① THE PARTITION FUNCTION FOR THIS SYSTEM IS

$$q = g_1 \exp(-\epsilon_1/kT) + g_2 \exp(-\epsilon_2/kT)$$

IN THIS CASE $\quad g_1 = g_2 = 1 \quad \epsilon_1 = -\mu F \quad \epsilon_2 = \mu F$

SO

$$q = e^{\mu F/kT} + e^{-\mu F/kT}$$

THE FRACTION OF MOLECULES WITH DIPOLE ALLIGNED WITH THE FIELD IS

$$\frac{N_{AL}}{N} = \frac{g_1 e^{-\epsilon_1/kT}}{q} = \frac{e^{+\mu F/kT}}{e^{\mu F/kT} + e^{-\mu F/kT}} = \left(1 + e^{-2\mu F/kT}\right)^{-1}$$

THE FRACTION OF MOLECULES WITH DIPOLE OPPOSED TO THE FIELD IS

$$\frac{N_{OP}}{N} = \frac{g_2 e^{-\epsilon_2/kT}}{q} = \frac{e^{-\mu F/kT}}{e^{\mu F/kT} + e^{-\mu F/kT}} = \left(e^{2\mu F/kT} + 1\right)^{-1}$$

IF PROBLEM 1. AN EXPRESSION FOR THE ENERGY OF SUCH A SYSTEM WAS DERIVED:

$$E = N\left[\frac{g_1 \epsilon_1 e^{-\epsilon_1/kT} + g_2 \epsilon_2 e^{-\epsilon_2/kT}}{g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT}}\right]$$

THUS

$$\langle E \rangle = \frac{E}{N} = \frac{-\mu F e^{\mu F/kT} + \mu F e^{-\mu F/kT}}{e^{\mu F/kT} + e^{-\mu F/kT}} = \frac{-\mu F\left(e^{\mu F/kT} - e^{-\mu F/kT}\right)}{\cosh(\mu F/kT)}$$

$$= \frac{-\mu F \sinh(\mu F/kT)}{\cosh(\mu F/kT)} = -\mu F \tanh(\mu F/kT)$$

(a)

$$\frac{N_{ALLIGNED}}{N} = (1 + e^{-2\mu F/kT})^{-1}$$

$$\frac{N_{OPPOSED}}{N} = (1 + e^{2\mu F/kT})^{-1}$$

$$\langle E \rangle = \frac{E}{N} = -\mu F \tanh(\mu F/kT)$$

FOR HCl $\mu = 1.03 \times 10^{-18}$ esu cm   GIVEN $V = 10^5$ V cm^{-1} T = 300 K

$$\frac{\mu F}{kT} = \frac{1.03 \times 10^{-18} \text{ esu-cm} \times 10^5 \text{ V/cm}}{1.3807 \times 10^{-16} \frac{ERG}{K} \times 300 K} \times \frac{10^7 ERG}{J} \times \frac{COUL}{2.9979 \times 10^9 \text{ esu}} \checkmark = 8.295 \times 10^{-3}$$

THUS FOR HCl

$$\frac{N_{ALLIGNED}}{N} = [1 + \exp(-2 \times 8.295 \times 10^{-3})]^{-1} = .504$$

$$\frac{N_{OPPOSED}}{N} = \{1 + \exp(2 \times 8.295 \times 10^{-3}\}^{-1} = .496$$

$$\langle E \rangle = 1.03 \times 10^{-16} \times 10^5 \times \frac{1}{2.9979 \times 10^9} \tanh(8.295 \times 10^{-3}) = 5.70 \times 10^{-23} \frac{JOULE}{MOLECULE}$$

(b)

$$\frac{N_{ALLIGNED}}{N} = .504 \qquad \frac{N_{OPPOSED}}{N} = .496 \quad \checkmark$$

$$\langle E \rangle = 5.70 \times 10^{-23} \frac{JOULE}{MOLECULE}$$

TO ALLIGNED   55 %. OF THE   HCl MOLECULES WITH THE. FIELD

$$\frac{N_{ALLIGNED}}{N} = .55 = \left[1 + \exp(-2\mu F/kT)\right]^{-1} \quad ; \quad 1 + \exp(-2\mu F/kT) = \frac{1}{.55}$$

$$\exp(-2\mu F/kT) = .\overline{81} \quad ; \quad F = \frac{-kT \ln .\overline{81}}{2\mu}$$

$$F = \frac{-1.3807 \times 10^{-16} \text{ ERG/K} \times 300 \text{ K} \ln .\overline{81}}{2 \times 1.03 \times 10^{-18} \text{ esu-cm}} \times \frac{1}{10^{7} \frac{\text{erg}}{\text{erg}}} \times 2.9979 \times 10^{9} \frac{\text{esu}}{\text{coul}} = 1.21 \times 10^{6} \text{ volt}$$

(c) TO ALLIGN 55% OF THE MOLECULES WITH THE FIELD
REQUIRES A FIELD OF 1.21 X10⁶ VOLTS. ⟵ 1 million volts
THUS FOR SUCH A SYSTEM IT IS NOT so PRACTICAL
such as 55% or more
LINE UP A LARGE FRACTION / THE MOLECULES WITH THE FIELD

(2) THE ENTROPY IS $\quad S = kN\ln\frac{q}{N} + E/T + kN$

FOR ATOMS $\quad q/N = (q_{TRANS}/N)q_{elec}$

THE TRANSLATIONAL PARTITION FUNCTION q_{TRANS}/N CAN BE WRITTEN

$$q_{TRANS}/N = C M^{3/2} T^{5/2}$$

THE CONSTANT C DEPENDS ON THE CHOICE OF STANDARD STATE, AND NOT ON THE PARTICULAR SUBSTANCE; M IS THE MOLECULAR WEIGHT, T THE TEMPERATURE.

THE SUBSCRIPT 1 AND 2 WILL REFER TO THE TWO ISOTOPES, AND THE SUBSCRIPT ISO WILL REFER TO THE ISOTOPIC MIXTURE.

THEN $\quad \Delta S = (S_1 + S_2) - S_{ISO}$

$$= kN_1\ln q_1/N_1 + E_1/T + kN_1 + kN_2\ln q_2/N_2 + E_2/T + kN_2$$
$$- kN_{ISO}\ln q_{ISO}/N_{ISO} - E_{ISO}/T - kN_{ISO}$$

$$\Delta S = kN_1\ln C M_1^{3/2} T^{5/2} q_{elec} + kN_2\ln C M_2^{3/2} T^{5/2} q_{elec} - kN_{ISO}\ln C M_{ISO}^{3/2} T^{5/2} q_{elec}$$
$$+ k(N_1 + N_2 - N_{ISO}) + (E_2 + E_1 - E_{ISO})/T$$

THE ELECTRONIC PARTITION FUNCTIONS ARE IDENTICAL, ALSO $N_1 + N_2 = N_{ISO}$, $E_1 + E_2 = E_{ISO}$

SO

$$\Delta S = kN_1\ln M_1^{3/2} + kN_2\ln M_2^{3/2} - kN_{ISO}\ln M_{ISO}^{3/2} + k\ln C T^{5/2} q_{elec}(N_1 + N_2 - N_{ISO})$$

$$= \frac{3k}{2}\left[N_1\ln M_1 + N_2\ln M_2 - N_{ISO}\ln M_{ISO}\right] = \frac{3kN_{ISO}}{2}\left[\frac{N_1\ln M_1}{N_{ISO}} + \frac{N_2\ln M_2}{N_{ISO}} - \ln M_{ISO}\right]$$

THE MOLE FRACTIONS OF ISOTOPES 1 AND 2 ARE RESPECTIVELY $X_1 = \frac{N_1}{N_{ISO}}$, $X_2 = \frac{N_2}{N_{ISO}}$

WE MAY CONSIDER ONE MOLE OF THE ISOTOPIC MIXTURE

SO THAT $\quad kN_{ISO} = R$. THE MOLECULAR WEIGHT OF THE ISOTOPE

IS $M_{ISO} = X_1 M_1 + X_2 M_2$ THE EXPRESSION FOR ΔS THEN BECOMES

$$\Delta S = \frac{3R}{2}\left[X_1 \ln M_1 + X_2 \ln M_2 - \ln\left(X_1 M_1 + X_2 M_2\right)\right]$$

$$\Delta S = \frac{3R}{2} \ln\left(\frac{M_1^{X_1} M_2^{X_2}}{X_1 M_1 + X_2 M_2}\right)$$

FOR Ne(g)   90% OF THE GAS IS THE ISOTOPE OF ATOMIC WT 20, AND

10% OF THE ISOTOPE OF ATOMIC WT 22,   THEN

$$\Delta S = \frac{3 \times 1.9872 \text{ cal}}{2 \text{ mol-K}} \ln\left(\frac{(20)^{.9} \times (22)^{.1}}{.9 \times 20 + .1 \times 22}\right) = -1.25 \times 10^{-3} \frac{\text{cal}}{\text{mol-K}^\circ}$$

(a) $\underset{1}{S_{ISOTOPE}} + \underset{2}{S_{ISOTOPE}} - \underset{\substack{\text{MIXTURE OF} \\ 1 \& 2}}{S_{ISOTOPIC}} = \Delta S = \frac{3R}{2} \ln\left(\frac{M_1^{X_1} M_2^{X_2}}{X_1 M_1 + X_2 M_2}\right)$

(b) FOR Ne(g) $\Delta S = -1.25 \times 10^{-3} \frac{\text{cal}}{\text{mol-K}}$

③ (a) Let $X_1 = X_{35Cl} = 0.75$ Let $X_2 = X_{37Cl} = 0.25$

If pairs of atoms are taken at random to form Cl_2 molecules,

$$X_{35,35} = X_1^2 = (0.75)^2$$ $$X_{37,37} = X_2^2 = (0.25)^2$$

$$X_{35,37} = X_1 \cdot X_2 + X_2 \cdot X_1 = 2 X_1 X_2 = 2(0.75)(0.25)$$

that is, the fractions of the isotopomers of Cl_2 molecules are the same as the probability of choosing that combination of atoms.

(b) The entropy of mixing is given by

$$S_{mixing} = -k \sum_i N_i \ln X_i = -kN \sum_i X_i \ln X_i$$

for the 3 types of molecules where i corresponds to $35Cl \, 35Cl$, $37Cl \, 37Cl$ and $35Cl \, 37Cl$ in turn.

$$S_{mixing} = -R \left[X_1^2 \ln X_1^2 + X_2^2 \ln X_2^2 + 2 X_1 X_2 \ln (2 X_1 X_2) \right]$$

$$= -R \left[0.5625 \ln 0.5625 + 0.375 \ln 0.375 + 0.0625 \ln 0.0625 \right]$$

$$= 1.718 \text{ cal mol}^{-1} \text{ K}^{-1}$$

(c) The entropy of mixing of 2 moles of Cl atoms ~~(if molecules exist)~~ is given by (if no diatomic molecules exist):

$$S_{mixing} = -2R \left[X_1 \ln X_1 + X_2 \ln X_2 \right]$$

$$= -2R \left[0.75 \ln 0.75 + 0.25 \ln 0.25 \right]$$

$$= 2.235 \text{ cal mol}^{-1} \text{ K}^{-1}$$

This is different from $1.718 \text{ cal mol}^{-1} \text{ K}^{-1}$ as should be.

④ S_{mixing} (2 moles atoms)

$$= 2 \{ -R[X_1 \ln X_1 + X_2 \ln X_2] \}$$

S_{mixing} (1 mole of molecules)

$$= -R[X_1^2 \ln X_1^2 + X_2^2 \ln X_2^2 + 2X_1 X_2 \ln 2X_1 X_2]$$

The difference between them is:

S_{mixing} (1 mole of molecules) $- S_{mixing}$ (2 moles atoms)

$$= -2R[X_1^2 \ln X_1 + X_2^2 \ln X_2 + \boxed{X_1 X_2 \ln 2 X_1 X_2}]$$
$$+ 2R[X_1 \ln X_1 + X_2 \ln X_2]$$

$$X_1(1-X_1)\ln X_1 + X_2(1-X_2)\ln X_2$$
$$+ X_1 X_2 \ln 2$$

$$= -2R X_1 X_2 \ln 2 \quad Q.E.D.$$

why $\ln 2$?

This difference arises from the difference in symmetry numbers (1) for $^{35}Cl\,^{37}Cl$ and (2) for $^{35}Cl_2$ and $^{37}Cl_2$, which in turn arises from the nuclear spin portion of the partition function. Both ^{35}Cl and ^{37}Cl have spin $3/2$ so these nuclei are fermions. The total wavefunction must be antisymmetric with respect to interchange of any two fermions. For the ground electronic state of Cl_2 ($^1\Sigma_g^+$), this means that the 6 para nuclear spin states go with $J = 0, 2, 4...$ the 10 ortho nuclear spin states go with $J = 1, 3, 5,..$ In the high temperature limit this means that for both $^{35}Cl_2$ and $^{37}Cl_2$ each rotational state has about half ($\frac{6}{16}$ and $\frac{10}{16}$ alternating) of the population that is available to the rotational states of $^{35}Cl\,^{37}Cl$ where no restriction occurs.

Note that the S_{mixing} (1 mole of molecules) $\neq 0$ where the natural abundance of ^{35}Cl and ^{37}Cl occur, means that at $0K$, the absolute entropy of Cl_2 is not zero but is equal to S_{mixing}, which is temperature independent and is that part of S that remains the same under P, V, T transformations of Cl_2.