# ASSIGNMENT 5 SOLUTIONS

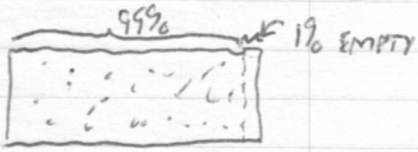
1 a) IMAGINE BOX CONSISTS OF 2 EQUAL SIZE COMPARTMENTS!

$N = 100$ MOLECULES

THE PROBABILITY FOR EACH MOLECULE TO BE ON THE LEFT IS $\frac{1}{2}$
THERE IS ONLY $\binom{100}{0} = 1$ WAY FOR ALL $N$ TO BE ON THE LEFT
WITH PROBABILITY $P = \binom{100}{0}\left(\frac{1}{2}\right)^{100}$

SO $P = 2^{-100} = e^{-100\ln 2} \simeq \boxed{7.9 \times 10^{-31}}$

b)




$N = 100$

THE PROBABILITY OF 1 MOLECULE ON THE LEFT IS $0{,}99$
THE PROBABILITY FOR $N$ MOLECULES ON LEFT IS $(0{,}99)^{100} \simeq \boxed{0.37}$

c) FOR $N = 10000$, $P = (0{,}99)^{10000} \simeq \boxed{2.3 \times 10^{-44}}$

2) a) $\Omega \sim \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \underset{U=q\varepsilon}{=} \left(\frac{U/\varepsilon + N}{U/\varepsilon}\right)^{U/\varepsilon}\left(\frac{U/\varepsilon+N}{N}\right)^N$

$\Rightarrow S = k \ln\Omega = k\left\{\frac{U}{\varepsilon}\left[\ln\left(\frac{U}{\varepsilon}+N\right) - \ln\left(\frac{U}{\varepsilon}\right)\right] + N\left[\ln\left(\frac{U}{\varepsilon}+N\right) - \ln N\right]\right\}$

$\Rightarrow T^{-1} = \left(\frac{\partial S}{\partial U}\right)_N$

$= k\left\{\frac{1}{\varepsilon}\left[\ln\left(\frac{U}{\varepsilon}+N\right) - \ln\left(\frac{U}{\varepsilon}\right)\right] + \frac{U}{\varepsilon}\left[\frac{1/\varepsilon}{U/\varepsilon+N} - \frac{1/\varepsilon}{U/\varepsilon}\right] + N\left[\frac{1/\varepsilon}{U/\varepsilon+N}\right]\right\}$

$= \frac{k}{\varepsilon}\left\{\ln\left(1+N\frac{\varepsilon}{U}\right) + \left[\frac{U/\varepsilon}{U/\varepsilon+N} - 1\right] + \left[\frac{N}{U/\varepsilon+N}\right]\right\}$

$= \frac{k}{\varepsilon}\ln\left(1+N\frac{\varepsilon}{U}\right)$

So $\boxed{T = \frac{\varepsilon}{k}\left[\ln\left(1+N\frac{\varepsilon}{U}\right)\right]^{-1}}$

b) REARRANGE RESULT IN a) TO FIND $U$ AS A FUNCTION OF $T$

$\Rightarrow \quad 1 + N\frac{\varepsilon}{U} = \exp\left(\frac{\varepsilon}{kT}\right)$

$\Rightarrow \quad U = N\varepsilon\left[\exp\left(\frac{\varepsilon}{kT}\right) - 1\right]^{-1}$

So $C = \left(\frac{\partial U}{\partial T}\right)_N$

$= -N\varepsilon\left[\exp\left(\frac{\varepsilon}{kT}\right)-1\right]^{-2}\left(-\frac{\varepsilon}{kT^2}\right)\exp\left(\frac{\varepsilon}{kT}\right)$

$\Rightarrow \boxed{C = N\frac{\varepsilon^2}{kT^2}\exp\left(\frac{\varepsilon}{kT}\right)\Big/\left[\exp\left(\frac{\varepsilon}{kT}\right)-1\right]^2}$

[OPTIONALLY COULD SIMPLIFY FURTHER BY NOTING

$$\frac{e^x}{(e^x-1)^2} = \frac{1}{(e^{x/2}-e^{-x/2})^2} = \frac{1}{4\sinh^2(x/2)}$$

$\Rightarrow C = N\frac{\varepsilon^2}{kT^2}\frac{1}{4}\left(\sinh\left(\frac{\varepsilon}{2kT}\right)\right)^{-2}$ ]

3) $S = kN\left\{ \ln\left[\frac{V}{N}\frac{1}{\Lambda^3}\right] + 5/2 \right\}$ WITH $\Lambda \equiv \left(\frac{3Nh^2}{4\pi mE}\right)^{1/2}$

GIVEN $n=1$ MOLE OF AR GAS AT $T = 293\,K$ AND $P = 1\,BAR = 10^5\,Pa$

SO $N = N_A = 6.02 \times 10^{23}$

$V = NkT/P \;\; (= nRT/P) = (1)(8.315)(293)/10^5 \simeq 0.0244\, m^3$

↙ 3 DEGREES OF FREEDOM FOR ATOM

$E = U = \frac{3}{2} NkT \;\; \left(= \frac{3}{2}(nRT)\right) = \frac{3}{2}(1)(8.315)(293) \simeq 3.65 \times 10^3\, J$

↙ MEAN ATOMIC MASS OF ARGON

$m = 39.9 \times 1.67 \times 10^{-27} \simeq 6.68 \times 10^{-26}\, kg$

WE NOW HAVE ALL THE QUANTITIES WE NEED TO EVALUATE $S$:

$kN \;\; (= nR) = 8.315\, J/K$

$V/N \simeq (0.0244\, m^3)/(6.02 \times 10^{23}) \simeq 4.05 \times 10^{-26}\, m^3$

$\Lambda^2 = \frac{3Nh^2}{4\pi mE} \overset{E=U=\frac{3}{2}NkT}{=} \frac{1}{2\pi}\frac{h^2}{mkT} \simeq \frac{1}{2\pi} \frac{(6.63\times 10^{-34}\, J\cdot s)^2}{(6.68 \times 10^{-26}\, kg)(1.38 \times 10^{-23}\, J/K)(293)}$

$\Rightarrow \Lambda^2 \simeq 2.59 \times 10^{-22}\, m^2$

$\Rightarrow \Lambda^3 \simeq 4.17 \times 10^{-33}\, m^3$

SO (AT LAST!)

$S \simeq (8.315\, J/K)\left\{ \ln\left[(4.05 \times 10^{-26}\, m^3)/(4.17 \times 10^{-33}\, m^3)\right] + 5/2 \right\}$

$\simeq (8.315\, J/K)\{16.1 + 2.5\}$

$\Rightarrow \boxed{S \simeq 155\, J/K}$

4a) GENERALLY, THE NUMBER OF ATOMS, $n_i$, IN A STATE WITH ENERGY $E_i$ WHICH CAN BE MANIFEST $g_i$ DIFFERENT WAYS IS GIVEN BY

$$n_i = \mathcal{E} g_i e^{-E_i/kT}$$ , WHERE $\mathcal{E}$ IS A CONSTANT.

IN THIS PROBLEM WE HAVE 2 STATES:

$i=0$ ; $g_0 = 1$, $E_0 = -13.6\,eV$

$i=1$ ; $g_1 = 4$, $E_1 = -3.4\,eV$

PROBABILITY OF BEING IN STATE 1 IS

$$P = \frac{\mathcal{E} g_1 e^{-E_1/kT}}{\mathcal{E} g_0 e^{-E_0/kT} + \mathcal{E} g_1 e^{-E_1/kT}} = \frac{g_1 e^{-E_1/kT}}{g_0 e^{-E_0/kT} + g_1 e^{-E_1/kT}}$$

$$= \left[\frac{g_0}{g_1} e^{-(E_0 - E_1)/kT} + 1\right]^{-1}$$

FOR $T = 293K$, $kT = (1.38 \times 10^{-23}\,J/K)(293\,K) \simeq 4.04 \times 10^{-21}\,J$

$\simeq 2.53 \times 10^{-2}\,eV$

HENCE $-(E_0 - E_1)/kT = -(-10.2\,eV)/(0.0253\,eV) \simeq 404 \gg 1$

BECAUSE THE EXPONENT IS SO LARGE WE MAY APPROXIMATE $P$ BY

$$P \approx \left[\frac{g_0}{g_1} e^{-(E_0 - E_1)/kT}\right]^{-1} = \frac{g_1}{g_0} e^{(E_0 - E_1)/kT} \qquad (*)$$

$$\simeq \frac{4}{1} e^{-404} \simeq \boxed{4 \times 10^{-176}}$$ VIRTUALLY IMPOSSIBLE

b) WITH $T = 9500K$, $kT \simeq 0.82\,eV$

$\Rightarrow -(E_0 - E_1)/kT \simeq 12.5$

THIS IS STILL A LARGE EXPONENT. SO CAN USE $(*)$

$$P \simeq 4 e^{-12.5} \simeq \boxed{1.5 \times 10^{-5}}$$ IMPROBABLE, BUT NOT IMPOSSIBLE.