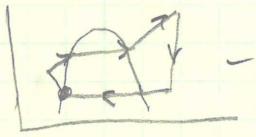
Concept 1 Enthalpy is a state function



- Enthalpy is independent of path
- Always talk about ΔH from some reference condition
- Steam tables → triple point ⇒ $\hat{H}=0$
- other tables are different
- don't mix and match!!

Concept 2 (Heat Capacities)

$\hat{H} = f(T,P)$ $\quad$ $\hat{U} = f(T,P)$

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_P dT + \left(\frac{\partial \hat{H}}{\partial P}\right)_T dP$$

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T d\hat{V}$$

$$C_P \equiv \left(\frac{\partial \hat{H}}{\partial T}\right)_P \qquad C_V \equiv \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}}$$

For ideal gases,

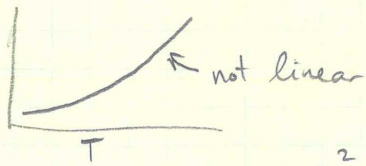
$$d\hat{H} = \hat{C}_P dT \qquad d\hat{U} = \hat{C}_V dT$$

for solids & liquids

$$d\hat{H} = \hat{C}_P dT + \hat{V} dP$$

so for ideal gases

$$\Delta\hat{H} = \int_{T_1}^{T_2} \hat{C}_P dT$$



$$\hat{C}_P = a + bT + cT^2 + dT^3 \ldots \quad \left(\text{DIPPR} = A + B\left(\frac{C/T}{\sinh C/T}\right)^2 + D\left(\frac{E/T}{\cosh E/T}\right)^2\right)$$

so

$$\Delta H_{(T_1 \to T_2)} = \int_{T_1}^{T_2} \left(a + bT + cT^2 + dT^3\right) dT$$

$$= a(T_2 - T_1) + \frac{b}{2}\left(T_2^2 - T_1^2\right) + \frac{c}{3}\left(T_2^3 - T_1^3\right) + \frac{d}{4}\left(T_2^4 - T_1^4\right)$$

Ideal gases $C_P = C_V + R$ (8.3-12)

Solids & liquids $C_P \cong C_V$

Concept 3 Phase change (pure substance)

$\Delta\hat{H}_{melt} = \hat{H}_l - \hat{H}_s$ ⇒ tabulated

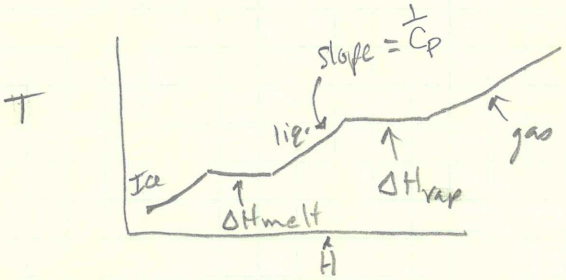
$\Delta\hat{H}_{vap} = \hat{H}_g - \hat{H}_l$ ⇒ tabulated

$\Delta\hat{H}_{freezing} = -\Delta\hat{H}_{melt}$

$\Delta H_{condens} = -\Delta H_{vap}$

also ΔH_{sub}

water



for pure component, T is constant during phase change

* Look at Tables (ppt files)
  - Cautions
  - Kopp's rule

* Sometimes we get lazy

$$\bar{C}_p = \frac{H_2 - H_1}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C_p\, dT}{T_2 - T_1}$$

Then $H_2 - H_1 = \bar{C}_p (T_2 - T_1)$ (like on an exam)

$$\Delta H_{sys} = H_{out} - H_{in}$$

$$= \left(\sum n_i \hat{H}_i\right)_{out} - \left(\sum n_i \hat{H}_i\right)_{in}$$

okay if same reference enthalpies are used

$$= \sum n_i \Delta H_i \quad \text{(if moles}_i \text{ are constant)}$$

$$= \left(\sum n_i a_i\right)(T_{out} - T_{in}) + \left(\sum n_i b_i\right)\frac{T_{out}^2 - T_{in}^2}{2} + \left(\sum n_i c_i\right)\frac{\left(T_{out}^3 - T_{in}^3\right)}{3} \quad \text{etc.}$$

→ What if moles$_i$ are not constant? (like with a chemical reaction!)

Concept 4 ΔH_f°

- Can use ΔH_f° as reference at 25°C, 1 atm
- Good for reaction chemistry
- $\Delta H_f^\circ = 0$ for species whose natural state is at 25°C, 1 atm

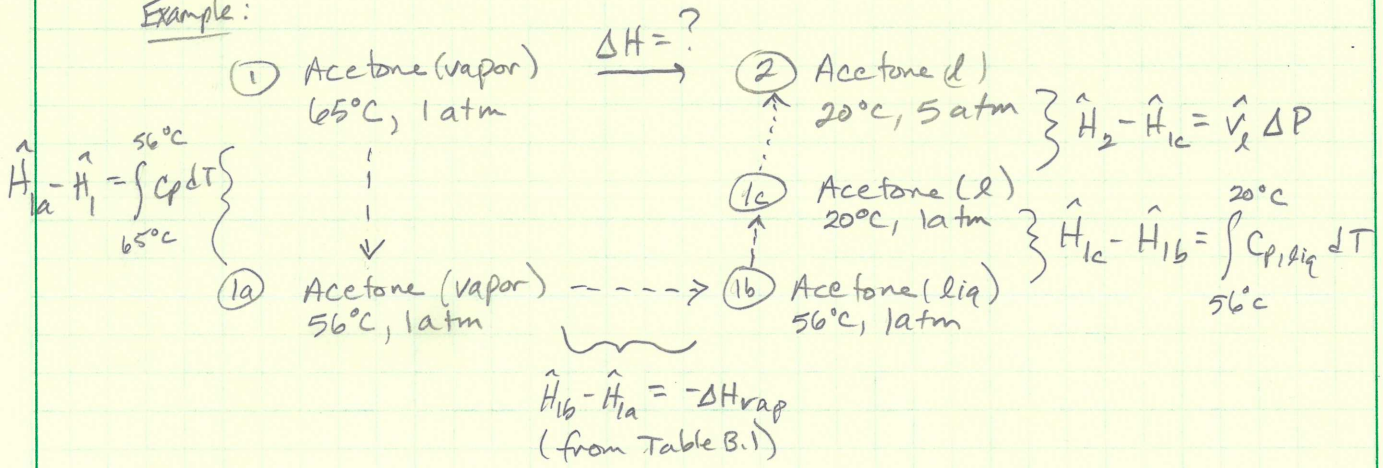
(N_2, O_2, C(graphite), H_2)

$$\hat{H}_i = \Delta H_{f,i}^\circ + \int_{25^\circ C}^{T} C_{p,i}\, dT$$

↑ Tabulated (B.1)

Concept 5 ΔH along a path

Example:



$$\Delta H = \hat{H}_2 - \hat{H}_1 = \Delta\hat{H}_{2-1c} + \Delta\hat{H}_{1c-1b} + \Delta\hat{H}_{1b-1a} + \Delta\hat{H}_{1a-1}$$

$$= \hat{V}_l \Delta P + \int_{56^\circ C}^{20^\circ C} C_{p_{liq}}\, dT - \Delta H_{v\ at\ 56^\circ C} + \int_{65^\circ C}^{56^\circ C} C_{p_{gas}}\, dT$$

Alternate

$$\hat{H}_1 = \Delta H_{f,vapor}^\circ + \int_{25^\circ C}^{65^\circ C} C_{p_{vap}}\, dT$$

$$\hat{H}_2 = \Delta\hat{H}_{f,liq}^\circ + \int_{25^\circ C}^{20^\circ C} C_{p_{liq}}\, dT + \hat{V}_l \Delta P$$

$$\hat{H}_2 - \hat{H}_1 = \underbrace{\left(\Delta H_{f,liq}^\circ - \Delta H_{f,vap}\right)}_{-\Delta H_{vap}\ at\ 25^\circ C} + \int_{25^\circ C}^{20^\circ C} C_{p_{liq}}\, dT + \hat{V}_l \Delta P - \int_{25^\circ C}^{65^\circ C} C_{p_{vap}}\, dT$$