Solutions HW #5

1) SCHROEDER 2.38

SCHROEDER'S DESCRIPTION OF AN IDEAL MIXTURES SUGGESTS THE EXISTENCE OF A MULTIPLICITY FUNCTION $\tilde{\Omega}(N)$ WHICH DESCRIBES THE MULTIPLICITY OF A MIXTURE OF N_A MOLECULES OF SPECIES A AND N_B MOLECULES OF SPECIES B BY THE RULE:

$$\Omega^{DIST}_{A\oplus B}(N_A, N_B) = \tilde{\Omega}(N_A+N_B)$$

THIS MULTIPLICITY FUNCTION $\Omega^{DIST}_{A\oplus B}$ IS VALID FOR THE PURELY HYPOTHETICAL CASE WHERE DIFFERENT MOLECULES OF THE SAME SPECIES ARE DISTINGUISHABLE. SINCE THE TWO SPECIES HAVE IDENTICAL PHYSICAL PROPERTIES EXCEPT FOR THEIR IDENTITY. IT MAKES

SENSE THAT THE MULTIPLICITY OF THEIR MIXTURE WOULD THEN DEPEND ONLY ON THEIR TOTAL PARTICLE # $N_A + N_B$.

TO MODIFY $\Omega^{DIST}_{A \oplus B}$ TO ACCOUNT FOR THE INDISTINGUISHABILITY OF MOLECULES OF THE SAME SPECIES WE DIVIDE BY THE NUMBER OF PERMUTATIONS MIXING MOLECULES OF THE SAME SPECIES, i.e. $N_A!$ FOR THE N_A MOLECULES OF SPECIES A AND N_B FOR SPECIES B. IN OTHER WORDS:

$$\Omega^{INDIST}_{A \oplus B}(N_A, N_B) = \frac{\Omega^{DIST}(N_A, N_B)}{N_A!\,N_B!}$$

$$= \frac{\overset{u}{\Omega}(N_A + N_B)}{N_A!\,N_B!}$$

THE ENTROPY OF MIXING IS THE DIFFERENCE IN ENTROPY BETWEEN A MIXTURE OF A AND B AND A PURE SYSTEM CONTAINING ONLY A OR B, i.e.

$$\Delta S_{mix} = S(N_A, N_B) - S(N_A + N_B, 0)$$

$$= k_B \ln \Omega^{INDIST}_{A\oplus B}(N_A, N_B)$$

$$- k_B \ln \Omega^{INDIST}_{A\oplus B}(N_A + N_B, 0)$$

$$= k_B \ln \left[\frac{\tilde{\Omega}(N_A + N_B)}{N_A!\, N_B!} \right]$$

$$- k_B \ln \left[\frac{\tilde{\Omega}(N_A + N_B)}{(N_A + N_B)!\, 0!} \right]$$

$$= k_B \ln \left[\frac{N!}{N_A!\,(N - N_A)!} \right] \qquad N \equiv N_A + N_B$$

$$= k_B \ln \binom{N}{N_A}$$

FROM Stirling's approximation WE HAVE: $\ln \binom{N}{N_A}$

$$= \ln \frac{N!}{N_A!\,(N-N_A)!}$$

$$= \ln N! - \ln N_A! - \ln (N-N_A)!$$

$$= N \ln N - \cancel{N} - N_A \ln N_A + \cancel{N_A}$$

$$- (N-N_A)\ln(N-N_A) + \cancel{N} - \cancel{N_A}$$

$$= N\Big[\cancel{\ln N} - x\big[\cancel{\ln N} + \ln x\big] - (1-x)\big[\cancel{\ln N} + \ln(1-x)\big]\Big]$$

$$= -N\big[x \ln x + (1-x)\ln(1-x)\big]$$

$$x \equiv N_A/N$$

2) a) SINCE THE WALL SEPARATING A + B IS FIXED WE HAVE

$$dV_1 = 0 \quad , \quad dV_2 = 0$$

SINCE THE WALL IS CLOSED [NO HOLES] WE HAVE

$$dN_1 = 0 \qquad dN_2 = 0$$

FROM ENERGY CONSERVATION WE HAVE

$$dU_1 = -dU_2 \equiv dU$$

SO THAT:

$$dS_{TOT} = \sum_{j=1}^{2} \frac{\partial S_{TOT}}{\partial U_j} dU_j + \frac{\partial S}{\partial V_j} \cancelto{0}{dV_j} + \frac{\partial S}{\partial N_j} \cancelto{0}{dN_j}$$

$$= \left[\frac{\partial S_{TOT}}{\partial U_1} - \frac{\partial S_{TOT}}{\partial U_2} \right] dU$$

$$= \left[\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \right] dU$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right] du$$

SO THAT THE ENERGY TRANSFER IS IRREVERSIBLE UNLESS T_1 IS VERY CLOSE TO T_2 (IF T_1 IS EXACTLY T_2 THEN NO ENERGY TRANSFER OCCURS AT *ALL*].

b) HERE WE AGAIN HAVE A CLOSED WALL SO

$$dN_1 = 0 \quad , \quad dN_2 = 0$$

THE WALL CAN MOVE BUT THE TOTAL VOLUME OF THE COMBINED SYSTEM IS FIXED SO

$$dV_1 = -dV_2 \equiv dV$$

AGAIN ENERGY IS CONSERVED SO

$$dU_1 = -dU_2 \equiv dU$$

WE ALSO ASSUME THE THERMAL CONTACT IS GOOD SO THAT

$dT_1 = dT_2$ OR

~~$\frac{\partial}{\partial U_1}\frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial}{\partial V_1}\frac{\partial S}{\partial U_1} dV_1 =$~~

~~$\frac{\partial}{\partial U_2}\frac{\partial S_2}{\partial U_2} dU_2 + \frac{\partial}{\partial V_2}\frac{\partial S}{\partial U_2} dV_2$~~

~~$\frac{3}{2}NkT$~~

$$d\left(\frac{U_1}{\frac{3}{2}N_1 k_B}\right) = d\left(\frac{U_2}{\frac{3}{2}N_2 k_B}\right)$$

$$\frac{1}{N_1}\, dU_1 = \frac{1}{N_2}\, dU_2$$

$$\frac{dU}{N_1} = \frac{-dU}{N_2}$$

$$dU\left(\frac{1}{N_1} + \frac{1}{N_2}\right) = 0$$

$$dU = 0$$

SO :

$$dS_{TOT} = \left[\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right] dV$$

* BUT ~~FOR~~ FROM SACKUR TETRODE EQ^N :

$$\frac{\partial}{\partial V} S = \frac{\partial}{\partial V} N k_B \ln V + f(U, N)$$

← NO V DEP.

$$= \frac{N k_B}{V} = \frac{P}{T}$$

SO $$dS_{TOT} = \left[\frac{P_1}{T_1} - \frac{P_2}{T_2} \right] dV$$

BUT $T_1 = T_2 \equiv T$ SO

$$dS_{TOT} = \frac{1}{T} \left[P_1 - P_2 \right] dV$$

SO PROCESS IS IRREVERSIBLE UNLESS P_1 IS VERY CLOSE TO P_2 [IF P_1 IS EXACTLY P_2 NO VOLUME TRANSFER OCCURS].

c) NOW WE HAVE:

$$dU_1 = -dU_2 \equiv dU \qquad [\text{ENERGY CONS.}]$$

$$dV_1 = dV_2 = 0 \qquad [\text{FIXED WALL}]$$

$$dN_1 = -dN_2 \equiv dN \qquad [\text{PARTICLE \# CONS.}]$$

$$dT_1 = dT_2$$

~~$\Rightarrow d\left(\frac{3}{2}N_1 k_B T_1\right.$~~

~~But~~ $$d\left(\frac{U_1}{\frac{3}{2}N_1 k_B}\right) = d\left(\frac{U_2}{\frac{3}{2}N_2 k_B}\right)$$

$$\frac{dU_1}{N_1} - \frac{U_1}{N_1^2}dN_1 = \frac{dU_2}{N_2} - \frac{U_2}{N_2^2}dN_2$$

BUT ~~$\frac{dU}{N}$ $\frac{U}{N}$~~ $$\frac{dU}{N} - \frac{U}{N}\frac{dN}{N}$$

$$= \frac{dU}{N} - \frac{3}{2}kT\frac{dN}{N}$$

$$= \frac{3}{2}kT\left(\frac{dU}{U} - \frac{dN}{N}\right)$$

So $$dT_1 = dT_2 \Longrightarrow dU\left(\frac{1}{U_1} + \frac{1}{U_2}\right) = dN\left(\frac{1}{N_1} + \frac{1}{N_2}\right)$$

~~SO~~ SINCE

$$dS = \frac{\partial S}{\partial u}\, du + \frac{\partial S}{\partial N}\, dN$$

AND $\frac{\partial S}{\partial u} = \frac{3}{2} \frac{N K_B}{u} = \frac{3}{2} \frac{N k_B}{N k_B T \cdot \frac{3}{2}} = \frac{1}{T}$

AND $\frac{\partial S}{\partial N} = -\frac{5}{2} \frac{N k_B}{N} + \frac{S}{N}$

$$= \frac{S}{N} - \frac{5}{2} k_B$$

WE GET

$$dS_{TOT} = \frac{1}{T} \cancel{du_1} + \left(\frac{S_1}{N_1} - \frac{5}{2} k_B \right) dN_1$$

$$+ \frac{1}{T} \cancel{du_2} + \left(\frac{S_2}{N_2} - \frac{5}{2} k_B \right) dN_2$$

$du_1 = -du_2$

$$= \left(\frac{S_1}{N_1} - \frac{S_2}{N_2} \right) dN$$

SO IN THIS CASE WE FIND THE <u>MOLAR ENTROPIES</u> NEED TO BE NEARLY EQUAL FOR THE PROCESS TO BE REVERSIBLE.

NOTE: IT TURNS OUT THAT IN GENERAL

[illegible]

IT IS THE $\frac{\partial S}{\partial N}$ WHICH MUST BE EQUAL FOR REVERSIBLE PARTICLE TRANSFER.

THERE IS A QUANTITY

$$\mu \equiv \cancel{T \partial u} - T \frac{\partial S}{\partial N}$$

CALLED THE CHEMICAL POTENTIAL WHICH ALSO SERVES TO DETERMINE THE IRREVERSIBILITY OF A ~~PROCESS~~ PARTICLE TRANSFER.