Chapter 3 Interactions and Implications

This chapter is about relationships between thermodynamic parameters.

Section 3.1 Temperature

In Chap 2, I did the example of an ideal gas and found

$\left(\frac{\partial S}{\partial U}\right)_{N,V} = 1/T$ This is true in general!!!

To see why this is true in general remember: 1) two objects in thermal equilibrium have the same temperature, 2) two objects, a and b, are in thermal equilibrium when $\Omega_a \cdot \Omega_b = \max$ for $U_a + U_b = U = \text{const}$, $(V_a, V_b, N_a, N_b) = \text{const}$, 3) $S_{TOT} = S_a + S_b = k \ln(\Omega_a \cdot \Omega_b) = \max$

Our two systems can only exchange energy and are in equilibrium $dU_a = -dU_b$

$$\left(\frac{\partial S_{TOT}}{\partial U_a}\right)_{U,N_a V_a, N_b, V_b} = 0 = \left(\frac{\partial S_a}{\partial U_a}\right)_{U,N_a,V_a} + \left(\frac{\partial S_b}{\partial U_a}\right)_{U,N_b,V_b} = \left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} - \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b}$$

At thermal equilibrium $\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} = \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b}$ is always true

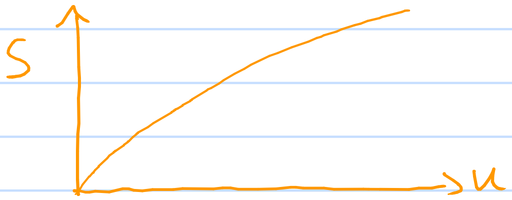
Since the unit of S is $\frac{J}{K}$, the unit of $\frac{\partial S}{\partial U}$ is $\frac{1}{K}$

<u>Also</u> we showed $\left(\frac{\partial S}{\partial U}\right)_{N,V} = 1/T$ for ideal gas. So make system a an ideal gas.

$$\underbrace{\underbrace{\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} = \frac{1}{T_a}}_{\text{ideal gas}} \underbrace{= \frac{1}{T_b}}_{\text{therm. equil.}} = \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b}}_{\text{statistical mechanics}} \Rightarrow \left(\frac{\partial S}{\partial U}\right)_{N,V} = 1/T \quad \underline{\text{in general}}$$

This relation defines temperature for any system in terms of the underlying microscopic properties of the system.

Temperature = 1/(rate of change of entropy with respect to internal energy) all else fixed



typical case $\left(\frac{\partial S}{\partial U}\right)_{N,V}$ decreases as U increases

$\Rightarrow$ T increases as U increases

(sec 3.3 exception when only looking at <u>part</u> of system)

All physical systems in full thermal equilibrium look like typical case

Why reach thermal equil.? Suppose start $\overset{\text{colder}}{\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a}} > \overset{\text{hotter}}{\left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b}}$

Suppose $dU_a > 0$ $\quad dS_{TOT} = \left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} dU_a - \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b} dU_a > 0$ allowed

Suppose $dU_a < 0$ $\quad$ " $\quad$ " $\quad$ " $\quad < 0$ not allowed

Heat is added to a and removed from b

Can also write $T = \left(\frac{\partial U}{\partial S}\right)_{N,V}$ but typically have $S(U,V,N)$ but not $U(S,V,N)$

Example: Einstein model $\quad S = Nk_B \ln\left[\left(\frac{q}{N}+1\right)\left(1+\frac{N}{q}\right)^{q/N}\right] \quad U = \hbar\omega q$

$$\frac{1}{T} = \frac{1}{\hbar\omega}\frac{dS}{dq} = \frac{Nk}{\hbar\omega}\frac{d}{dq}\left[\ln\left(\frac{q}{N}+1\right) + \frac{q}{N}\ln\left(1+\frac{N}{q}\right)\right] = \frac{Nk}{\hbar\omega}\left[\cancel{\frac{1}{N}\frac{1}{\frac{q}{N}+1}} + \frac{1}{N}\ln\left(1+\frac{N}{q}\right) - \cancel{\frac{q}{N}\frac{N}{q^2}\frac{1}{1+N/q}}\right]$$

$$\frac{\hbar\omega}{kT} = \ln\left(1+\frac{N}{q}\right) \Rightarrow 1+\frac{N}{q} = e^{\hbar\omega/kT} \Rightarrow q = \frac{N}{e^{\hbar\omega/kT}-1} \Rightarrow U = \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}$$

Example: Einstein model $\quad kT \gg \hbar\omega$

$$e^{\frac{\hbar\omega}{kT}} \simeq 1 + \frac{\hbar\omega}{kT} \Rightarrow U = \frac{N\hbar\omega}{\hbar\omega/kT} = NkT$$ Equipartition Thm!

Example: Einstein model $\quad \hbar\omega \gg kT$

$$e^{\frac{\hbar\omega}{kT}} - 1 \simeq e^{\hbar\omega/kT} \Rightarrow U = N\hbar\omega e^{-\hbar\omega/kT} \rightarrow 0 \text{ as } T \rightarrow 0$$

Example: Einstein model $\quad$ Find $S(T)$ $\quad$ define $x = \frac{\hbar\omega}{kT}$

$$1+\frac{N}{q} = e^x \qquad 1+\frac{q}{N} = \frac{e^x}{e^x-1}$$

$$\begin{aligned} S &= Nk\ln\left(\frac{q}{N}+1\right) + qk\ln\left(1+\frac{N}{q}\right) \\ &= Nkx - Nk\ln(e^x-1) + qkx \\ &= \frac{N\hbar\omega}{T} - Nk\ln\left(e^{\frac{\hbar\omega}{kT}}-1\right) + U/T = \frac{U}{T} - Nk\ln\left(1-e^{-\frac{\hbar\omega}{kT}}\right) \\ &= \frac{N\hbar\omega}{T}\frac{1}{e^{\frac{\hbar\omega}{kT}}-1} - Nk\ln\left(1-e^{-\frac{\hbar\omega}{kT}}\right) \end{aligned}$$

$$S(T\rightarrow 0) \rightarrow \frac{N\hbar\omega}{T}e^{-\frac{\hbar\omega}{kT}} + Nke^{-\frac{\hbar\omega}{kT}} \rightarrow 0$$ faster than any power

Reverse Prob 3.6 For an ideal gas with f quadratic degrees of freedom we had $U = \frac{f}{2}Nk_BT$. What is Ω?

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T} = \frac{1}{U/(\frac{f}{2}Nk_B)} = \frac{f/2\,Nk_B}{U} \Rightarrow S = \frac{f}{2}Nk_B\ln U + g(V,N)$$

$$\Omega = e^{S/k} = G(V,N)\,e^{\frac{f}{2}N\ln U} = G(V,N)\,U^{\frac{f}{2}N}$$

This can't be correct as $U \rightarrow 0$ because $\Omega \rightarrow 0$ $\quad S \rightarrow -\infty$

Section 3.3 Paramagnetism (weird example)

A point dipole in a uniform B-field has $PE = -\vec{\mu}\cdot\vec{B}$

A spin ½ in a uniform B-field has 2 energies $\overset{\text{spin up}}{\epsilon_\uparrow = -\mu B}$, $\overset{\text{spin down}}{\epsilon_\downarrow = \mu B}$

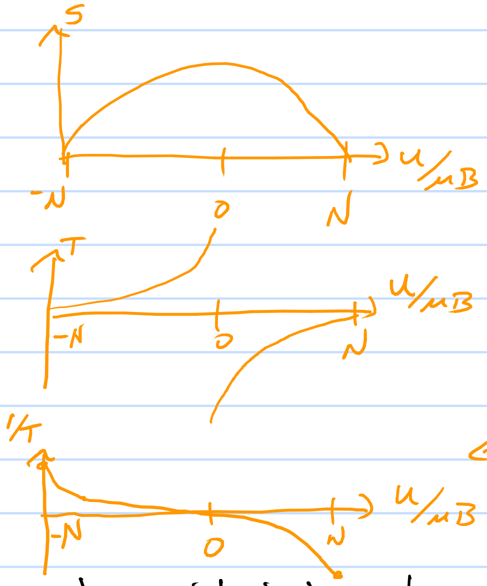
Treat a system of N spin ½ particles (This is only a partial treatment because no KE and no spatial PE. The spins can be isolated in some systems for a time: spins only weakly interact with other degrees of freedom.)

$$U = \mu B\,(N_\downarrow - N_\uparrow) = \mu B\,(N - 2N_\uparrow)$$

M = total magnetization $= -U/B$

This is just a 2 state system so $\Omega = \dfrac{N!}{N_\uparrow!\,N_\downarrow!}$

N=6	$N_\uparrow$	$N_\downarrow$	$U/\mu B$	Ω	S/k_B
	6	0	-6	1	0
	5	1	-4	6	1.79
	4	2	-2	15	2.71
	3	3	0	20	3.00
	2	4	2	15	2.71
	1	5	4	6	1.79
	0	6	6	1	0



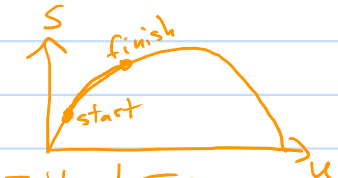
max(s) is not at max(u)??!!

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

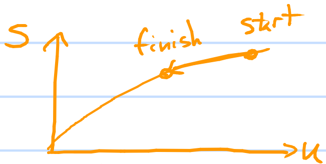
at every point $u \neq 0$ bigger $u \Rightarrow$ bigger T

$\leftarrow \frac{1}{T}$ always decreasing $\Rightarrow$ OK?

How does this system behave when it interacts with a normal system

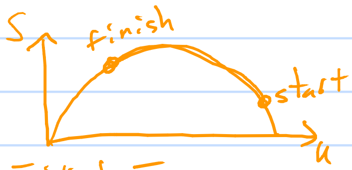


Initial $T_a > 0$



$T_b > T_a$

Very similar to usual system heat goes from larger T to smaller T



Initial $T_a < 0$

$1/T_b >_{\text{always}} 1/T_a$

Negative T_a interacting with normal system always loses energy to normal sys. $\Rightarrow T_a < 0$ always behaves like higher T

Heat does not always flow from a system with high T to one with low T. In the thermodynamic limit, heat always flows so that S_{TOT} increases.

For large system $N, N_\uparrow, N_\downarrow$ all $\gg 1$ analytically find S

$$\Omega = \frac{N!}{N_\uparrow!(N-N_\uparrow)!} = \frac{\sqrt{2\pi N}\, N^N e^{-N}}{\sqrt{2\pi N_\uparrow}\, N_\uparrow^{N_\uparrow} e^{-N_\uparrow} \sqrt{2\pi(N-N_\uparrow)}\,(N-N_\uparrow)^{(N-N_\uparrow)} e^{-(N-N_\uparrow)}} = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{N}{N_\uparrow(N-N_\uparrow)}}\,\frac{N^N}{N_\uparrow^{N_\uparrow}(N-N_\uparrow)^{N-N_\uparrow}}$$

$$S/k_B = \ln(\Omega) = N\ln N - N_\uparrow \ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow) + \cancel{\frac{1}{2}\ln\left(\frac{N}{N_\uparrow(N-N_\uparrow)2\pi}\right)} \to \text{normal} = 0$$

Prob 3.19 Determine $U(T,N)$

$$1/T = \left(\frac{\partial S}{\partial U}\right)_{N,V} = -\frac{1}{2\mu B}\left(\frac{\partial S}{\partial N_\uparrow}\right)_N = \frac{k}{2\mu B}\left(1 + \ln N_\uparrow - 1 - \ln(N-N_\uparrow)\right) = \frac{k}{2\mu B}\ln\left(\frac{N_\uparrow}{N-N_\uparrow}\right)$$

$$\frac{N_\uparrow}{N-N_\uparrow} = e^{\frac{2\mu B}{kT}} \Rightarrow N_\uparrow = N\frac{e^{2\mu B/kT}}{e^{2\mu B/kT}+1}$$

$$U = \mu B(N - 2N_\uparrow) = N\mu B\,\frac{1-e^{2\mu B/kT}}{1+e^{2\mu B/kT}} \qquad M = -\frac{U}{B} = N\mu\,\frac{e^{2\mu B/kT}-1}{e^{2\mu B/kT}+1}$$

Typical values $\frac{\mu}{k_B} \simeq \frac{2}{3}\frac{\text{Kelvin}}{\text{Tesla}}$ for electron ($\sim\frac{1}{100}$ or $\frac{1}{1000}$ for nuclei)

Example: Evaluate $kT \gg \mu B$

$$e^{2\mu B/kT} \simeq 1 + \frac{2\mu B}{kT} \Rightarrow M = N\mu^2 B/kT \qquad \text{Curie's Law}$$

Example: Probability for a spin to be up?

$$P_\uparrow = N_\uparrow/N = e^{2\mu B/kT}/(e^{2\mu B/kT}+1) = e^{\mu B/kT}/(e^{\mu B/kT}+e^{-\mu B/kT})$$
$$= e^{-\varepsilon_\uparrow/kT}/(e^{-\varepsilon_\uparrow/kT}+e^{-\varepsilon_\downarrow/kT})$$
$$P_\downarrow = 1 - P_\uparrow = e^{-\varepsilon_\downarrow/kT}/(e^{-\varepsilon_\uparrow/kT}+e^{-\varepsilon_\downarrow/kT})$$

always true that
$$P_j \overset{?}{=} e^{-\varepsilon_j/kT}/(e^{-\varepsilon_1/kT}+e^{-\varepsilon_2/kT}+\dots)$$

Prob 3.23 Find S in terms of $x = \frac{\mu B}{kT}$

$$N_\uparrow = N\frac{e^{2x}}{e^{2x}+1} = N\frac{e^x}{e^x+e^{-x}}$$

$$S/k_B = N\ln N - N_\uparrow\ln(N_\uparrow) - (N-N_\uparrow)\ln(N-N_\uparrow)$$

$$= N\left[\cancel{\ln N} - \frac{e^x}{e^x+e^{-x}}\left(\cancel{\ln N} + x - \ln(e^x+e^{-x})\right) - \frac{e^{-x}}{e^x+e^{-x}}\left(\cancel{\ln N} - x - \ln(e^x+e^{-x})\right)\right]$$

$$= N\left[-x\frac{e^x-e^{-x}}{e^x+e^{-x}} + \ln(e^x+e^{-x})\right] = N\{\ln[2\cosh(x)] - x\tanh(x)\}$$

as $T\to\infty$ $x\to 0$ $S/k \to N\ln 2$ ✓ all states equally likely

as $T\to 0$ $x\to\infty$ $2\cosh(x) \to e^x(1+e^{-2x})$ $x\tanh(x) \to x\frac{1-e^{-2x}}{1+e^{-2x}} = x - x2e^{-2x}$

$S/k_B \to N\{x + e^{-2x} - x + 2xe^{-2x}\} \to 0$ ✓ only ground state

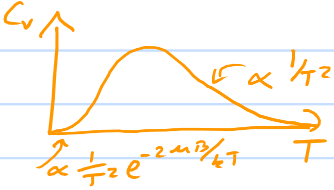
Section 3.2 Entropy and Heat

Remember the definition $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V}$ To compute from first principles $\Omega(U,V,N) \rightarrow S(U,V,N) = k \ln[\Omega(U,V,N)] \rightarrow$
$1/T = \left(\frac{\partial S}{\partial U}\right)_{V,N} \rightarrow$ solve for U vs. T $\rightarrow$ $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$

Example Ideal gas $U = \frac{f}{2} NkT \Rightarrow C_V = \frac{f}{2} Nk$

Example Einstein model $U = \frac{N\hbar\omega}{e^{\hbar\omega/kT}-1} \Rightarrow C_V = \frac{N\hbar\omega}{(e^{\hbar\omega/kT}-1)^2} e^{\frac{\hbar\omega}{kT}} \frac{\hbar\omega}{kT^2}$
as $T \rightarrow \infty$ $C_V \rightarrow Nk$
as $T \rightarrow 0$ $C_V \rightarrow 0$

Example Spin 1/2 paramagnet $U = N\mu B \frac{e^{-\mu B/kT} - e^{\mu B/kT}}{e^{-\mu B/kT} + e^{\mu B/kT}}$ $X = \frac{\mu B}{kT}$
$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = N\mu B \left(-\frac{\mu B}{kT^2}\right) \left[\frac{-e^{-x} - e^{x}}{e^{-x}+e^{x}} + \left(\frac{e^{-x}-e^{x}}{e^{-x}+e^{x}}\right)^2\right]$
$= -NkX^2\left(-4/(e^{x}+e^{-x})^2\right) = NkX^2/\cosh^2(x)$



Why $C_B \rightarrow 0$ as $T \rightarrow 0$?
" " " $T \rightarrow \infty$?] Physics reason

In many respects, it's easier to measure entropy than to calculate it.
$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T} \Rightarrow dS = dU/T = Q/T$ last step because $dV = 0 \Rightarrow W = 0$

If $\Delta T = 0$ (example, phase change with latent heat) $\Delta S = Q/T$ exact

If you measure (or know) $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \Rightarrow dU = C_V\,dT \Rightarrow dS = C_V \frac{dT}{T}$
$S_f - S_i = \int_{T_i}^{T_f} C_V(T) \frac{1}{T}\,dT$

In many materials there's a large range of T where $C_V(T) \simeq$ const
$S_f - S_i \simeq C_V\left(\frac{T_i + T_f}{2}\right) \ln(T_f/T_i)$

Textbook example: 200 g of water from 20°C to 100°C
$C_V = 840\ \mathrm{J/K} \Rightarrow S_f - S_i = 840\ \mathrm{J/K} \ln\left(\frac{373}{293}\right) = 200\ \mathrm{J/K}$
How big increase in multiplicity? $\Omega_f = \Omega_i e^{(S_f - S_i)/k} = \Omega_i e^{1.5\times10^{25}}$ very large

$S_f - S(0) = \int_0^{T_f} \frac{C_V(T)}{T}\,dT \Rightarrow C_V \rightarrow 0$ as $T \rightarrow 0$
Our full calculation of Einstein model and paramagnet had $C_V \rightarrow 0$ as $T \rightarrow 0$
Ideal gas did not have correct $C_V(T \rightarrow 0)$ because of approximations

3rd 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. Thus, some aspects of the system is not in thermal equil. ⇒ don't actually reach ground state as $T \to 0$

Examples: orientation of molecules, orientation of nuclear spin, mixing of different isotopes, frustrated systems, ...

Example 2 large systems $\Delta U_a = 1500\,J$ $T_a = 500\,K$ $T_b = 200\,K$ $\Delta T \simeq 0$

$\Delta S_a = \frac{-1500\,J}{500\,K} = -3\,J/K$ $\Delta S_b = \frac{1500\,J}{200\,K} = 7.5\,J/K$

$\Delta S_{TOT} = 4.5\,J/K$ $\Omega_f = \Omega_i\, e^{\Delta S/k} = \Omega_i\, e^{3.3\times10^{23}}$

Prob 3.11 50 liter @ 55°C mix with 25 liters @ 10°C

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

50 liter = 50 kg

$\Delta S = 50{,}000\,g\ 4.2\,\frac{J}{gK} \ln\left(\frac{313}{328}\right) + 25{,}000\,g\ 4.2\,\frac{J}{gK} \ln\left(\frac{313}{283}\right)$

$= -9830\,J/K + 10579\,J/K = 749\,J/K$

Prob 3.13 1 year = $3.16\times10^7\,s$ ⇒ $1000\,W \cdot 1\,yr = 3.16\times10^{10}\,J$

a) $\Delta S = -\frac{3.16\times10^{10}\,J}{6000\,K} + \frac{3.16\times10^{10}\,J}{300\,K} = 1.0\times10^{8}\,J/K$

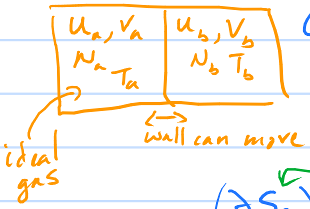
b) Growing grass violates 2nd law?

Section 3.4 Mechanical equilibrium and pressure

In Chap 2, we saw that an ideal gas had $\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{Nk}{V} = \frac{P}{T}$

Is this true in general? Yes, but tricky to show because hard to come up with situation where the work done on a, b kills the U, N = fixed

If $T_a = T_b$, $\Delta U_a \neq 0$ is OK



$$0 = \Delta S_{TOT} = \underbrace{\left(\frac{\partial S_a}{\partial U_a}\right)_{N_a V_a} \Delta U_a + \left(\frac{\partial S_b}{\partial U_b}\right)_{N_b V_b} (-\Delta U_a)}_{\text{cancel}} + \left(\frac{\partial S_a}{\partial V_a}\right)_{U_a N_a} \Delta V_a + \left(\frac{\partial S_b}{\partial V_b}\right)_{U_b N_b} (-\Delta V_a)$$

$S_{TOT} = \max$

statistical mech.

$$\underbrace{\left(\frac{\partial S_a}{\partial V_a}\right)_{U_a N_a} = \frac{P_a}{T_a}}_{\text{ideal gas}} = \underbrace{\frac{P_b}{T_b}}_{\substack{T_a = T_b \\ \text{and mech. equil}}} = \left(\frac{\partial S_b}{\partial V_b}\right)_{U_b N_b}$$

$\left(\frac{\partial S}{\partial V}\right)_{U,N} = P/T$ in general

In general think of S as a function of U, V, N. If $dN=0$

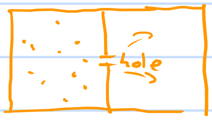
$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV = \frac{1}{T} dU + \frac{P}{T} dV$$

Rearrange to get $dU = TdS - PdV$

This is similar to but not exactly equal to the 1st law $dU = Q + W$

If the changes are quasistatic, $W = -PdV \Rightarrow Q = TdS$

Non quasistatic examples : fast compression, free expansion



Example: free expansion $S = Nk_B \ln(V) + \frac{3N}{2}\ln(U) + f(N)$

Free expansion $\Rightarrow$ $U = \text{const} \Rightarrow S_f - S_i = Nk_B \ln(V_f/V_i)$

Different derivation

$$dS = \cancelto{0}{\frac{dU}{T}} + P/T\, dV = \frac{Nk}{V} dV \Rightarrow \int_i^f dS = S_f - S_i = \int_{V_i}^{V_f} \frac{Nk}{V} dV = Nk \ln\left(\frac{V_f}{V_i}\right)$$

Example: Adiabatic expansion $Q = 0 = dU - W = TdS - PdV + PdV$
$= dS = 0$

Adiabatic changes can be undone because $dS = 0$

In general $dS = \frac{dU}{T} + \frac{P}{T} dV = \frac{Q}{T} + (W + PdV)/T$

If $W > -PdV$ then $dS > Q/T$ This happens when transformation occurs too fast. In the free expansion example $-P\Delta V < 0$ and $W = 0$

$W > -P\Delta V \Rightarrow \Delta S > Q/T = 0/T$

Prob 3.28 1 liter air heated at constant P until doubles in V; $\Delta S = ?$

$$dS = \frac{1}{T}(dU + PdV) = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

$\left(\frac{\partial U}{\partial T}\right)_P = \frac{f}{2} nR$ $\qquad P\left(\frac{\partial V}{\partial T}\right)_P = nR$

$$dS = \left(\frac{f}{2} + 1\right) nR\, dT/T \Rightarrow S_f - S_i = \left(\frac{f}{2} + 1\right) nR \ln\left(\frac{T_f}{T_i}\right)$$

For air $f = 5$ doubling V at const. $P \Rightarrow T_f = 2T_i$

$$\Delta S = \frac{7}{2} \frac{PV}{T} \ln(2) = \frac{7}{2}\, 1.01 \times 10^5 \frac{N}{m^2}\, 10^{-3} m^3 / 300K \ln 2 = 0.81\ J/K$$

$$\Omega_f = \Omega_i e^{5.9 \times 10^{22}}$$

Section 3.5 Diffusive equilibrium and Chemical Potential

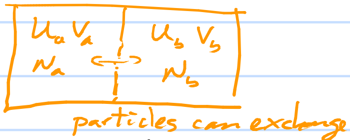
The chemical potential was invented by J. Willard Gibbs (arguably the greatest American scientist. In his textbook, he's clearly amused by the awe over the chemical potential.)

$$S(U,V,N) \Rightarrow dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{-\mu}{T} dN$$

μ = chemical potential - has units of energy

What does μ represent



Thermal equil. implies

$$\left(\frac{\partial S_a}{\partial N_a}\right)_{U_a V_a} = \left(\frac{\partial S_b}{\partial N_b}\right)_{U_b N_b}$$

$\Rightarrow \mu_a = \mu_b$ since $T_a = T_b$

μ can be positive or negative

Chemical potential is the quantity that's the same in the two systems that can exchange particles (diffuse into each other)

Example: $\Delta S = ?$ if you add 1 particle to system keeping $U, V = \text{const}$

$$\Delta S = -\frac{\mu}{T}\Delta N = -\frac{\mu}{T}$$

Systems with smaller μ get larger ΔS

Example $\mu_a = -0.1\,\text{eV} = -1.6\times10^{-20}\,\text{J}$, $\mu_b = -0.3\,\text{eV} = -4.8\times10^{-20}\,\text{J}$ $\quad T_a = T_b = 160\,\text{K}$

Move 1 particle from a to b keeping $U_a, U_b, V_a, V_b = \text{const.}$

$$\left.\begin{aligned} \Delta S_a &= -\frac{-1.6\times10^{-20}\,\text{J}}{160\,\text{K}}(-1) = -10^{-22}\,\text{J/K} \\ \Delta S_b &= -\frac{-4.8\times10^{-20}}{160\,\text{K}}(1) = 3\times10^{-22}\,\text{J/K} \end{aligned}\right\} \Delta S = \Delta S_a + \Delta S_b = 2\times10^{-22}\,\text{J/K}$$

Moving 1 particle from b to a gives $\Delta S = -2\times10^{-22}\,\text{J/K}$

In this example, $\mu_a > \mu_b \Rightarrow$ to increase entropy particles go from high chemical potential to lower chemical potential.

Rearrange $dU = TdS \underbrace{- PdV}_{\text{mech. work}} + \underbrace{\mu dN}_{\text{chem work}}$ only 1 species

Many species $dU = TdS - PdV + \sum_j \mu_j dN_j$

This relation can be used to derive relations between S, U, V, N and P, T, μ

Example $dS = 0 \quad dV = 0 \qquad dU = \mu dN \Rightarrow \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$

Example $dU = 0 \quad dS = 0 \qquad 0 = -PdV + \mu dN \Rightarrow \left(\frac{\partial V}{\partial N}\right)_{U,S} = \frac{\mu}{P}$

Example: chemical potential for monatomic ideal gas

$$S = Nk\left\{\ln\left[V\left(\frac{4\pi U m}{3h^2}\right)^{3/2}\right] - \frac{5}{2}\ln N + 5/2\right\}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = k\left\{\ln\left[V\left(\frac{4\pi U m}{3h^2}\right)^{3/2}\right] - \frac{5}{2}\ln N + \cancel{5/2}\right\} + \cancel{Nk\left(-\frac{5}{2N}\right)} = -\frac{\mu}{T}$$

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right] = -kT\ln\left[\frac{kT}{P}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$

Trends: increasing $P \Rightarrow$ decreasing [ ] $\Rightarrow$ increasing μ ✓
higher $m \Rightarrow$ increasing [ ] $\Rightarrow$ decreasing μ
T is complicated $\left(\frac{\partial \mu}{\partial T}\right)_P = \frac{\mu}{T} - \frac{5}{2}k \Rightarrow \frac{\partial \mu}{\partial T} < 0$ if $\mu < \frac{5}{2}kT$

Example: difference in μ for two ideal gases at same T but diff P?

$$\mu(P_1, T) - \mu(P_2, T) = kT\ln(P_1/P_2)$$

Example: μ for Einstein model $S = k\left[q\ln(q+N) - q\ln q + N\ln(q+N) - N\ln N\right]$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_q = -kT\left[\cancel{\frac{q}{q+N}} + \ln(q+N) + \cancel{\frac{N}{q+N}} - \ln(N) \cancel{-1}\right] = -kT\ln\left(\frac{q+N}{N}\right)$$

$\Rightarrow q = N\left(e^{-\frac{\mu}{kT}} - 1\right)$? weird?

For $N \gg q$ (low T) $\mu = -kT\ln(1 + q/N) = -kT\,q/N$

$\Rightarrow$ for each particle added at fixed E $\Delta S = -\mu/T = k\,q/N$ (small $q/N \ll 1$)

For $q \gg N$ $\mu = -kT\ln(q/N)$ $\Delta S = -\mu/T = k_B\ln(q/N)$

Remember $q = U/\hbar\omega$ at high T $U = NkT$

Adding a particle when there are few quanta doesn't greatly increase entropy. Adding a particle when there are many quanta per particle gives large ΔS.

Section 3.6 Summary

Type of process	Exchanged quantity	Governing variable	Relation
thermal	energy	temperature	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Classical Thermodynamics $dU = TdS - PdV + \sum_j \mu_j dN_j$ quasistatic

These are statistical relations that hold in the thermodynamic limit.
For large number of particles, fluctuations are minor and classical thermodynamics is deterministic.

In the thermodynamic limit, entropy increases or stays constant.

Two systems in thermal equilibrium must have $\Delta S_a = -\Delta S_b$ for any process that exchanges between a and b.

$$\left(\frac{\partial S_a}{\partial U_a}\right)_{V_a N_a} = \left(\frac{\partial S_b}{\partial U_b}\right)_{V_b N_b} \Rightarrow T_a = T_b$$

$$\left(\frac{\partial S_a}{\partial V_a}\right)_{U_a N_a} = \left(\frac{\partial S_b}{\partial V_b}\right)_{U_b N_b} \Rightarrow P_a = P_b$$

$$\left(\frac{\partial S_a}{\partial N_a}\right)_{U_a V_a} = \left(\frac{\partial S_b}{\partial N_b}\right)_{U_b N_b} \Rightarrow \mu_a = \mu_b$$