Concept 1: Enthalpy is a state function

- Enthalpy is independent of path
- Always talk about \( \Delta H \) from some reference condition
- Steam tables \( \Rightarrow \) triple point \( \Rightarrow \) \( H = 0 \)
- Other tables are different
- Don’t mix and match!

Concept 2: (Heat Capacities)

\[
\hat{H} = f(T,P) \\
\hat{U} = f(T,P) \\
C_P = \left( \frac{\partial \hat{H}}{\partial T} \right)_P \\
C_v = \left( \frac{\partial \hat{U}}{\partial T} \right)_P
\]

\[
\begin{align*}
\Delta H & = \int_{T_1}^{T_2} C_P dT \\
\hat{C}_P & = a + bT + cT^2 + dT^3 \ldots \quad (DIPPR = A + B\left(\frac{C/T}{\sinh(C/T)}\right)^2 + D\left(\frac{E/T}{\cosh(E/T)}\right)^2) \\
\Delta H_{(T_1 \rightarrow T_2)} & = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3) dT \\
& = a(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + \frac{c}{3} (T_2^3 - T_1^3) + \frac{d}{4} (T_2^4 - T_1^4)
\end{align*}
\]

\[
C_P \quad \text{area} = \Delta \hat{H}
\]

Ideal gases \( C_P = C_v + R \) \( (8.3 - 12) \)

Solids \& liquids \( C_P \leq C_v \)
Concept 3: Phase change (pure substance)

\[ \Delta H_{\text{melt}} = \hat{H}_f - \hat{H}_s \Rightarrow \text{tabulated} \]

\[ \Delta H_{\text{mp}} = \hat{H}_g - \hat{H}_l \Rightarrow \text{tabulated} \]

\[ \Delta H_{\text{freezing}} = -\Delta H_{\text{melt}} \]

\[ \Delta H_{\text{condens}} = -\Delta H_{\text{vap}} \]

Also: \[ \Delta H_{\text{sub}} \]

For pure compound,

\( T \) is constant during phase change

* Look at Tables (ppt files)

Cautions
- Kopp's rule

* Sometimes we get lazy

\[ \bar{C}_p = \frac{H_2 - H_1}{T_2 - T_1} = \frac{\int C_p dT}{T_2 - T_1} \]

Then \( H_2 - H_1 = \bar{C}_p (T_2 - T_1) \)

(like an \( \bar{C}_p \) average)

\[ \Delta H_{\text{sys}} = H_{\text{out}} - H_{\text{in}} \]

\[ = (E_n; H_i)_{\text{out}} - (E_n; H_i)_{\text{in}} \]

Okay if same reference enthalpies are used

\[ = E_n; \Delta H_i \quad \text{(if moles are constant)} \]

\[ = (E_n; a; (T_{\text{out}} - T_i)) + (E_n; b; \frac{T_{\text{out}}^2 - T_i^2}{2}) + (E_n; c; \frac{T_{\text{out}}^3 - T_i^3}{3}) \]

\[ \Rightarrow \text{What if moles are not constant?} \]

(like with a chemical reaction!!)
Concept 4: \( \Delta H_f^\circ \)
- Can use \( \Delta H_f^\circ \) 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
  \( (N_2, O_2, C(graphite), H_2) \)

\[ H_i = \Delta H_f^\circ_i + \int_{25^\circ C}^{T} C_p \, dT \]

Tabulated (8.1)

Concept 5: \( \Delta H \) along a path

Example:

1. Acetone (vapor) \( \Delta H = ? \)
   - \( 55^\circ C, 1 \text{ atm} \)
   - \( 20^\circ C, 5 \text{ atm} \)
   - \( \hat{H}_2 - \hat{H}_{1c} = \hat{V}_x \Delta P \)
   - \( \hat{H}_{1c} \)
   - \( 20^\circ C, 1 \text{ atm} \)
   - \( \hat{H}_{1b} = \int_{50^\circ C}^{55^\circ C} C_p \, dT \)

\( \hat{H}_{ib} - \hat{H}_{ia} = \Delta H_{\text{vap}} \)
   (from Table 8.1)

\[ \Delta H = \hat{H}_2 - \hat{H}_1 = \Delta H_{2-1c} + \Delta H_{1c-1b} + \Delta H_{1b-1a} + \Delta H_{1a-1} \]

Alternate

\[ \hat{H}_1 = \Delta H_{f,vap}^\circ + \int_{25^\circ C}^{65^\circ C} C_p \, dT \]

\[ \hat{H}_2 = \Delta H_{f,liq}^\circ + \int_{25^\circ C}^{20^\circ C} C_p \, dT + \hat{V}_x \Delta P \]

\[ \hat{H}_2 - \hat{H}_1 = (\Delta H_{f,liq}^\circ - \Delta H_{f,vap}^\circ) + \int_{25^\circ C}^{20^\circ C} C_p \, dT + \hat{V}_x \Delta P - \int_{25^\circ C}^{65^\circ C} C_p \, dT \]