

## Answers to second Exam

1. a) a closed system in a temperature bath is described by the canonical ensemble. The probability for observing a closed (fixed  $N$ ) thermally equilibrated system with a particular energy  $E$  is

$$P_E = \frac{e^{-E/kT}}{Q} \quad \text{where } Q \equiv \sum_j e^{-E_j/kT}$$

b) configuration integral

$$Z(T, V) = \int_{\vec{r}_1} \int_{\vec{r}_2} \dots \int_{\vec{r}_N} e^{-U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)/kT} d^3r_1 d^3r_2 \dots d^3r_N$$

where  $U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is the potential energy as a function of the coordinates of the  $N$  particles of the system.

c)  $\int_{\vec{r}_1} \dots \int_{\vec{r}_N} d^3r_1 d^3r_2 \dots d^3r_N = V^N$  when  $U=0$

- d) average density of particles at  $\vec{r}$  given that a tagged particle is at the origin =

$$\frac{N}{V} g(r) \quad \text{where } g(r) = \frac{V^2 \int_{\vec{r}_3} \dots \int_{\vec{r}_N} e^{-U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)/kT} d^3r_3 \dots d^3r_N}{Z(T, V)}$$

- e) When each particular point in phase space  $X_{\approx l}$  is selected according to the probability  $\propto e^{-E(X_{\approx l})/kT}$

then the thermal average of some property which depends on the configuration  $X$  of the system becomes

a simple arithmetic average

$$\langle A(\underline{x}) \rangle = \frac{1}{M} \sum_{l=1}^M A(\underline{x}_l)$$

This is based on the theorem (proven by Metropolis) that a Markov chain actually has the property that in the limit of  $M \rightarrow \infty$  the distribution function tends toward the equilibrium distribution.

f) Simple sampling does not sample well enough those regimes of phase space that contribute important terms to the thermal average, since phase space is sampled without regard to its contribution. Therefore a poor thermal average will be obtained for those properties that are different from a simple arithmetic average over all configurations.

g) in order to avoid edge artifacts that arise from having a finite simulation box where molecules are close to the edges of the box, so as to simulate a macroscopic system in which most molecules are in the interior.

$$2. \text{ Given } g_{elec} = g_0 + g_1 \exp(-E_1/kT)$$

$$\text{fraction of molecules with energy } E_0 = N_0 = \frac{N}{g} g_0$$

$$\text{fraction of molecules with energy } E_1 = N_1 = \frac{N}{g} g_1 \exp(-E_1/kT)$$

$$E = N_0 E_0 + N_1 E_1 = \frac{N}{g} [g_0 E_0 + g_1 \exp(-E_1/kT) E_1]$$

$$= \frac{N}{g} g_1 E_1 \exp(-E_1/kT)$$

$$C_V \equiv \left( \frac{\partial E}{\partial T} \right)_V = N g_1 E_1 \frac{\partial}{\partial T} \left[ \frac{\exp(-E_1/kT)}{g} \right]$$

$$\frac{d(u/v)}{v^2} = \frac{v du - u dv}{v^2}$$

$$du = -\left(\frac{E_1}{k}\right) \left(-\frac{1}{T^2}\right) \exp\left(\frac{-E_1}{kT}\right) = \frac{E_1}{kT^2} \exp\left(\frac{-E_1}{kT}\right)$$

$$dv = g_1 du$$

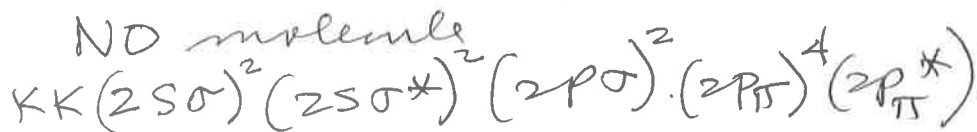
$$d\left(\frac{u}{v}\right) = \frac{[g_0 + g_1 \exp(-\frac{E_1}{kT})] du - \exp(-\frac{E_1}{kT}) g_1 du}{g^2}$$

$$= \frac{g_0 E_1}{g^2 kT^2} \exp(-E_1/kT)$$

$$C_V = \frac{N g_1 E_1 g_0 E_1}{g^2 kT^2} \exp(-E_1/kT) = \frac{N g_0}{g} \cdot \frac{N}{g} g_1 \exp(-\frac{E_1}{kT}) \cdot \frac{E_1^2}{N kT^2}$$

$$C_V = \frac{N_0 \cdot N_1 E_1^2}{N kT^2}$$

NO molecule



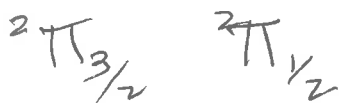
one unpaired electron in  $2p\pi^*$

$S = 1/2$   $2S+1 = 2$

$\Lambda = 1$  for  $(2p\pi^*)$

$\Omega = 1 + 1/2, 1 - 1/2$   
 $= 3/2, 1/2$

Term symbol  $2S+1\Lambda_\Omega$



these two spin-split substates are separated by  $121 \text{ cm}^{-1}$  with  $\Omega=3/2$  lower than  $\Omega=1/2$

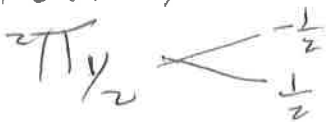
ground state

$g_0 = 4$



first excited state

$g_1 = 2$



[Gordy et al. Phys Rev 98(4): 1034-1038]

they only split in a magnetic field

$E_1 = 121 \text{ cm}^{-1}$

3. For the reaction  $\text{Na}_2(g) \rightleftharpoons 2\text{Na}(g)$

Let  $N_{\text{Na}}$  = number of Na atoms;  $N_{\text{Na}_2}$  = number of  $\text{Na}_2$  molecules

$P = \frac{NkT}{V}$  ideal gas assumption

$$P_{\text{Na}} = \frac{N_{\text{Na}} kT}{V} \quad P_{\text{Na}_2} = \frac{N_{\text{Na}_2} kT}{V}$$

$$K_p = \frac{(N_{\text{Na}})^2}{N_{\text{Na}_2}} \cdot \frac{kT}{V} = \frac{(q_{\text{Na}})^2}{q_{\text{Na}_2}}$$

For a Na atom:  $q_{\text{Na}} = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{nuc spin}}$   
 (ground state) is  $2S_{\frac{1}{2}}$  degeneracy is 2  
 $= \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V \cdot 2 \cdot (2I+1)$   
 nuclear spin of  $^{23}\text{Na}$  is  $3/2$

For Na molecule:  $q_{\text{Na}_2} = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{nuc spin}}$   
 (ground state is singlet)  
 $q_{\text{vib}} = \sum_{v=0}^{\infty} 1 \cdot e^{-\frac{v h \nu}{kT}} = \text{infinite series with a known sum}$   
 $= \frac{1}{1 - e^{-h\nu/kT}}$

$$q_{\text{rot}} = \sum (2J+1) e^{-B_e J(J+1)/kT} \approx \int_0^{\infty} (2J+1) e^{-J(J+1) B_e/kT} dJ$$

$$= \frac{kT}{B_e} = \frac{kT}{\frac{h^2}{2I_0}} = 8\pi^2 I_0 kT / h^2$$

for high T limit  $\rightarrow$  Symmetry number = 2  
 $q_{\text{nuc spin}} = \frac{1}{2} (2I+1)(2I+1)^*$

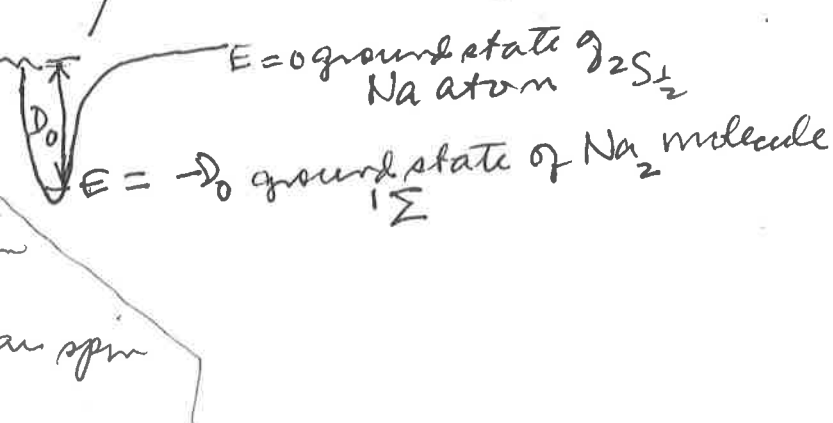
$$q_{\text{Na}_2} = \left(\frac{2\pi(2m)kT}{h^2}\right)^{3/2} V \cdot 1 \cdot e^{-(-D_0)/kT} \cdot \frac{1}{1 - e^{-h\nu/kT}} \cdot \frac{kT}{B_e} \cdot \frac{1}{2} \cdot (2I+1)(2I+1)$$

comes from  $E=0$  ground state of Na atom  $2S_{\frac{1}{2}}$

\* Accurate picture is as follows:

Odd goes with ortho nuclear spin  
 $(\frac{3}{2}+1)(2 \cdot \frac{3}{2}+1) = 10$

Even goes with para nuclear spin  
 $(\frac{3}{2})(2 \cdot \frac{3}{2}+1) = 6$



$$K_p = \frac{kT}{V} \cdot \frac{\left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \cdot V \cdot 2 \right]^2}{\left[ \left( \frac{2\pi 2m kT}{h^2} \right)^{3/2} \cdot V \cdot e^{\frac{D_0/kT}{1-e^{-h\nu/kT}}} \cdot \frac{8\pi^2 I_0 kT}{h^2} \cdot \frac{1}{2} \right]}$$

$$= kT \frac{\left( \frac{2\pi m kT}{h^2} \right)^{3/2} \cdot 4 \cdot (1-e^{-h\nu/kT}) \cdot 2h^2}{2^{3/2} e^{D_0/kT} \cdot \frac{8\pi^2 I_0 kT}{h^2}}$$

$$K_p = (\pi m kT)^{3/2} \frac{(1-e^{-h\nu/kT})}{e^{D_0/kT}} \cdot \frac{1}{\pi^2 I_0 h}$$

$$m = 23 \text{ (actually } 22.98985)$$

$$m = 23 \text{ amu} \cdot \frac{1 \text{ gram}}{6.022 \times 10^{23} \text{ amu}} = 3.819 \times 10^{-23} \text{ gram}$$

$$I_0 = Mr_0^2 = \frac{m}{2} r_0^2 = \frac{23}{2} \cdot (3.078 \times 10^{-8} \text{ cm})^2 \cdot \frac{1 \text{ gram}}{6.022 \times 10^{23} \text{ amu}}$$

$$I_0 = 21.1 \times 10^{-39} \text{ g cm}^2$$

$$\frac{D_0}{kT} = \frac{0.73 \text{ eV} \times 8106 \text{ cm}^{-1}}{208.5 \text{ cm}^{-1} \text{ eV}} \cdot \frac{300 \text{ K}}{T} = 8514/T \quad (300 \text{ K} = 208.5 \text{ cm}^{-1})$$

$$\frac{h\nu}{kT} = \frac{159.23 \text{ cm}^{-1}}{208.5 \text{ cm}^{-1}} \cdot \frac{300 \text{ K}}{T} = 229.1/T$$

$$\frac{(m kT)^{3/2}}{\pi^{1/2} I_0 h} = \frac{(38.19 \times 10^{-24} \times 1.3805 \times 10^{-16} \text{ T})^{3/2}}{\pi^{1/2} 21.1 \times 10^{-39} \times 6.624 \times 10^{-27}} = 1.545 \times 10^6 \frac{\text{T}^{3/2}}{\text{erg cm}^{-3}}$$

$$= 1.545 \times 10^6 \text{ T}^{3/2} \text{ erg cm}^{-3} \left( \frac{82.05 \text{ cm}^3 \text{ atm mole}^{-1}}{8.3143 \times 10^7 \text{ erg K}^{-1}} \right)$$

$$= 1.5247 \text{ T}^{3/2} \text{ atm}$$

$$K_p = 1.5247 \text{ T}^{3/2} \text{ atm} \cdot (1 - e^{-229.1/T}) (e^{-8514/T})$$

$$\text{at } T = 1000 \text{ K}, K_p = 1.5247 (1000)^{3/2} \cdot (1 - e^{-0.229}) (e^{-8.514})$$

$$K_p = 2.83 \text{ atm} \quad \begin{matrix} 0.2047 & 0.000287 \end{matrix}$$

4. The nuclei in this homonuclear diatomic molecule are fermions (spin half integer). So the rotational and nuclear spin states are (ground electronic state is  $^1\Sigma_g^+$ )

$J=2 \text{ --- } 1 \text{ --- } \text{para}$

$J=1 \text{ --- } 3 \text{ --- } \text{ortho}$   
 $J=0 \text{ --- } 1 \text{ --- } \text{para}$   
 ↑ rotational q. no.    ↑ nucl spin degeneracy    ↑ nuclear spin state

$$f_{\text{rot}} \cdot f_{\text{nuclear spin}} = \sum_J (2J+1) (1 \text{ or } 3) \exp\left(-\frac{B_e J(J+1)}{kT}\right)$$

$J$  where  $J_{\text{odd}}$  goes with 3  
 $J_{\text{even}}$  goes with 1

In contact with a paramagnetic solid means that the molecules can make transitions freely ortho  $\leftrightarrow$  para nuclear spin states.

(a) If remaining in contact with paramagnetic solid, then ortho  $\leftrightarrow$  para interconversion can occur at any temperature, which means that all  $J$  levels are permitted to be populated. With only the ground electronic <sup>and vibrational</sup> state populated:

$$f = f_{\text{rot}} f_{\text{nuclear spin}} = \sum_{J=0}^{\text{Even}} (2J+1)(1) \exp\left(-\frac{B_e J(J+1)}{kT}\right) + \sum_{J=1}^{\text{Odd}} (2J+1)(3) \exp\left(-\frac{B_e J(J+1)}{kT}\right)$$

$$q = 1 \left[ 1 + 5 \exp\left(\frac{-6\text{Be}}{kT}\right) + 9 \exp\left(\frac{-20\text{Be}}{kT}\right) + 13 \exp\left(\frac{-42\text{Be}}{kT}\right) + 17 \exp\left(\frac{-72\text{Be}}{kT}\right) + \dots \right]$$

$$+ 3 \left[ 3 \exp\left(\frac{-2\text{Be}}{kT}\right) + 7 \exp\left(\frac{-12\text{Be}}{kT}\right) + 11 \exp\left(\frac{-30\text{Be}}{kT}\right) + 15 \exp\left(\frac{-56\text{Be}}{kT}\right) + \dots \right]$$

$$N_0 = \frac{N}{g} \cdot 1 \quad N_2 = \frac{N}{g} 5 \exp\left(\frac{-6\text{Be}}{kT}\right) \quad N_4 = \frac{N}{g} 9 \exp\left(\frac{-20\text{Be}}{kT}\right)$$

$$N_6 = \frac{N}{g} 13 \exp\left(\frac{-42\text{Be}}{kT}\right) \quad N_8 = \frac{N}{g} 17 \exp\left(\frac{-72\text{Be}}{kT}\right)$$

$$N_1 = 3 \frac{N}{g} 3 \exp\left(\frac{-2\text{Be}}{kT}\right) \quad N_3 = 3 \frac{N}{g} 7 \exp\left(\frac{-12\text{Be}}{kT}\right), \quad N_5 = 3 \frac{N}{g} 11 \exp\left(\frac{-30\text{Be}}{kT}\right)$$

$$N_7 = 3 \frac{N}{g} 15 \exp\left(\frac{-56\text{Be}}{kT}\right), \dots$$

$$E_0 = 0 \quad E_1 = 2\text{Be} \quad E_2 = 6\text{Be} \quad E_3 = 12\text{Be} \quad E_4 = 20\text{Be}$$

$$E_5 = 30\text{Be} \quad E_6 = 42\text{Be}, \quad E_7 = 56\text{Be} \quad E_8 = 72\text{Be} \dots$$

$$E = N_0 E_0 + N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4 + \dots$$

$$= \frac{N}{g} \left\{ 0 + 5(6\text{Be}) \exp\left(\frac{-6\text{Be}}{kT}\right) + 9(20\text{Be}) \exp\left(\frac{-20\text{Be}}{kT}\right) + 13(42\text{Be}) \exp\left(\frac{-42\text{Be}}{kT}\right) + 17(72\text{Be}) \exp\left(\frac{-72\text{Be}}{kT}\right) + \dots \right\}$$

$$+ 3 \frac{N}{g} \left\{ 3(2\text{Be}) \exp\left(\frac{-2\text{Be}}{kT}\right) + 7(12\text{Be}) \exp\left(\frac{-12\text{Be}}{kT}\right) + 11(30\text{Be}) \exp\left(\frac{-30\text{Be}}{kT}\right) + 15(56\text{Be}) \exp\left(\frac{-56\text{Be}}{kT}\right) + \dots \right\}$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V \quad \frac{\partial}{\partial T} \exp\left(\frac{-a\text{Be}}{kT}\right) = \frac{a\text{Be}}{kT^2} \exp\left(\frac{-a\text{Be}}{kT}\right)$$



$$C_v = \frac{N}{kq} \left\{ 0 + 5 \left( \frac{6Be}{T} \right)^2 \exp\left(-\frac{6Be}{kT}\right) + 9 \left( \frac{20Be}{T} \right)^2 \exp\left(-\frac{20Be}{kT}\right) \right. \\ \left. + 13 \left( \frac{42Be}{T} \right)^2 \exp\left(-\frac{42Be}{kT}\right) + 17 \left( \frac{72Be}{T} \right)^2 \exp\left(-\frac{72Be}{kT}\right) \dots \right\} \\ + \frac{3N}{kq} \left\{ 3 \left( \frac{2Be}{T} \right)^2 \exp\left(-\frac{2Be}{kT}\right) + 7 \left( \frac{12Be}{T} \right)^2 \exp\left(-\frac{12Be}{kT}\right) \right. \\ \left. + 11 \left( \frac{30Be}{T} \right)^2 \exp\left(-\frac{30Be}{kT}\right) + 15 \left( \frac{56Be}{T} \right)^2 \exp\left(-\frac{56Be}{kT}\right) \dots \right\}$$

where  $q$  is as derived above.

(b) Equilibrated at 4K means the only populated rotational state is  $J=0$  which goes with the nuclear spin state para, a degeneracy of 1. When this system is then separated and isolated from any paramagnetic substances, while  $T$  is raised, the nuclear spins can not undergo any transitions, will remain para. Since para nuclear spin state is only permitted to go with  $J=\text{even}$ , when the  $T$  is raised, the only rotational states that can be populated are  $J=\text{even}$ .

Therefore,

$$q_{\text{even}} = q_{\text{rot}} q_{\text{nuc}} = \sum_{J=0}^{J=\text{even}} (1)(2J+1) \exp\left(-\frac{Be J(J+1)}{kT}\right)$$

now  $N_0, N_2, N_4, N_6, \dots, N_{\text{even}}$  are as in part (a) but  $N_1 = N_3 = N_5 = N_7 = N_{\text{odd}} = 0$

$$C_v = \frac{N}{q_{\text{even}}} \left\{ 0 + 5 \left( \frac{6Be}{T} \right)^2 \exp\left(-\frac{6Be}{kT}\right) + 9 \left( \frac{20Be}{T} \right)^2 \exp\left(-\frac{20Be}{kT}\right) \right. \\ \left. + 13 \left( \frac{42Be}{T} \right)^2 \exp\left(-\frac{42Be}{kT}\right) + 17 \left( \frac{72Be}{T} \right)^2 \exp\left(-\frac{72Be}{kT}\right) \dots \right\}$$

Note that  $q_{\text{even}}$ , not the full  $q$  is used here.

5. Derive the ratio  $\langle N_A \rangle / \langle N_B \rangle$  from the condition of chemical equilibrium  $\mu_A = \mu_B$  for  $A \rightleftharpoons B$  isomerization process

a) Treat the system as corrected Boltzons

$$t_{CB} = \prod_i \frac{g_i^{N_i}}{N_i!}$$

$$t = t^A \cdot t^B = \prod_i \frac{(g_i^A)^{N_i^A}}{N_i^A!} \prod_j \frac{(g_j^B)^{N_j^B}}{N_j^B!}$$

$$\ln t = \sum_i N_i^A \left( \ln \frac{g_i^A}{N_i^A} + 1 \right) + \sum_j N_j^B \left( \ln \frac{g_j^B}{N_j^B} + 1 \right)$$

To find most probable distribution, maximize  $t$  (or  $\ln t$ ):  
 constraints are  $\sum_i N_i^A + \sum_j N_j^B = N$  and  $E = \sum_i N_i^A \epsilon_i^A + \sum_j N_j^B \epsilon_j^B$

$$\left. \begin{aligned} \frac{\partial(\ln t)}{\partial N_i^A} = \alpha - \beta \epsilon_i^A = 0 \quad i=1, \dots \\ \frac{\partial(\ln t)}{\partial N_j^B} = \alpha - \beta \epsilon_j^B = 0 \quad j=1, \dots \\ \ln \frac{g_i^A}{N_i^A} + \alpha - \beta \epsilon_i^A = 0 \end{aligned} \right\} \begin{aligned} &\text{only one } \alpha \\ &\text{since } \mu_A = \mu_B \\ &\text{only one } \beta, \\ &\text{same temperature} \end{aligned}$$

$$\ln \frac{g_j^B}{N_j^B} + \alpha - \beta \epsilon_j^B = 0$$

From which we get

$$N_i^A = g_i^A e^\alpha e^{-\beta \epsilon_i^A}$$

$$N_j^B = g_j^B e^\alpha e^{-\beta \epsilon_j^B}$$

$$\langle N_A \rangle = \sum_i N_i^A = e^\alpha \sum_i g_i^A e^{-\beta \epsilon_i^A}$$

$$\langle N_B \rangle = \sum_j N_j^B = e^\alpha \sum_j g_j^B e^{-\beta \epsilon_j^B}$$

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{\sum_i g_i^A e^{-\beta \epsilon_i^A}}{\sum_j g_j^B e^{-\beta \epsilon_j^B}}$$

If the degeneracies are  $g_A$  and  $g_B$  and

if A states and B states differ in energy by

$$\Delta \epsilon, \text{ then } \sum_i g_i^A e^{-\beta \epsilon_i^A} = g_A \sum_j e^{-\beta (\epsilon_j^B + \Delta \epsilon)} = g_A e^{-\beta \Delta \epsilon} \sum_j e^{-\beta \epsilon_j^B}$$

$$\sum_j g_j^B e^{-\beta \epsilon_j^B} = g_B \sum_j e^{-\beta \epsilon_j^B}$$

$$\therefore \frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A}{g_B} e^{-\beta \Delta \epsilon} \quad \text{Q.E.D.}$$

$$(6) \quad Q = \frac{1}{N!} g^N$$

a) Partition the sum,

$$g = \underbrace{\sum_i g_i^A e^{-\beta \epsilon_i^A}}_{g_A} + \underbrace{\sum_j g_j^B e^{-\beta \epsilon_j^B}}_{g_B}$$

$$Q = \frac{1}{N!} (g_A + g_B)^N$$

$$Q = \frac{1}{N!} \left\{ \frac{N!}{(N-0)!0!} g_A^0 g_B^N + \frac{N!}{(N-1)!1!} g_A^1 g_B^{N-1} + \frac{N!}{(N-2)!2!} g_A^2 g_B^{N-2} + \frac{N!}{(N-3)!3!} g_A^3 g_B^{N-3} + \dots \right\}$$

$$= \sum_{\substack{N_A, N_B \\ N_A + N_B = N}} \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$$

$$= \sum_P \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$$

P is each particular set of  $N_A, N_B$

Fundamental relation in canonical ensemble is

$$A = -kT \ln Q$$

For a particular set of  $N_A, N_B$

$$A(N_A, N_B) = -kT \ln \left( \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right)$$

$$\frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} = e^{-\frac{A(N_A, N_B)}{kT}}$$

$$Q = \sum_P e^{-\beta A(N_A, N_B)}$$

Q.E.D

b) minimize  $A \rightarrow$  derive the result in Prob 1:

$$\left( \frac{\partial A}{\partial \langle N_A \rangle} \right) = \left( \frac{\partial A}{\partial \langle N_B \rangle} \right) = 0 \quad \text{subject to } \langle N_A \rangle + \langle N_B \rangle = N_{\text{fixed}}$$

$$A(N_A, N_B) = -kT \ln \left( \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right)$$

$$= -kT \left\{ N_A \ln g_A + N_B \ln g_B - \ln N_A! - \ln N_B! \right\}$$

Use Stirling's approximation,

$$A(N_A, N_B) = -kT \left\{ N_A \ln g_A + N_B \ln g_B - N_A \ln N_A + N_A - N_B \ln N_B + N_B \right\}$$

The properties,  $A(N_A, N_B)$  for example corresponds to the average distribution  $A(\langle N_A \rangle, \langle N_B \rangle)$ . At equilibrium,

$$\left( \frac{\partial A}{\partial \langle N_A \rangle} \right)_{T,V} = -kT \left\{ \ln g_A - (\ln \langle N_A \rangle + 1) + 1 \right\} = -kT (\ln g_A - \ln \langle N_A \rangle) = 0$$

$$\left( \frac{\partial A}{\partial \langle N_B \rangle} \right)_{T,V} = -kT \left\{ \ln g_B - (\ln \langle N_B \rangle + 1) + 1 \right\} = -kT (\ln g_B - \ln \langle N_B \rangle) = 0$$

From which we get

$$\frac{g_A}{g_B} = \frac{\langle N_A \rangle}{\langle N_B \rangle}$$

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{\sum_i g_i^A e^{-\beta \epsilon_i^A}}{\sum_j g_j^B e^{-\beta \epsilon_j^B}}$$

again use degeneracy  $g_A, g_B$  and energy difference

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A \sum_i e^{-\beta(\epsilon_i^B + \Delta E)}}{g_B \sum_j e^{-\beta \epsilon_j^B}} = \frac{g_A}{g_B} e^{-\beta \Delta E} \quad \text{Q.E.D.}$$

⑦ Start from  $Q = \frac{(g_A + g_B)^N}{N!} = \sum_{N_A, N_B} \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$

to show that  $\langle N_A \rangle = g_A \left( \frac{\partial \ln Q}{\partial g_A} \right)_{g_B, N}$

To find any average value

$$\langle M \rangle = \sum_j P_j M_j$$

where  $j$  runs through all the system quantum states, but in this case we can choose  $j$  to run through all the possible  $N_A, N_B$  combinations and the probability is given by

$$P(N_A, N_B) = \frac{\left( \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right)}{Q}$$

To find  $\langle N_A \rangle$  we do

$$\langle N_A \rangle = \sum_{N_A, N_B} \frac{g_A^{N_A} g_B^{N_B} N_A}{N_A! N_B! Q} = \frac{\sum_{N_A, N_B} \frac{g_A^{N_A} g_B^{N_B} N_A}{N_A! N_B!}}{Q} \quad (x)$$

Note also that 
$$\frac{\partial}{\partial g_A} \left[ \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right] = N_A \frac{g_A^{N_A-1} g_B^{N_B}}{N_A! N_B!}$$

So that 
$$g_A \frac{\partial}{\partial g_A} \left[ \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right] = N_A \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$$

This is exactly what we have in our expression (X)

Therefore

$$\langle N_A \rangle = \frac{1}{Q} \cdot \sum_{N_A, N_B} g_A \frac{\partial}{\partial g_A} \left( \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right)$$

Noting that  $g_A$  is independent of  $N_A$  we can put  $g_A$  outside the sum over  $N_A, N_B$  combinations

$$= \frac{1}{Q} \cdot g_A \frac{\partial}{\partial g_A} \sum_{N_A, N_B} \left( \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right)$$

since  $\frac{1}{Q} dQ = d \ln Q$  we can write  $\frac{\partial \ln Q}{\partial g_A}$  but this is  $Q$  itself

$$\langle N_A \rangle = g_A \left( \frac{\partial \ln Q}{\partial g_A} \right)_{g_B, N} \quad \text{Q.E.D.}$$

$$\langle N_A \rangle = g_A \left( \frac{\partial \ln \left[ \frac{(g_A + g_B)^N}{N!} \right]}{\partial g_A} \right)_{g_B, N} = g_A \left( \frac{\partial N \ln (g_A + g_B)}{\partial g_A} \right)$$

$$\langle N_A \rangle = g_A \left( \frac{N}{g_A + g_B} \right) \quad \text{Q.E.D.}$$

Since the expression is symmetrical with respect to A and B we would also find

$$\langle N_B \rangle = g_B \frac{N}{g_A + g_B}$$

Now the ratio  $\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A}{g_B}$  Q.E.D.

Fluctuations from these averages:

$$\langle [N_A - \langle N_A \rangle]^2 \rangle = \langle [N_A^2 - 2N_A \langle N_A \rangle + \langle N_A \rangle^2] \rangle$$

$$= \langle N_A^2 \rangle - \langle N_A \rangle^2$$

We have  $\langle N_A \rangle$  already

We just need  $\langle N_A^2 \rangle$ , again by the same approach,

$$\langle N_A^2 \rangle = \sum_{N_A, N_B} N_A^2 \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B! Q}$$

Take  $g_A \frac{\partial}{\partial g_A} \left[ \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right] = \frac{N_A g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$

$$\langle N_A^2 \rangle = \frac{1}{Q} \sum_{N_A, N_B} N_A g_A \frac{\partial}{\partial g_A} \left[ \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!} \right] = \frac{1}{Q} g_A \frac{\partial}{\partial g_A} \sum_{N_A, N_B} N_A \frac{g_A^{N_A} g_B^{N_B}}{N_A! N_B!}$$

But this is  $Q \langle N_A \rangle$

$$\frac{1}{Q} g_A \frac{\partial}{\partial g_A} (Q \langle N_A \rangle) = \frac{1}{Q} g_A \left[ \frac{\partial Q}{\partial g_A} \langle N_A \rangle + Q \frac{\partial \langle N_A \rangle}{\partial g_A} \right]$$

$$\langle N_A^2 \rangle = g_A \left[ \langle N_A \rangle \frac{\partial \ln Q}{\partial g_A} + \frac{\partial \langle N_A \rangle}{\partial g_A} \right]$$



But we already have shown  $g_A \left( \frac{\partial \ln \Omega}{\partial g_A} \right)_{g_B, N} = \langle N_A \rangle$

Therefore,  $\langle N_A^2 \rangle = \langle N_A \rangle^2 + g_A \left( \frac{\partial \langle N_A \rangle}{\partial g_A} \right)$  Q.E.D.

$\therefore$  The fluctuation  $\langle N_A^2 \rangle - \langle N_A \rangle^2 = g_A \left( \frac{\partial \langle N_A \rangle}{\partial g_A} \right) \left[ \frac{g_A + g_B - g_A}{(g_A + g_B)^2} \right]$

Further,  $\frac{\partial}{\partial g_A} \langle N_A \rangle = \frac{\partial}{\partial g_A} \left[ \frac{N g_A}{g_A + g_B} \right] = N \frac{g_A + g_B - g_A}{(g_A + g_B)^2}$

$$= \frac{N g_B}{(g_A + g_B)^2} = \frac{\langle N_B \rangle}{g_A + g_B}$$

$$= \frac{\langle N_A \rangle g_B}{g_A (g_A + g_B)} \quad \left\langle \frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A}{g_B} \right.$$

$$\therefore g_A \frac{\partial \langle N_A \rangle}{\partial g_A} = \langle N_A \rangle \frac{g_B}{g_A + g_B} = \langle N_A \rangle \frac{\langle N_B \rangle}{N}$$

Therefore the fluctuation is

$$\langle N_A^2 \rangle - \langle N_A \rangle^2 = \frac{\langle N_A \rangle \langle N_B \rangle}{N} \quad \text{Q.E.D.}$$