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* $\overline{C}_V$

Determining Enthalpy

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: $H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^{\text{s}}(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{fus}}}^{T} C_P^{\text{l}}(T')\,dT'$

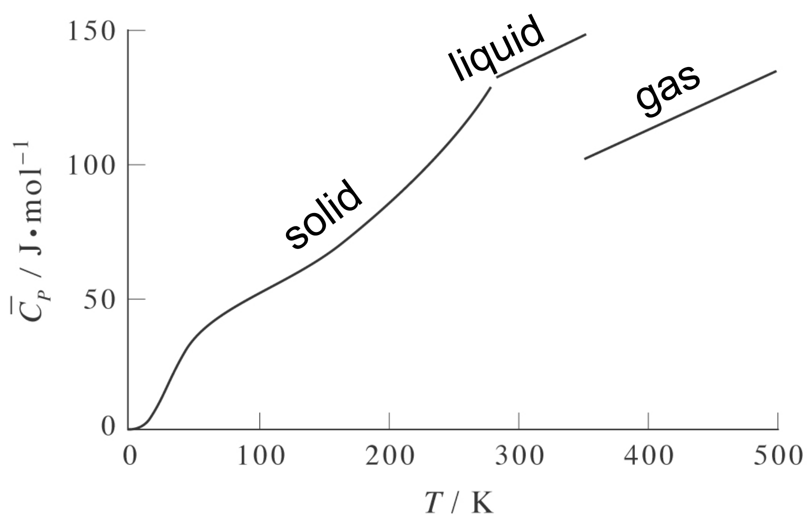
Solid, from $T=0$ to $T=T_{\text{fus}}$

Enthalpy of fusion $\Delta_{\text{fus}}H = H^{\text{l}}(T_{\text{fus}}) - H^{\text{s}}(T_{\text{fus}})$

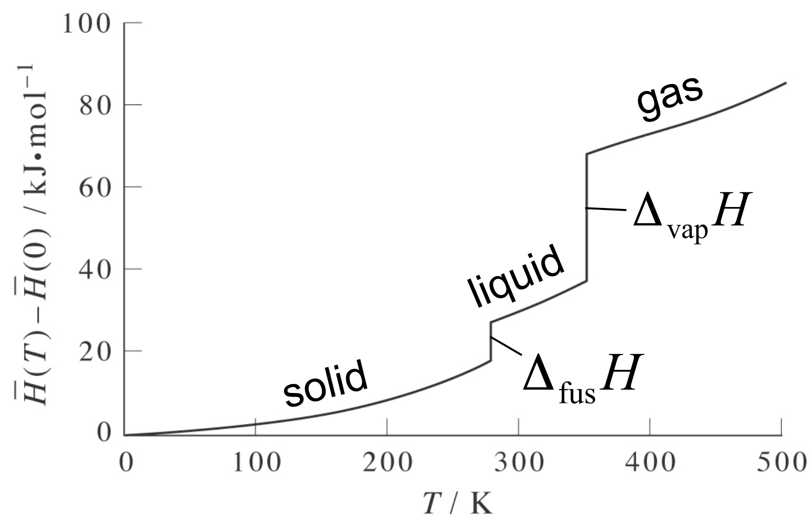
Liquid, from $T=T_{\text{fus}}$ to $T=T$

Enthalpy of Benzene

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



Measuring the heat capacity, temperature by temperature



Integrating the heat capacity, adding phase changes

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

$$H(T) - H(0) = \int_0^{T_{\text{fus}}} C_P^{\text{s}}(T')\,dT' + \Delta_{\text{fus}}H + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_P^{\text{l}}(T')\,dT' + \Delta_{\text{vap}}H + \int_{T_{\text{vap}}}^{T} C_P^{\text{g}}(T')\,dT'$$