59-240 Lecture 12: Third Law & Entropy Changes for Processes

Third Law of Thermodynamics

- T = 0 K
- Thermal motion quenched
- Arrangement of atoms not taken into account
- Nernst Heat Theorem
  - $\Delta S \rightarrow 0$ as $T \rightarrow 0$
- Statement of 3rd Law
  - If the entropy of every element in its most stable state at T = 0 is taken as zero, then every substance has a positive entropy which at T = 0 may become zero, which is also zero for all perfect crystalline substances, including compounds.
  - This does not mean that the entropy at T = 0 is really zero!
  - Choosing S = 0 at T = 0 for each pure substance allows for comparison of relative entropies
- Standard Reaction Entropies
  - $\Delta_r S^\circ = \sum_{\text{products}} \nu S_m^\circ - \sum_{\text{reactants}} \nu S_m^\circ = \sum_J \nu_J S_m^\circ(\text{J})$
- Reaching Low Temperatures
  - Adiabatic Demagnetization

Helmholz and Gibbs energies

- Heat transfer at constant V
  - $dS - \frac{dU}{T} \geq 0$
    $T\,dS \geq dU$
  - Constant $dU = 0$ or $dS = 0$:
    $dS_{U,V} \geq 0 \qquad dU_{S,V} \leq 0$
  - **Helmholtz Energy, *A***
    $A = U - TS$
    $dA = dU - T\,dS$
    $dA_{T,V} \leq 0$
- Heat transfer at constant p
  - $dS - \frac{dH}{T} \geq 0$
    $T\,dS \geq dH$
  - Constant $dH = 0$ or $dS = 0$:
    $dS_{H,p} \geq 0 \qquad dH_{S,p} \leq 0$
  - **Gibbs Energy, *G***
    $G = H - TS$
    $dG = dH - T\,dS$
    $dG_{T,p} \leq 0$
- Criteria for spontaneity
  - H and U not satisfactory
  - S not satisfactory
  - Limiting conditions for these state functions
  - require conditions where either p, T or V, T can be controlled

Gibbs energy

- $G = H - TS$
  $dG = dH - T\,dS$
  $dG_{T,p} \leq 0$
- reversibility, $dG = 0$
- spontaneous, $dG < 0$
- max. non-exp work
  - $dw_{\text{e,max}} = dG$
  - $dG = dw_{\text{e,rev}} + V\,dp$
  - calculation
  - $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$
  - standard Gibbs energy of formation
  - $\Delta_r G^\circ = \sum_{\text{products}} \nu \Delta_f G^\circ - \sum_{\text{reactants}} \nu \Delta_f G^\circ = \sum_J \nu_J \Delta_f G^\circ(\text{J})$

Helmholz energy

- $A = U - TS$
  $dA = dU - T\,dS$
  $dA_{T,V} \leq 0$
- reversibility, $dA = 0$
- spontaneous, $dA < 0$
- maximum expansion work
  - $dw_{\text{max}} = dA$
  - $dw_{\text{max}} = dU - T\,dS$
  - $\Delta A = \Delta U - T\Delta S$
  - examples
  - calculating max. work