Chapter 3

Equilibrium occurs when $\frac{\partial S_{total}}{\partial q_A} = 0$ ← Einstein solid

generalize a bit

$$\frac{\partial S_{total}}{\partial U_A} = 0$$

$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

$$U_B = U - U_A$$

$$dU_B = - dU_A$$

$$\frac{\partial S_A}{\partial U_A} + \frac{S_B}{\partial U_A} = 0$$

$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

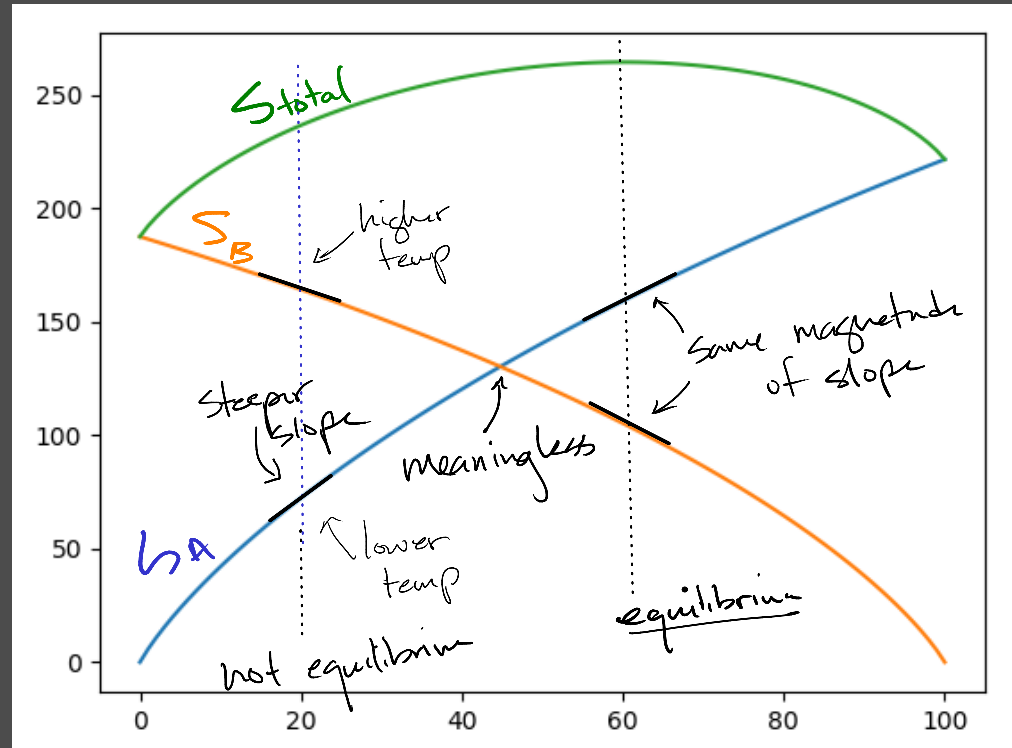
$$\boxed{\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}}$$

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

$$\boxed{T = \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V}}$$

this the definition of temperature

Entropy



q_A

HW: 1, 3

Anaconda
miniconda

Apply to hot Einstein solid ($q >> N$)

$$\Omega = \left(\frac{eq}{N}\right)^N \qquad q >> N \text{ limit}$$

\# of packets of energy

energy of one energy packet

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} \qquad S = k_B \ln \Omega = k_B N \ln\left(\frac{eq}{N}\right)$$

$$U = q \cdot \epsilon$$

$$q = \frac{U}{\epsilon}$$

$$S = k_B N \left(\ln \frac{U}{N\epsilon} + \cancel{\ln} e \right)$$

1

$$S = k_B N \ln U - k_B N \ln N\epsilon + k_B N$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B N}{U}$$

$$T = \frac{U}{N k_B} \Rightarrow \underbrace{U = N k_B T}$$

→ Equipartition Theorem

$f = 2$

→ 1-D kinetic energy

→ 1-D potential energy

What about an ideal gas

Sackur-Tetrode equation

$$\Omega = f(N) \cdot V^N \cdot U^{3N/2}$$

$$S = k_B \ln \Omega = k_B \ln V^N + k_B \ln U^{3N/2} + k_B \ln f(N)$$

$$= k_B N\left(\ln V + \frac{3}{2} \ln U + \ln f(N)\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3}{2} \frac{k_B N}{U}$$

$$U = \frac{3}{2} N k_B T \quad \checkmark\checkmark$$

$f = 3 \rightarrow$ 3-D kinetic energy

Entropy + Heat

Experiment to determine <u>heat</u> capa<u>city</u>.

Also have a theory to make a prediction

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$\hookrightarrow U(T)$

high temp solid

$$C_V = \frac{\partial}{\partial T}(Nk_BT)$$

$$= Nk_B = n_m R$$

ideal gas (monoatomic)

$$C_V = \frac{3}{2}Nk_B = \frac{3}{2}n_m R$$

Review the process for any material to predict heat capacity

1. Use combinatorics + QM to find an expression for Ω in terms of U, V, N etc. } probably impossible!
2. $S = k_B \ln \Omega$
3. $T = \left(\frac{\partial S}{\partial U}\right)_{N,V\text{ etc}}$
4. solve for U in terms of T
5. take partial of U w.r.t. $T \rightarrow C_V$

stat mech give an alternative $\rightarrow$ Ch. 6

We can measure S, by going <u>backwards</u>.

$$dS = \underbrace{\frac{\partial S}{\partial U}}_{\frac{1}{T}} \cdot dU$$

$$dS = \frac{dU}{T}$$

constant volume (isochoric)

$$đW = 0$$

$$dU = đQ$$

$$\boxed{dS = \frac{đQ}{T}}$$

original definition of entropy

T does not change much w/ a little $đQ$ added

$$\Delta S = \frac{Q}{T} \Big\} \text{ phase change}$$

rewrite in terms of heat capacity

$$dS = \frac{C_v dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v \, dT}{T}$$

can be constant but can also be a function of temp itself.

$$đW = p dV$$

$$dU = đQ + đW$$

$$dU = đQ - p dV$$

$$dU = T dS - p dV$$

$$S(T_f) - S(0) = \int_0^{T_f} \frac{C_V}{T}\, dT$$

need to know all the way to zero.

0 or some constant → residual entropy

→ much experimental data for many substances tabulated by chemists!