

Measuring entropy from heat capacity data:

Under constant volume conditions:

From $dU = \delta q_{\text{rev}} + \delta w_{\text{rev}}$ we have $dU = TdS - PdV$

$$dV = 0 \Rightarrow dU = TdS \Rightarrow dS = \frac{1}{T} dU$$

$$\Rightarrow \left. \frac{\partial S}{\partial T} \right|_V = \frac{1}{T} \left. \frac{\partial U}{\partial T} \right|_V = \frac{C_V}{T}$$

$$\text{Integrate: } \Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

Under constant pressure conditions:

$$H = U + PV \Rightarrow dH = dU + PdV + VdP$$

$$= TdS - PdV + PdV + VdP = TdS$$

$$\text{Thus } dS = \frac{1}{T} dH \Rightarrow \left. \frac{\partial S}{\partial T} \right|_P = \frac{1}{T} \left. \frac{\partial H}{\partial T} \right|_P = \frac{C_P}{T}$$

$$\text{Integrate: } \Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

3rd Law: $S(T=0) = 0$

Thus we can write $S(T) = \int_0^T \frac{C_P(T')}{T'} dT'$ *absolute entropy*

One last hitch: $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}}$

ie extra contribution from phase transitions

Show Fig 21.2

section 21-9: Entropy changes of chemical reactions (30a)

Since we know how to compute the entropy of a substance from $S(T) = \int_0^T \frac{C_p(T')}{T'} dT'$ (+ phase transitions)

we can generate a table of standard molar entropies, see Table 21.2

Then, for the chemical reaction $aA + bB \rightarrow yY + zZ$ the standard entropy change is given by

$$\Delta S_{\text{rxn}}^{\circ} = yS^{\circ}(Y) + zS^{\circ}(Z) - aS^{\circ}(A) - bS^{\circ}(B).$$



$$\Delta S_{\text{rxn}}^{\circ} = S^{\circ}(\text{H}_2\text{O}(\text{l})) - S^{\circ}(\text{H}_2(\text{g})) - \frac{1}{2}S^{\circ}(\text{O}_2(\text{g}))$$

$$= 70.0 - 130.7 - \left(\frac{1}{2}\right)205.2$$

$$= -163.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

large negative value because we are converting gas to liquid which is more ordered.