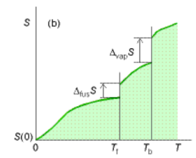
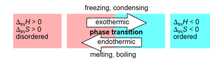
59-240 Lecture 11 Entropy Changes and Processes

Measurement of Entropy

- $$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)\,dT}{T} + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)\,dT}{T} + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(g)\,dT}{T}$$
- 

- N_2 example
- Debye extrapolation
  - $$S(T) = S(0) + \int_0^{T_f} \frac{aT^3\,dT}{T}$$

Phase transitions

- phase trans: reversible
  - transfer of heat is reversible
  - phases are in equilibrium
- $$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$
- 

- Trouton's Rule
  - Most solvents
  - H_2O case
  - CH_4 case

Entropy equations summary

- $$\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = \int_{T_i}^{T_f} \frac{C_V\,dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$
- $$\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = \int_{T_i}^{T_f} \frac{C_p\,dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right)$$
- $$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{P_i}{P_f}\right)$$
- $$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

Perfect Gas Expansion

- See Lecture 10
- $$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$
- Reversible change
  - $\Delta S_{tot} = 0$
  - $\Delta S_{sur} = -\Delta S = -nR \ln (V_f / V_i)$
- Free expansion
  - $w = 0$, $q = 0$
  - $\Delta S_{sur} = 0$ and $\Delta S_{tot} = \Delta S = nR \ln (V_f / V_i)$

Temperature Change

- $$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$
- $$dq_{rev} = C_p\,dT$$
- $$S(T_f) = S(T_i) + \int_i^f \frac{C_p\,dT}{T}$$
- Example of simultaneous expansion and heating

Melting an ice cube

- Adiabatic case
  - Steps
    - Calculate q_1 and ΔS_1 for cooling water to Tfus from Ti
    - At Tfus, calculate q_2 and ΔS_2 to melt ice cube
    - Figure out Tf, calculate q_3 and ΔS_3 to reach this temp
  - Equations
    - $$\Delta S_1 = \int_{T_i}^{T_{fus}} \frac{dq}{T} = C_p \int_{T_i}^{T_{fus}} \frac{dT}{T} = C_p \ln\left(\frac{T_{fus}}{T_i}\right)$$
    - $$\Delta S_2 = \frac{q_{fus}}{T} = \frac{\Delta H_{fus}}{T}$$
    - $$\Delta S_3 = C_p \ln\left(\frac{T_f}{T_{fus}}\right)$$
  - Homework problem
- Isothermal case
  - Same steps
  - But...you already know Tf!