

1. Sucrose is denser than water. But if an aqueous solution of sucrose is prepared, the sucrose molecules do not settle to the bottom of the solution. In other words, a 1.0 M sucrose solution does not become a 1.1 M solution near the bottom of the solution and a 0.9 M solution near the top. (A big relief for analytical chemists!) *Why?*

At 25 °C, the diffusion coefficient of sucrose ($342.30 \text{ g mol}^{-1}$) in water ($18.015 \text{ g mol}^{-1}$) is $0.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the specific volumes of sucrose and water are $0.616 \text{ cm}^3 \text{ g}^{-1}$ and $1.002 \text{ cm}^3 \text{ g}^{-1}$, respectively, and the viscosity of water is $0.0100 \text{ g cm}^{-1} \text{ s}^{-1}$.

2. a) Show that the sedimentation speed of a spherical particle is proportional to the *square* of its radius. Does this help to explain, at least qualitatively, the observation made in question 1?
- b) To illustrate the result obtained in part a, calculate the sedimentation speeds for spherical clay particles (density 3.5 g cm^{-3}) of radius $1 \text{ }\mu\text{m}$ and $0.01 \text{ }\mu\text{m}$ suspended in water at 25 °C.
- c) Also calculate the sedimentation speeds for bubbles of air of radius $1 \text{ }\mu\text{m}$ and $0.01 \text{ }\mu\text{m}$ in water at 25 °C. *Watch the sign of v_z !*

3. Sedimentation is a useful technique for separating substances. In practice, however, gravitational acceleration (about 9.81 cm s^{-1} near the surface of the earth) is often too weak to provide significant separations at a reasonable rate. In these cases, a centrifuge can be used.

a) A particle rotating at a distance r from the axis of rotation experiences the acceleration $\omega^2 r$, where ω is the angular velocity (2π times the number of rotations per second). In the notes for Lab #4, we derived

$$C(z) = C(0)\exp(-m_{\text{eff}}gz/kT)$$

for the equilibrium distribution of particles in a gravitational field. Derive the corresponding expression for $C(r)$, the equilibrium distribution of particles in a centrifugal field.

b) Calculate the acceleration 6 cm from the axis of an ultracentrifuge running at 60,000 rpm. How many times stronger is this acceleration relative to g ?

4. Perfect crystals have zero entropy at $T = 0 \text{ K}$. Phosgene (Cl_2CO) crystals, however, have an entropy of $9.1 \text{ J K}^{-1} \text{ mol}^{-1}$ at 0 K. Why?
5. The natural isotopic abundances for bromine are: 50.54 atom % ^{79}Br and 49.46 atom % ^{81}Br . Calculate the mole percentages of $^{79}\text{Br}_2$, $^{81}\text{Br}_2$, and $^{79}\text{Br}^{81}\text{Br}$ in a sample of bromine gas.
6. A sample of methane (CH_4) is randomly enriched to 85 atom % deuterium. Calculate the mole percentage of each of the following species: CD_4 , CHD_3 , CH_2D_2 , CH_3D , and CH_4 . Describe an experimental technique that could be used to verify this composition.

7. The purpose of this question is to summarize (*in one shot!*) the basic statistical thermodynamic equations for systems with nondegenerate energy levels E_1, E_2, E_3, \dots

a) Using Boltzmann's distribution law and the molecular partition function z defined as

$$z = \sum_{i=1}^{\infty} \exp(-E_i / kT)$$

show that the probability P_i of finding a molecule in energy level i is

$$P_i = \frac{\exp(-E_i / kT)}{z}$$

b) Prove that energy E of a system of N molecules

$$E = \sum_{i=1}^{\infty} N_i E_i$$

is given by

$$E = N \sum_{i=1}^{\infty} P_i E_i = -NkT^2 \left(\frac{\partial \ln z}{\partial T} \right)_{N,V}$$

c) Use Boltzmann's entropy equation $S = k \ln W$ and

$$\ln W = \ln \left(\frac{N!}{N_1! N_2! N_3! \dots} \right)$$

to show that the entropy is

$$S = -Nk \sum_{i=1}^{\infty} P_i \ln P_i$$

Can you explain why this result is analogous to the entropy change for mixing?

d) Show that the expression derived for the entropy in part c is equivalent to

$$S = \frac{E}{T} + Nk \ln z$$

e) Derive the expression $A = -NkT \ln z$ for the Helmholtz energy (an auxiliary thermodynamic function defined as $A = E - TS$ which is convenient for processes at fixed T, V).

f) Use the Maxwell relation $p = -(\partial A / \partial V)_{N,T}$ for the Helmholtz energy ($dA = -SdT - pdV$) to derive an expression for the pressure p .

g) Derive statistical thermodynamic expressions for the enthalpy ($H = E + pV$), Gibbs energy ($G = H - TS$), and the heat capacity at constant volume [$C_V = (\partial E / \partial T)_{N,V}$].

8. a) Show that each of the following distributions (labeled A, B and C) has the same number of molecules N and the same energy E .

i	$\frac{E_i/k}{\text{K}}$	N_i (dist. A)	N_i (dist. B)	N_i (dist. C)
1	0	33	31	32
2	100	15	17	16
3	200	7	9	8
4	300	5	3	4

- b) Calculate the number of configurations (W) for each of the three distributions.
- c) Identify the distribution that obeys Boltzmann's law and verify that it corresponds to the maximum value of W . Calculate the temperature.
- d) Suggest a simple graphical procedure to test for a Boltzmann distribution.

9. For one mole of molecules with the three available molecular energy levels

$$E_1 = 0$$

$$E_2 = k(100 \text{ K})$$

$$E_3 = k(200 \text{ K})$$

Complete the following table:

	$T = 0 \text{ K}$	$T = 50 \text{ K}$	$T = 500 \text{ K}$	$T = 5000 \text{ K}$	$T = \infty$
z					
$P_1 = N_1/N$					
$P_2 = N_2/N$					
$P_3 = N_3/N$					
$E_m/(\text{J mol}^{-1})$					
$S_m/(\text{J K}^{-1} \text{ mol}^{-1})$					

10. The cost of packaging products in metal cans can be reduced by using the smallest amount of metal per can, thereby minimizing the surface area. For a cylindrical can of volume $V = 355 \text{ cm}^3$, use Lagrange's method to find the optimum radius r and height h to minimize the surface area, A .
11. Two nondegenerate energy levels are separated by $\Delta E = k(8700 \text{ K})$. If there are 10 times more molecules in the lower level at equilibrium, calculate the temperature.
12. The entropy of an ideal monatomic gas can be interpreted as a measure of the "disorder" caused by arranging the gas atoms over a vast number of translational energy levels. According to quantum mechanics, the spacing of the translational energy levels for a particle in a box of length a , width b , and height c is inversely proportional to the mass of the particle.

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Use this result to explain qualitatively why the molar entropy of helium ($126.15 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C and 1 bar) is smaller than the molar entropy of argon ($154.84 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C and 1 bar) at a given temperature and pressure.

13. 24 molecules of pure substance A and 40 molecules of pure substance B mix under conditions of constant temperature and pressure.
- Calculate the number of possible molecular arrangements before and after mixing (W_i and W_f), and use Boltzmann's equation $S = k_B \ln W$ to calculate ΔS for the mixing process. (Do not use Sterling's approximation.)
 - Calculate ΔS for the mixing process using the thermodynamic equation.
 - The value of ΔS calculated using molecular theory (part a) and the value of ΔS calculated using thermodynamics (part b) do not agree! Is the molecular theory wrong? Explain briefly.
14. In class we considered the problem of 10,000 indistinguishable molecules distributed over the three energy levels: $E_1 = kT$, $E_2 = 2kT$, $E_3 = 3kT$. If the total energy is constant at $E = 15,000kT$, direct calculations indicated that the most probable number of molecules in each level are $N_1 = 6162$, $N_2 = 2676$ and $N_3 = 1162$.
- Calculate $\ln W_{\text{max}}$ for the most probable distribution. (Use Sterling's approximation.)
 - To check that W_{max} is indeed the maximum value, calculate $\ln W$ for the slightly altered distribution with $N_1 = 6163$, $N_2 = 2674$ and $N_3 = 1163$ produced by a fluctuation (at constant E and constant N). Calculate ΔS for the fluctuation and its probability.

- 1) The sedimentation speed of an aqueous sucrose molecule might be too slow to produce a measurable separation. To check this possibility, calculate v_z for an aqueous sucrose molecule

$$v_z = (\text{force}) \times (\text{mobility}) = -(m_{\text{eff}} g) \times (U)$$

$$m_{\text{eff}} = m \left(1 - \frac{\rho_{\text{water}}}{\rho_{\text{sucrose}}} \right) = \frac{M}{L} \left(1 - \frac{V_{m, \text{sucrose}}}{V_{m, \text{water}}} \right)$$

(molar volumes)

$$= \frac{0.34230 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \left(1 - \frac{0.616 \text{ cm}^3 \text{ g}^{-1}}{1.002 \text{ cm}^3 \text{ g}^{-1}} \right)$$

$$m_{\text{eff}} = 2.190 \times 10^{-25} \text{ kg} \quad g = 9.81 \text{ m s}^{-2}$$

$$U = \frac{D}{kT} = \frac{(0.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \left(10^{-4} \frac{\text{m}}{\text{cm}} \right)^2}{1.381 \times 10^{-23} \text{ J K}^{-1} (298.15 \text{ K})} \quad (\leftarrow \text{SI units})$$

$$U = 1.239 \times 10^{-11} \text{ m s}^{-1} \text{ N}^{-1}$$

sedimentation speed	$v_z = -m_{\text{eff}} g U = -2.190 \times 10^{-25} (9.81) (1.239 \times 10^{-11})$
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is negligibly small	$v_z = -2.660 \times 10^{-15} \text{ m s}^{-1} \quad (-8.39 \times 10^{-6} \text{ m year}^{-1})$
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or // show that the concentration gradient dc/dz produced by sedimentation is negligibly small for aqueous sucrose:

$$c(z) = c(0) e^{-m_{\text{eff}} g z / kT} \quad \frac{dc}{dz} = -c_0 \frac{m_{\text{eff}} g}{kT} e^{-m_{\text{eff}} g z / kT}$$

$$\frac{dc}{dz} = -c \frac{m_{\text{eff}} g}{kT} \quad \frac{1}{c} \frac{dc}{dz} = -\frac{m_{\text{eff}} g}{kT} = \text{relative change in } c \text{ per unit height}$$

$$= -0.000522 \quad (\text{only } -0.05\% \text{ per meter})$$

② a) sedimentation speed for a spherical particle

$$v_z = \overset{\text{"down"}}{\downarrow} -m_{\text{eff}} g \downarrow = -m_{\text{eff}} g \frac{1}{6\pi r \eta}$$

$$m_{\text{eff}} = V_{\text{particle}} \rho_{\text{particle}} - V_{\text{particle}} \rho_{\text{solvent}}$$

$$= \frac{4}{3} \pi r^3 \rho_{\text{particle}} - \frac{4}{3} \pi r^3 \rho_{\text{solvent}} = \frac{4}{3} \pi r^3 (\rho_{\text{particle}} - \rho_{\text{solvent}})$$

$$= \frac{4}{3} \pi r^3 \rho_{\text{particle}} \left(1 - \frac{\rho_{\text{solvent}}}{\rho_{\text{particle}}}\right)$$

$$v_z = -m_{\text{eff}} g \frac{1}{6\pi r \eta} = -\frac{4}{3} \pi r^3 \rho_{\text{particle}} \left(1 - \frac{\rho_{\text{solvent}}}{\rho_{\text{particle}}}\right) \frac{1}{6\pi r \eta}$$

$$v_z = -\frac{2}{9} (\rho_{\text{particle}} - \rho_{\text{solvent}}) \frac{r^2}{\eta}$$

v_z is proportional to r^2

a sucrose molecule is a very small "particle", so the sedimentation speed of a sucrose molecule ($\propto r^2$) should be negligible

$$b) \eta = (0.0100 \text{ g cm}^{-1} \text{ s}^{-1}) (10^{-3} \text{ kg g}^{-1}) (100 \text{ cm m}^{-1}) \\ = 0.00100 \text{ kg m}^{-1} \text{ s}^{-1} \quad (\leftarrow \text{SI})$$

$$\rho_{\text{particle}} = (3.5 \text{ g cm}^{-3}) 10^{-3} (\text{kg g}^{-1}) 10^6 (\text{cm}^3 \text{ m}^{-3}) = 3500 \text{ kg m}^{-3}$$

$$\rho_{\text{solvent}} = \frac{1}{V_{\text{solvent}}} = \frac{1}{1.002} \text{ g cm}^{-3} = 998 \text{ kg m}^{-3}$$

$$r = 1 \mu\text{m} = 10^{-6} \text{ m} \\ (\text{clay particles})$$

$$v_z = -\frac{2}{9} (3500 - 998) \frac{(10^{-6})^2}{0.00100} = \boxed{-5.56 \times 10^{-6} \frac{\text{m}}{\text{s}}}$$

(\leftarrow 4.8 cm per day)

$$r = 0.01 \mu\text{m} = 10^{-8} \text{ m}$$

$$v_z = -\frac{2}{9} (3500 - 998) \frac{(10^{-8})^2}{0.00100} = \boxed{-5.56 \times 10^{-11} \frac{\text{m}}{\text{s}}}$$

(\leftarrow 0.00048 cm/day)

(2 cont.)

c) the "average molar mass" of air ($\approx 80 \text{ mol\% N}_2, 20 \text{ mol\% O}_2$)
is $M = 0.80 M_{\text{N}_2} + 0.20 M_{\text{O}_2} = 0.80(28.01) + 0.20(32.00) \frac{\text{g}}{\text{mol}}$

$$M = 28.80 \text{ g mol}^{-1} = 0.02880 \text{ kg mol}^{-1}$$

$$\begin{aligned} \text{density of air (assume 1 atm)} &= M \frac{n}{V} = M \frac{P}{RT} = 0.02880 \frac{101325}{8314(298.15)} \\ &= 1.18 \text{ kg m}^{-3} \end{aligned}$$

$$\text{air bubble, } r = 1 \mu\text{m}, \quad v_z = -\frac{2}{9} \left(\rho_{\text{bubble}} - \rho_{\text{solvent}} \right) \frac{r^2}{\eta}$$

$$v_z = -\frac{2}{9} (1.18 - 998) \frac{(10^{-6})^2}{0.00100} = \boxed{+2.21 \times 10^{-7} \text{ m s}^{-1}} \quad \left(\begin{array}{l} \text{"up"} \\ (1.91 \text{ cm day}^{-1}) \end{array} \right)$$

air bubble, $r = 0.01 \mu\text{m}$

$$v_z = (2.21 \times 10^{-7} \text{ m s}^{-1}) 10^{-4} = \boxed{2.21 \times 10^{-11} \text{ m s}^{-1}}$$

③ a) at equilibrium: centrifugal force + diffusion force = 0
 $m_{\text{eff}} \omega^2 r - \frac{d\mu}{dr} = 0 \quad (\mu = \text{constant} + kT \ln c)$

$$m_{\text{eff}} \omega^2 r - kT \frac{d \ln c}{dr} = 0 \quad d \ln c = -\frac{m_{\text{eff}} \omega^2}{kT} r dr$$

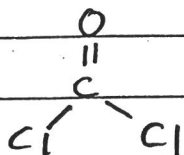
$$\int d \ln c = -\frac{m_{\text{eff}} \omega^2}{kT} \int r dr \quad \ln c(r) - \ln c(0) = -\frac{m_{\text{eff}} \omega^2}{2kT} r^2$$

$$\boxed{c(r) = c(r=0) \exp\left(-\frac{m_{\text{eff}} \omega^2 r^2}{2kT}\right)}$$

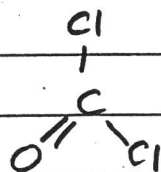
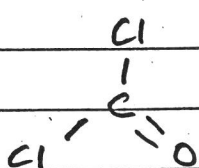
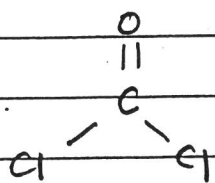
$$\text{b) } \omega^2 r = (2\pi 60000 \text{ min}^{-1})^2 \left(\frac{1}{60} \frac{\text{min}}{\text{s}}\right)^2 (0.06 \text{ m}) = \boxed{2.37 \times 10^6 \frac{\text{m}}{\text{s}^2}}$$

(241,000 times larger than g .)

4. Phosgene is a "propeller"-type planar molecule:



In a phosgene crystal, three nearly energetically identical orientations are possible:



For one mole of phosgene molecules, the number of configurations is $W = 3 \times 3 \times 3 \times 3 \dots$ (L times)

$$W = 3^L$$

↑ Avogadro number

$$\begin{aligned} S &= k \ln W = k \ln 3^L = Lk \ln 3 = R \ln 3 \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 3 \\ &= 9.13 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

5) Consider a crystal of bromine. At any atomic bromine site, the probability of finding ^{79}Br is 0.5054 and the probability of finding ^{81}Br is 0.4946.

$$\underline{^{79}\text{Br}} \quad \underline{^{79}\text{Br}} \quad (0.5054) (0.5054) = 0.2554 \text{ probability}$$

$$\underline{^{79}\text{Br}} \quad \underline{^{81}\text{Br}} \quad (0.5054) (0.4946) = 0.2500$$

$$\underline{^{81}\text{Br}} \quad \underline{^{79}\text{Br}} \quad (0.4946) (0.4946) = 0.2500$$

$$\underline{^{81}\text{Br}} \quad \underline{^{81}\text{Br}} \quad (0.4946) (0.4946) = 0.2446$$

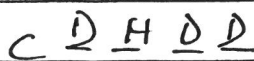
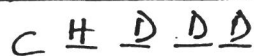
$$\text{sum } \underline{\underline{1.0000}}$$

$^{79}\text{Br}_2$ abundance 25.54%, $^{81}\text{Br}_2$ abundance 24.46%
isotopically mixed $^{79}\text{Br}^{81}\text{Br}$ 50.00% abundance

⑥ For CH_4 randomly enriched to 85 atom% D:

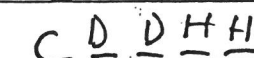
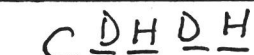
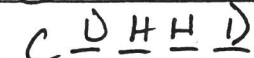
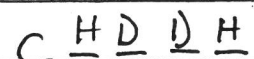
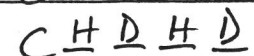
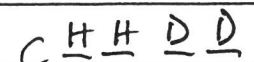


probability for $\text{CD}_4 = P(\text{CD}_4) = 0.85^4 = 0.522006$

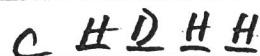
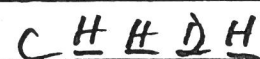
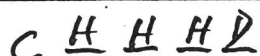


$P(\text{CHD}_3) = \frac{4!}{3!1!} 4(0.15)(0.85)^3 = 0.368475$

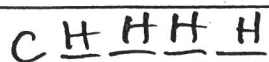
(all 4 sites are equivalent)



$P(\text{CH}_2\text{D}_2) = \frac{4!}{2!2!} 6(0.15)^2(0.85)^2 = 0.097538$



$P(\text{CH}_3\text{D}) = 4(0.15)^3(0.85) = 0.011475$



$P(\text{CH}_4) = (0.15)^4 = 0.000506$

sum 1.000000

composition:

CD_4	52.20	mol %
CHD_3	36.85	"
CH_2D_2	9.75	"
CH_3D	1.14	"
CH_4	0.05	"

mass
spectroscopy
detection?

⑦ a) P_i is proportional to $e^{-E_i/KT}$ $\sum_i P_i = 1$

$P_i = a e^{-E_i/KT}$ (a is a constant)

$$\sum_i P_i = \sum_j a e^{-E_j/KT} \quad 1 = a \sum_j e^{-E_j/KT}$$

$$a = \frac{1}{\sum_j e^{-E_j/KT}} \quad P_i = \frac{e^{-E_i/KT}}{\sum_j e^{-E_j/KT}} = \frac{e^{-E_i/KT}}{Z}$$

b) $E = \sum_i N_i E_i = \sum_i (P_i N) E_i = N \sum_i P_i E_i$

$$-NKT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} = -NKT^2 \frac{\partial}{\partial T} \ln \left(\sum_i e^{-E_i/KT} \right)$$

$$= \frac{-NKT^2 \sum_i \left(\frac{-E_i}{K} \right) \left(\frac{-1}{T^2} \right) e^{-E_i/KT}}{\sum_i e^{-E_i/KT}} = \frac{N \sum_i E_i e^{-E_i/KT}}{\sum_i e^{-E_i/KT}}$$

$$= N \sum_i P_i E_i = E$$

c) $S = k \ln W$

$$= k \ln \left(\frac{N!}{N_1! N_2! N_3! \dots} \right)$$

$$N = N_1 + N_2 + N_3 + \dots$$

$$= k (\ln N! - \ln N_1! - \ln N_2! - \ln N_3! - \dots)$$

$$= k (N \ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 - N_3 \ln N_3 + N_3 - \dots)$$

$$= k \left[(N_1 + N_2 + N_3 + \dots) \ln N - N_1 \ln N_1 - N_2 \ln N_2 - N_3 \ln N_3 \dots \right]$$

$$= k (-N_1 \ln N_1 + N_1 \ln N - N_2 \ln N_2 + N_2 \ln N - N_3 \ln N_3 + N_3 \ln N - \dots)$$

$$= -k \sum_i N_i \ln(N_i/N) = -k \sum_i (P_i N) \ln P_i = -k N \sum_i P_i \ln P_i$$

(7c cont.)

This result is analogous to the entropy change produced by mixing N_1 molecules of pure substance 1, N_2 molecules of pure substance 2, N_3 molecules of pure substance 3, ...

$$\Delta S_{\text{mix}} = -k \sum_i N_i \ln X_i = -kN \sum_i X_i \ln X_i$$

↖ mole fraction of i

in the expression $S = -NK \sum_i P_i \ln P_i$ we are mixing configurations

d) from part a: $P_i = \frac{e^{-E_i/KT}}{Z}$

so: $\ln P_i = \frac{-E_i}{KT} - \ln Z$

$$\therefore S = -NK \sum_i P_i (\ln P_i) = -NK \sum_i P_i \left(\frac{-E_i}{KT} - \ln Z \right)$$

$$S = \frac{N}{T} \sum_i P_i E_i + NK \sum_i P_i \ln Z = \frac{N \sum_i P_i E_i}{T} + (NK \ln Z) \left(\sum_i P_i \right)$$

1 ↘

$$S = \frac{E}{T} + NK \ln Z$$

e) $A \equiv E - TS = E - T \left(\frac{E}{T} + NK \ln Z \right) = -NKT \ln Z$

f) $p = - \left(\frac{\partial A}{\partial V} \right)_{N,T} = -NKT \left(\frac{\partial \ln Z}{\partial V} \right)_{N,T}$

g) $H \equiv E + pV = -NKT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} + NKTV \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}$

(7 g cont)

$$G \equiv H - TS = E + pV - TS$$

$$= E + NKT V \left(\frac{\partial \ln Z}{\partial V} \right)_{N,T} - T \left(\frac{E}{T} + Nk \ln Z \right)$$

$$= NKT V \left(\frac{\partial \ln Z}{\partial V} \right)_{N,T} + NKT \ln Z$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} \left[-NKT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} \right]$$

$$= -NKT^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_{N,V} + 2NKT \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V}$$

⑧ a) for Distribution A

$$N = N_1 + N_2 + N_3 + N_4 = 33 + 15 + 7 + 5 = 60$$

$$E = N_1 E_1 + N_2 E_2 + N_3 E_3 + N_4 E_4$$

$$E/k = 33(0) + 15(100 \text{ K}) + 7(200 \text{ K}) + 5(300 \text{ K}) = 4400 \text{ K}$$

for Distribution B $N = 31 + 17 + 9 + 3 = 60$

$$E/k = 31(0) + 17(100 \text{ K}) + 9(200 \text{ K}) + 3(300 \text{ K}) = 4400 \text{ K}$$

for distribution C $N = 32 + 16 + 8 + 4 = 60$

$$E/k = 32(0) + 16(100 \text{ K}) + 8(200 \text{ K}) + 4(300 \text{ K}) = 4400 \text{ K}$$

(8 cont.)

b) distribution A: $W_A = \frac{N!}{N_1! N_2! N_3! N_4!} = \frac{60!}{33! 15! 7! 5!}$

$$W_A = 1.2116 \times 10^{27}$$

distribution B: $W_B = \frac{60!}{31! 17! 9! 3!} = 1.3067 \times 10^{27}$

distribution C: $W_C = \frac{60!}{32! 16! 8! 4!} = 1.5619 \times 10^{27}$

c) for equally-spaced energy levels with $E_{i+1} - E_i = \Delta E$

$$\frac{N_{i+1}}{N_i} = \frac{e^{-(E_i + \Delta E)/KT}}{e^{-E_i/KT}} = e^{-\Delta E/KT} = \text{constant for a Boltzmann distribution}$$

only distribution C obeys this rule

$$\frac{N_2}{N_1} = \frac{16}{32} = \frac{N_3}{N_2} = \frac{8}{16} = \frac{N_4}{N_3} = \frac{4}{8} = \frac{1}{2}$$

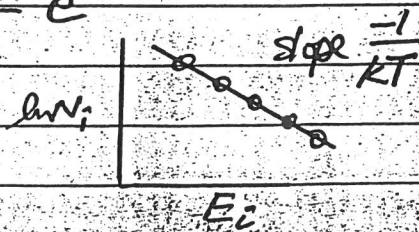
$$\frac{1}{2} = e^{-\Delta E/KT} \quad \ln\left(\frac{1}{2}\right) = -\frac{\Delta E}{KT}$$

$$T = -\frac{\Delta E}{k \ln\left(\frac{1}{2}\right)} = \frac{\Delta E/k}{\ln 2} = \frac{100 \text{ K}}{\ln 2} = 144 \text{ K}$$

d) $\frac{N_i}{N} = p_i = \frac{e^{-E_i/KT}}{Z}$

$$N_i = \frac{N}{Z} e^{-E_i/KT}$$

$$\ln N_i = \ln\left(\frac{N}{Z}\right) - \frac{E_i}{kT}$$



plot $\ln N_i$ against E_i : look for a straight line

$$(9) \quad z = \sum_i e^{-E_i/KT} = e^{-E_1/KT} + e^{-E_2/KT} + e^{-E_3/KT}$$

$$z = e^{-0} + e^{-100K/T} + e^{-200K/T}$$

$$\frac{N_1}{N} = P_1 = \frac{e^{-E_1/KT}}{z} = \frac{1}{1 + e^{-100K/T} + e^{-200K/T}}$$

$$\frac{N_2}{N} = \frac{e^{-100K/T}}{1 + e^{-100K/T} + e^{-200K/T}}$$

$$\frac{N_3}{N} = \frac{e^{-200K/T}}{1 + e^{-100K/T} + e^{-200K/T}}$$

as $T \rightarrow 0$ $\frac{N_1}{N} \rightarrow \frac{1}{1+0+0} = 1$ (all molecules in the ground state)

$$\frac{N_2}{N} \rightarrow \frac{0}{1+0+0} = 0$$

$$\frac{N_3}{N} \rightarrow \frac{0}{1+0+0} = 0$$

as $T \rightarrow \infty$

$$\frac{N_1}{N} \rightarrow \frac{1}{1+1+1} = \frac{1}{3}$$

$$\frac{N_2}{N} \rightarrow \frac{1}{1+1+1} = \frac{1}{3}$$

$$\frac{N_3}{N} \rightarrow \frac{1}{1+1+1} = \frac{1}{3}$$

(all 3 levels equally populated)

(9 cont.)

$$E = N_1 E_1 + N_2 E_2 + N_3 E_3 = N(P_1 E_1 + P_2 E_2 + P_3 E_3)$$

Avogadro's number

$$E_m = L \left(\frac{N_1}{N} E_1 + \frac{N_2}{N} E_2 + \frac{N_3}{N} E_3 \right) = Lk \left(\frac{N_1}{N} (0) + \frac{N_2}{N} 100K + \frac{N_3}{N} 200K \right)$$

$$E_m = R \left(\frac{N_2}{N} 100K + \frac{N_3}{N} 200K \right)$$

$$Nk = Lk = R$$

$$S = -Nk(P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3)$$

$$S = -R \left(\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N_2}{N} \ln \frac{N_2}{N} + \frac{N_3}{N} \ln \frac{N_3}{N} \right)$$

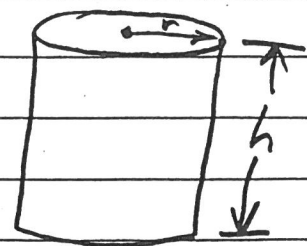
	T=0	T=50K	T=500K	T=5000K	T=∞
Z	1	1.153	2.489	2.941	3
N ₁ /N	1	0.867	0.402	0.340	1/3
N ₂ /N	0	0.117	0.329	0.330	1/3
N ₃ /N	0	0.016	0.269	0.327	1/3
E _m /(J mol ⁻¹)	0	124	721	820	831
S _m /(J mol ⁻¹ K ⁻¹)	0	3.66	9.02	9.13	9.13

qualitatively, the molecular partition function is a measure of the number of energy levels that are appreciably occupied

(10) The surface area of a can is

$$A = 2\pi r^2 + 2\pi rh$$

\swarrow 2 ends \searrow sidewall



The volume of a can is $V = \pi r^2 h = 355 \text{ cm}^3$

Minimize A subject to the constraint $g(r, h) = \pi r^2 h - 355 \text{ cm}^3 = 0$

define $F(r, h) = A(r, h) + \alpha g(r, h)$

$\alpha = \text{Lagrange multiplier}$

$$F(r, h) = 2\pi r^2 + 2\pi rh + \alpha(\pi r^2 h - 355 \text{ cm}^3)$$

find the unconstrained minimum in $F(r, h)$

$$\frac{\partial F}{\partial r} = 0 = 4\pi r + 2\pi h + \alpha 2\pi rh \Rightarrow 2r + h + \alpha rh = 0$$

$$\frac{\partial F}{\partial h} = 0 = 2\pi r + \alpha \pi r^2 \Rightarrow \alpha = -\frac{2}{r}$$

$$2r + h + \alpha rh = 0$$

$$2r + h - \frac{2}{r} rh = 0$$

$$2r = h$$

$$\frac{h}{2} = r$$

(or diameter = h)

$$V = \pi r^2 h = \pi r^2 2r = 2\pi r^3 = 355 \text{ cm}^3$$

$$r = 3.837 \text{ cm}$$

$$h = 2r = 7.674 \text{ cm}$$

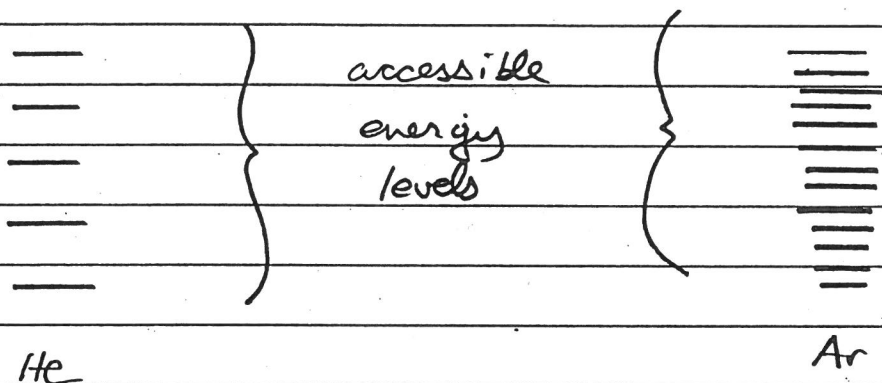
(check $\pi r^2 h = 355.00 \text{ cm}^3$)

$$(11) \quad \frac{N_{i+1}}{N_i} = \frac{e^{-(E_i + \Delta E)/kT}}{e^{-E_i/kT}} = e^{-\Delta E/kT} = \frac{1}{10}$$

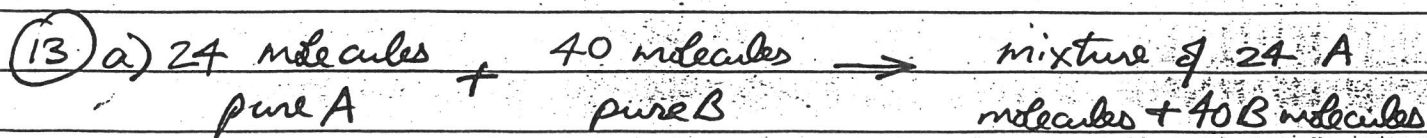
$$\frac{-\Delta E}{kT} = \ln\left(\frac{1}{10}\right) \quad T = \frac{-\Delta E}{k \ln\left(\frac{1}{10}\right)} = \frac{\Delta E}{k \ln 10}$$

$$T = \frac{k(8700 \text{ K})}{k \ln 10} = \boxed{3778 \text{ K}}$$

$$(12) \quad S_m = -R \sum_i P_i \ln P_i$$



For Ar, with energy levels more closely spaced, the atoms can be spread over a larger number of translational energy levels (analogous to "mixing" a larger number of components). This produces more "disorder" and a larger molar entropy.



$$W_i = \frac{24!}{24! 0!} \frac{40!}{40! 0!} = 1 \quad \left(\begin{array}{l} 24 \text{ A's on 24 sites} \\ 40 \text{ B's on 40 sites} \end{array} \right)$$

$$W_f = \frac{64!}{24! 40!} = 2.50649 \times 10^{17}$$

(13 a cont.)

$$\Delta S_{\text{mix}} = S_f - S_i = k \ln W_f - k \ln W_i$$

$$= (1.38066 \times 10^{-23} \text{ J K}^{-1}) \left[\ln(2.50649 \times 10^{17}) - \ln 1 \right]$$

$$\Delta S_{\text{mix}} = 5.5313 \times 10^{-22} \text{ J K}^{-1}$$

mole fraction A
mole fraction B

$$b) \Delta S_{\text{mix}} (\text{thermodynamic}) = -k (N_A \ln X_A + N_B \ln X_B)$$

$$= -(1.38066 \times 10^{-23} \text{ J K}^{-1}) \left(24 \ln \frac{24}{64} + 40 \ln \frac{40}{64} \right)$$

$$\Delta S_{\text{mix}} = 5.8457 \times 10^{-22} \text{ J K}^{-1} \quad (\approx 6\% \text{ larger})$$

c) No! Molecular theory is not "wrong"! In the limit of bulk macroscopic mixtures ($N \gg \gg 60$), ΔS_{mix} (molecular) and ΔS_{mix} (thermodynamic) are in perfect agreement

(14) a) $\ln W_{\text{max}} = \ln \frac{10000!}{6162! 2676! 1162!}$

$$= 10,000 \ln 10,000 - 10,000 - 6162 \ln 6162 + 6162 - 2676 \ln 2676 + 2676 - 1162 \ln 1162 + 1162$$

$$= 9012.347005$$

b) $\ln W = 10,000 \ln 10,000 - 6163 \ln 6163 - 2674 \ln 2674 - 1163 \ln 1163$
 $= 9012.345848$ $W < W_{\text{max}}$

$$\Delta S = k \ln W - k \ln W_{\text{max}} = k(-0.001157) = -1.598 \times 10^{-26} \text{ J K}^{-1}$$

$$\frac{W}{W_{\text{max}}} = \exp(\ln W - \ln W_{\text{max}}) = e^{-0.001157} = 0.9988$$

(very likely, not surprising because $\sigma_i \approx 100$)