3.2 Entropy and Heat

Remember $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V}$. To compute from first principles, need to find expression for $\Omega(U,V,N)$, get $S = k_B \ln \Omega$, compute $(\partial S/\partial U) = 1/T$, solve for U as a function of T, then finally $(\partial U/\partial T)_{N,V}$

Couple of simple systems $U = Nk_BT$ for high T Einstein model $\Rightarrow C_V = Nk_B$

also ideal gas $U = \frac{f}{2}Nk_BT \to C_V = \frac{f}{2}Nk_B$

also Einstein model any T $U = \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1} \Rightarrow C_V = \frac{N\hbar\omega}{(e^{\frac{\hbar\omega}{kT}}-1)^2} e^{\frac{\hbar\omega}{kT}} \frac{\hbar\omega}{k_BT^2}$

$C_V = Nk_B \left[\frac{\hbar\omega}{k_BT} / (1 - e^{-\frac{\hbar\omega}{k_BT}})\right]^2 e^{-\hbar\omega/k_BT}$

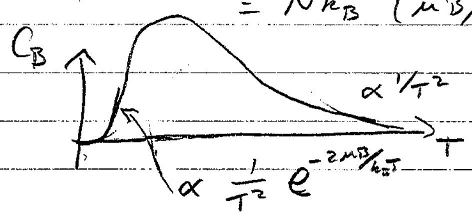
These are 3 examples

From 3.3 on paramagnets $U = N\mu B \frac{e^{-\frac{\mu B}{k_BT}} - e^{\mu B/k_BT}}{e^{-\frac{\mu B}{k_BT}} + e^{\mu B/k_BT}}$ $\quad x \equiv \frac{\mu B}{k_BT}$

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = N\mu B\left(-\frac{\mu B}{k_BT^2}\right)\left[\frac{-e^{-x} - e^{x}}{e^{-x}+e^{x}} + \frac{(e^{-x}-e^{x})^2}{(e^{-x}+e^{x})^2}\right]$$

$$= -Nk_B\left(\frac{\mu B}{k_BT}\right)^2 \left[\frac{-4}{(e^{-x}+e^{x})^2}\right] = Nk_B\left[\frac{\mu B}{k_BT}\frac{2}{e^{\frac{\mu B}{k_BT}} + e^{-\frac{\mu B}{k_BT}}}\right]^2$$

$$= Nk_B\,(\mu B/k_BT)^2 / \cosh^2\left(\frac{\mu B}{k_BT}\right)$$



In many respects, it is easier to measure entropy than to calculate it

Start with $\left(\frac{\partial S}{\partial U}\right)_{N,V} = 1/T \to dS = \frac{dU}{T} = \frac{Q}{T}$ ← because constant V no W.

Note this is an infinitesimal relation.

If $\Delta T = 0$ (like in phase change with latent heat) $\Delta S = \frac{Q}{T}$ ← exact

A different relation can be obtained if you know $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$

$\Rightarrow dU = C_V\,dT \Rightarrow dS = C_V\frac{dT}{T} \Rightarrow S_f - S_i = \int_{T_i}^{T_f} C_V(T)\frac{1}{T}\,dT$

In many materials $C_V(T) \simeq$ constant over a wide range of temperature. In this case $S_f - S_i = C_V \ln(T_f/T_i)$

Example from textbook 200 g of water from 20 to 100°C
$C_V = 840\ J/K \Rightarrow S_f - S_i = 840\ J/K \ln\left(\frac{373}{293}\right) = 200\ J/K$
How big an increase in multiplicity?
$\Omega_f = \Omega_i e^{(S_f - S_i)/k_B} = \Omega_i e^{1.5 \times 10^{25}}$ (a very large #)

In general $S_f - S(0) = \int_0^{T_f} \frac{C_V(T)}{T} dT$
$S(0) = ?$

3^{rd} Law of Thermodynamics $S(T) \to 0$ as $T \to 0$ because 1 ground state.
In practice, many systems have relaxation times >> age of universe. This means don't reach actual ground state; end up in a metastable state.
Examples: orientation of molecules, orientation of nuclear spins, mixing of different isotopes, ...

Because S is finite and positive $\Rightarrow C_V \to 0$ as $T \to 0$
Our result for ideal gas can't be correct as $T \to 0$. $[C_V = \frac{f}{2} N k_B]$

Our full calculation of Einstein solid + Paramagnet did $C_V \to 0$ as $T \to 0$

Suppose you have 2 large systems 1500 J goes from A at 500 K to B at 200 K. What happened to ΔS_A, ΔS_B, ΔS_{TOT}
$\Delta S_A = \frac{-1500\ J}{500\ K} = -3\ J/K \qquad \Delta S_B = \frac{1500\ J}{200\ K} = 7.5\ J/K$
$\Delta S = 4.5\ J/K \qquad \Omega_f = \Omega_i e^{\Delta S/k_B} = \Omega_i e^{3.3 \times 10^{23}}$

3.11 H_2O 50 liters at 55°C mix with 25 liters at 10°C

$50 \cdot (T_f - 55°C) + 25 \cdot (T_f - 10°C) = 0 \qquad T_f = \frac{50\ 55°C + 25\ 10°C}{75} = 40°C$

50 liters = 50 kg $\qquad$ 25 liters = 25 kg

$\Delta S = 50000\,g\ 4.2 \frac{J}{g\,K} \ln\left(\frac{313}{328}\right) + 25000\,g\ 4.2 \frac{J}{gK} \ln\left(\frac{313}{283}\right)$

$= -9830\ J/K \qquad + 10579\ J/K$

$= 749\ J/K$

3.13 1 year = 3.16×10^7 s

1000 W - 1 year = 3.16×10^{10} J

$\Delta S = -\frac{3.16 \times 10^{10} J}{6000 K} + \frac{3.16 \times 10^{10} J}{300 K} = 1.0 \times 10^8\ J/K$

b) Growing grass violates 2^{nd} law?