Statistical Molecular Thermodynamics

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Video 5.11

Review of Week 5

Critical Concepts from Week 5

- The First Law of Thermodynamics states that energy is conserved; mathematically $dU = \delta q + \delta w$ where U is internal energy, q is heat, and w is work; by convention, heat is positive when it is absorbed by the system, work is positive when it is done *on* the system, and vice versa in both cases
- Energy is a state function, while heat and work are path functions
- The work done by an expanding gas is $-P_{\text{ext}}dV$ where P_{ext} is the external pressure against which the gas expands
- A reversible processes happens in infinitesimally small steps; the maximum work that can be extracted from the isothermal expansion of a gas is the reversible work

Critical Concepts from Week 5

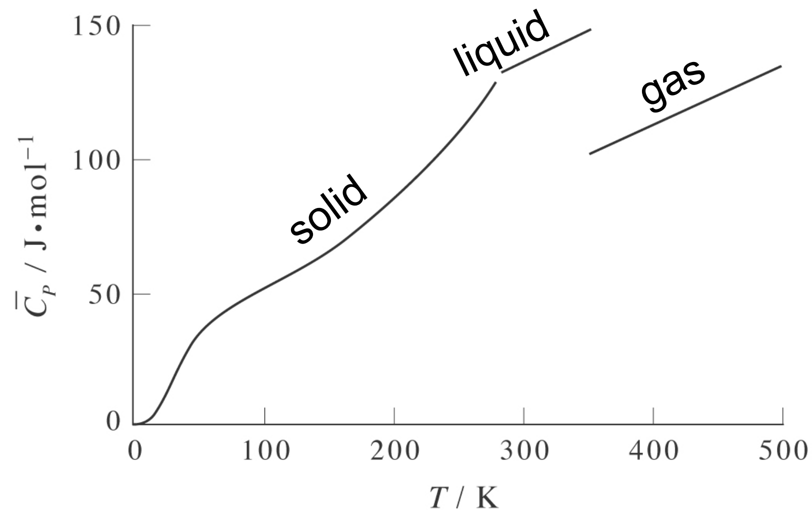
- An adiabatic process is one for which $\delta q = 0$, under which conditions w is a state function
- A gas cools as it expands adiabatically against external pressure
- Enthalpy H is defined as $U + PV$ and ΔH *for a constant pressure process* is equal to the heat transferred q_P
- The constant pressure heat capacity is defined as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

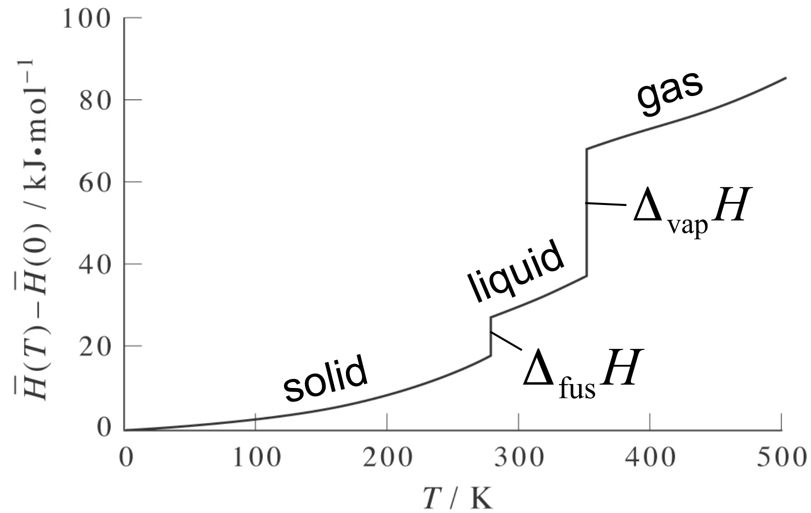
- For an ideal gas, $\overline{C}_P = \overline{C}_V + R$

Critical Concepts from Week 5

- Enthalpy changes with temperature can be determined from heat capacities, the latter can be determined experimentally



Measuring the heat capacity, temperature by temperature



Integrating the heat capacity, adding phase changes

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

For $T > T_{vap}$,

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

Critical Concepts from Week 5

- Hess' Law relies on the nature of enthalpy as a state function to assert that enthalpies are additive; this permits enthalpy changes for unknown reactions to be determined by the suitable addition (or subtraction) of enthalpy changes for *known* reactions
- Standard enthalpies of reaction are intensive and tabulated for defined standard states chosen by convention
- Standard molar enthalpies of formation are defined to be zero for pure elements in their most stable standard state forms; enthalpies of formation for all other molecules may then be determined from suitable reactions to form them from their precursor constituent elements

Critical Concepts from Week 5

- Given $\Delta_f H^o$ and C_P values for reactants and products, $\Delta_r H$ can be computed for any reaction

$$a\mathrm{A} + b\mathrm{B} \longrightarrow y\mathrm{Y} + z\mathrm{Z}$$

$$\boldsymbol{\Delta_r H = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})}$$

$$\Delta_r H = \left(y\Delta_f H^\circ[\mathrm{Y}] + z\Delta_f H^\circ[\mathrm{Z}]\right) - \left(a\Delta_f H^\circ[\mathrm{A}] + b\Delta_f H^\circ[\mathrm{B}]\right)$$

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2}\left[C_P(\text{products}) - C_P(\text{reactants})\right] dT$$