Phys 344.

Lecture 15.

Assignment #5.

3.35, 37 ; 4.1, 2, 4, 5, 10, 14, 15, 16.

- Thermal equilibrium — same Temperature.

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

- Mechanical equilibrium — Same pressure.

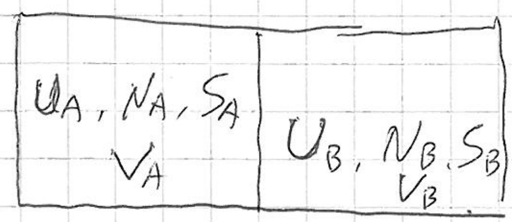
$$\left(P = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \right)$$

- What about diffusive equilibrium?

2 systems: A and B

Total U and N are fixed.

Can exchange energy and particles



same kind of particles.

e.g. Both are H_2O molecules.

Varying: U_A and N_A, and (V_A)

But $U = U_A + U_B$ = fixed.

$N = N_A + N_B$ = fixed.

$(V = V_A + V_B$ = fixed$)$

When the 2 systems are in equilibrium.

$$S \rightarrow S_{max}. \quad (S = S_{Total}).$$

$$\left(\frac{\partial S}{\partial U_A}\right)_{N_A, V_A} = 0, \quad \left(\frac{\partial S}{\partial N_A}\right)_{U_A, V_A} = 0 \quad \left(\frac{\partial S}{\partial V_A}\right)_{U_A N_A} = 0$$

$$\Downarrow \qquad\qquad \Downarrow \qquad\qquad \Downarrow$$

$$T_A = T_B \qquad ? \qquad P_A = P_B.$$

- $\left(\frac{\partial S}{\partial N_A}\right)_{U_A, V_A} = 0$: $N = N_A + N_B$ = fixed. $\delta N_B = -\delta N_A$.
  $S = S_A + S_B$.

$$\left(\frac{\partial S_A}{\partial N_A}\right) + \left(\frac{\partial S_B}{\partial N_A}\right) = 0 \qquad \frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B} = 0 \qquad \underline{\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}}$$

- Define : chemical potential.

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

Then, when two systems are in diffusive equilibrium,

$$\mu_A = \mu_B.$$

· If they are not in diffusive equilibrium, then, $\frac{\partial S_A}{\partial N_A} \neq \frac{\partial S_B}{\partial N_B}$

if $\left(\frac{\partial S_A}{\partial N_A}\right)_{U_A, V_A} > \left(\frac{\partial S_B}{\partial N_B}\right)_{U_B, V_B}$

Particles tend to move from B to A.

$\left(\because \; |\Delta S_A| > |\Delta S_B| \text{ for the same } |\Delta N_A| \right.$

i.e. gain in S_A

is greater than loss in S_B.)

i.e. When $\mu_B > \mu_A$.

particles tend to move from B to A.

$\therefore$ In general, particles tend to move from higher chemical potential to lower chemical potential.

Note: ① $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$.

"negative"

② Multiply by T. (NOT just $\left(\frac{\partial S}{\partial N}\right)_{U,V}$)

~~Question~~

- Entropy representation.

$$S = S(U, V, N, \cdots)$$

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN$$

$-pdV$ — mechanical work

μdN — chemical work (diffusive).

$\left(\begin{array}{l} đQ \text{ — NOT exact.} \\ \dfrac{dQ}{T} \text{ — exact.} \end{array}\right.$

- Energy representation.

$$U = U(S, V, N, \cdots).$$

$$dU = TdS - PdV + \mu dN$$

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

unit of μ — energy

Meaning of μ: Change in energy when you add a particle while keeping S and V unchanged.

U — Total energy of system (may include gravitational potential energy if we want)

- Sign of μ. $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$.

When you add a particle, S increases. ($S = \Sigma S_i$) at least.

to cancel that effect on S.

we need to reduce U $\left(\text{since } \frac{\Delta S}{\Delta U} > 0\right)$

i.e, when $\Delta N > 0$, $\Delta U < 0$

$\therefore$ chemical potential is always negative. $\mu < 0$.

e.g. Einstein solid: $N=3$, $q=3$ $U = q\varepsilon = qhf$.

$$\Omega = \binom{N+q-1}{q} = \binom{5}{3} = \frac{5!}{3!\,2!} = 10.$$

$$S_i = k \ln 10.$$

If we add one more oscillator: $N=4$. $q=3$.

S would increase to: $k\binom{6}{3} = k \ln 20$.

To reduce S back to S_i, we can reduce q to $q=2$.

Then: $\Omega = \binom{5}{2} = 10$.

$$\therefore \mu = \left(\frac{\Delta U}{\Delta N}\right)_{S,V} = \frac{(2-3)\varepsilon}{(4-3)} = -\varepsilon.$$

e.g. monatomic ideal gas.

Sackur-Tetrode equation:

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

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

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

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

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

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

Note: ① more than one species, $N_1, N_2, \cdots N_i, \cdots$
$\mu_1, \mu_2, \cdots \mu_i, \cdots$

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

$$\mu_i = -T\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_1,N_2\cdots}, \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_1,N_2\cdots}$$

② chemists: $\mu \equiv -T\left(\frac{\partial S}{\partial n}\right)_{U,V}$ (per mole).