)}{d(1/T)} = \frac{\Delta\hat{H}_v}{R}$$

$$\text{plot of } \ln p^* \text{ vs. } 1/T \rightarrow \text{slope} = \frac{\Delta\hat{H}_v}{R}$$

- Watson correlation : heat of vaporization for other temperature

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1) \left[\frac{T_c - T_2}{T_c - T_1} \right]^{0.38}$$

8.4c Energy Balances Involving Phase Changes

→ See example 8.4 -4

8.4d Psychrometric charts

- Psychrometric chart : plot of several properties of a gas -vapor mixture

Air – Water system at 1 atm : Figure 8.4 -1

- Wet bulb and dry bulb temperature

Dry bulb temperature : normal temperature

Wet bulb temperature : measure of saturation of the given liquid (water)

- How to read psychrometric chart ?

$$F = 2 + 2^{-1} = 3$$

P : 1 atm for psychrometric chart

Other 2 variables : Tdb and Twb

T db or hr ,

H : add enthalpy deviation to the H at saturation

- See example 8.4 -5 for reading the psychrometric chart

8.4e Adiabatic Humidification

- * Adiabatic humidification

evaporation of a liquid into gas -liquid mixture

latent heat required to evaporate liquid is provided by the sensible heat lost by the gas phase.

- * Adiabatic humidification

- drying of solid product

- production of humid air

* For air -water system, adiabatic saturation curve coincide with the constant wet -bulb temperature line.

8.5 Mixing and Solution

* Heat of Mixing

$$H = \sum x_i H_i + \Delta H_{mix}$$

- Heat effect accompanied by mixing of two different species
- $\Delta H_{mix} \approx 0$ for hydrocarbons and simple molecules. But for some mixtures heats of mixing are substantial.

8.5a Heat of Solution and Mixing

* Integral Heat of Solution $\Delta \hat{H}_s(T, n)$:

Enthalpy for process when 1 mol of solute is dissolved in n moles of liquid solvent at const. T

* Heat of solution at infinite dilution

$$: \Delta \hat{H}_s(T, n \rightarrow \infty)$$

* Calculation of Enthalpy

$$\Delta H = n \Delta \hat{H}_s : n \text{ is the moles of solvent at the given conc.}$$

* Two reference state

- i) Based on pure solvent and solute

$$\hat{H}_{ref} = \Delta \hat{H}_s(n)$$

- ii) Based on pure solvent and infinite dilution solution

(1 mol HCl, 10^6 mol H₂O) \rightarrow (1 mol HCl, 10 mol water) + (($10^6 - 10$) mol water)

$$\Delta \hat{H}_s(\infty) \qquad \Delta \hat{H}_s(n) \qquad 0$$

$$\hat{H}_{ref} = \Delta \hat{H}_s(n) - \Delta \hat{H}_s(\infty)$$

*** Note enthalpies are expressed per solute not moles of solution.**

8.5b Balances on Dissolution and Mixing Process

- * Prepare enthalpy table for each streams.
- * Use $n_i \hat{H}_i$ values
- * Calculate enthalpies based on 25 deg.C values.