Statistical Molecular Thermodynamics

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Video 5.8

Heat Capacities
Heat Capacity is a Path Function

The *amount of energy required to raise the temperature of a substance by one degree* is different if done at constant $V$ or constant $P$:

- At constant $V$, the energy added as heat is $q_V$, \( (\Delta U = q_V) \)
  \[
  C_V = \left( \frac{\partial U}{\partial T} \right)_V \approx \frac{\Delta U}{\Delta T} = \frac{q_V}{\Delta T}
  \]

- At constant $P$, the energy added as heat is $q_P$, \( (\Delta H = q_P) \)
  \[
  C_P = \left( \frac{\partial H}{\partial T} \right)_P \approx \frac{\Delta H}{\Delta T} = \frac{q_P}{\Delta T}
  \]
Heat Capacities of Ideal Gas

For an ideal gas: \[ H = U + PV \]
\[ = U + nRT \]

Differentiating: \[ \frac{dH}{dT} = \frac{dU}{dT} + nR \]

For an ideal gas, \( U \) and \( H \) depend only on \( T \), not \( P \) or \( V \)

So: \[ \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + nR \]

Or: \[ C_P = C_V + nR \]

Recall that for a monatomic ideal gas, \( \overline{C}_V = (3/2)R \), so the difference between \( \overline{C}_P \) and \( \overline{C}_V \) is 67% of \( \overline{C}_V \)
The difference in enthalpy at two different temperatures is determined from integration of $C_P$ over the temperature range:

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \rightarrow dH = C_P dT \rightarrow H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T) dT$$

This is true only if there is no phase transition occurring between $T_1$ and $T_2$. At a phase transition, there is no change in the temperature as you add heat ($C_P \rightarrow \infty$), so one must also add any enthalpy associated with a phase change where needed:

Example: $H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^S(T') dT' + \Delta_{\text{fus}} H + \int_{T_{\text{fus}}}^{T} C_P^L(T') dT'$

Solid, from $T=0$ to $T=T_{\text{fus}}$ \hspace{1cm} Enthalpy of fusion \hspace{1cm} Liquid, from $T=T_{\text{fus}}$ to $T=T_{\text{fus}}$ to $T=T$
Enthalpy of Benzene

Benzene: $T_{\text{fus}} = 278.7\ \text{K}$, $T_{\text{vap}} = 353.2\ \text{K}$

Measuring the heat capacity, temperature by temperature

Integrating the heat capacity, adding phase changes

For $T > T_{\text{vap}}$, 

$$H(T) - H(0) = \int_{0}^{T_{\text{fus}}} C_P^S(T')\,dT' + \Delta_{\text{fus}}\,H + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_P^l(T')\,dT' + \Delta_{\text{vap}}\,H + \int_{T_{\text{vap}}}^{T} C_P^g(T')\,dT'$$