

Physical Chemistry Course
December 5, 2002

1. (a) Probability distribution:

Given: the probability that a system will occupy an energy state with energy E is proportional to $\exp[-E/RT]$

$$P(E_i) = C \exp[-E_i/RT]$$

The normalization constant is obtained by setting the sum of probabilities to 1:

$$C [\exp^{-E_1/RT} + \exp^{-E_2/RT} + \exp^{-E_3/RT} + \exp^{-E_4/RT}] = 1.$$

Solve for C

$$C = \frac{1}{\sum_i \exp[-E_i/RT]} \leftarrow \text{This is the MOLECULAR PARTITION FUNCTION}$$

At $T = 298 \text{ K}$

$$C = \left[e^0 + e^{-1000/8.314 \times 298} + e^{-2000/8.314 \times 298} + e^{-3000/8.314 \times 298} \right]^{-1}$$

$$= [1 + 0.6679 + 0.4461 + 0.2979]^{-1} = 0.4146$$

$$P(E_i) = 0.4146 \exp[-E_i/RT] \quad \text{NORMALIZED Probability distribution}$$

(b) Average energy is given by

$$\langle E \rangle = \sum_{i=1}^4 E_i P(E_i)$$

$$\approx 0.4146 \left[0 + 1000 \exp\left(\frac{-1000}{8.314 \times 298}\right) + 2000 \exp\left(\frac{-2000}{8.314 \times 298}\right) + 3000 \exp\left(\frac{-3000}{8.314 \times 298}\right) \right]$$

$$= 0.4146 \{ 0 + 1000(0.6679) + 2000(0.4461) + 3000(0.2979) \}$$

$$= 1017.3 \text{ J}$$

(c) Contributions to the average energy are

$$0 ; 0.4146(1000)(0.6679) = 276.9 \text{ J}; 0.4146(2000)(0.4461) = 369.91 \text{ J}; 0.4146(3000)(0.2979) = 370.52 \text{ J}$$

We see that the largest value is 370.52 J, contributed by the state 4 with $E_4 = 3000 \text{ J}$

(d) Since state 1 has the highest probability (0.4146), it will be the most heavily populated (the ground state).

(e) There are 4 ways for the energy of two systems to combine to a total of 3000 joules

system I	E_I	Prob.	system II	E_{II}	Prob.	Combined Probability
state 1	0	0.4146	state 4	3000	0.1235	(.4146)(.1235)
state 4	3000	0.1235	state 1	0	0.4146	(.1235)(.4146)
state 2	1000	0.2769	state 3	2000	0.1850	(.2769)(0.1850)
state 3	2000	0.1850	state 2	1000	0.2769	(.1850)(.2769)

Total = 0.2050

∴ Therefore there is a 20.5% chance that the total energy of the two systems will add to 3000 J.

(f) The average total energy the two systems in (e) will have at 298 K is:

$$\langle E_{TOT} \rangle = \sum_{k=1}^{16} (E_i + E_j) P(E_i, E_j)$$

$k=1$ to 16 combinations
 \uparrow
 total energy for k^{th} combination
 combined probability for k^{th} combination

4 possibilities for the first system
 x 4 possibilities for the second system

k	state I	state II	E_{TOT}	$P(E_I, E_{II})$
1	1	1	0	$0.4146 \times 0.4146 = 0.1719$
2	1	2	1000	$0.4146 \times 0.2769 = 0.1148$
3	1	3	2000	$0.4146 \times 0.1850 = 0.07670$
4	1	4	3000	$0.4146 \times 0.1235 = 0.05120$
5	2	1	1000	$0.2769 \times 0.4146 = 0.1148$
6	2	2	2000	$0.2769 \times 0.2769 = 0.07667$
7	2	3	3000	$0.2769 \times 0.1850 = 0.05123$
8	2	4	4000	$0.2769 \times 0.1235 = 0.03420$
9	3	1	2000	$0.1850 \times 0.4146 = 0.07670$
10	3	2	3000	$0.1850 \times 0.2769 = 0.05123$
11	3	3	4000	$0.1850 \times 0.1850 = 0.03422$
12	3	4	5000	$0.1850 \times 0.1235 = 0.02285$
13	4	1	3000	$0.1235 \times 0.4146 = 0.05120$
14	4	2	4000	$0.1235 \times 0.2769 = 0.03420$
15	4	3	5000	$0.1235 \times 0.1850 = 0.02285$
16	4	4	6000	$0.1235 \times 0.1235 = 0.01525$

$$\langle E_{TOT} \rangle = 2034.8 \text{ J which is exactly } 2 \times \langle E \rangle$$

$$(2) (a) P(E_i) = C \sum_{i=1}^M \exp[-E_i/RT]$$

The normalization constant is

$$C = \left[\sum_{i=1}^M \exp[-E_i/RT] \right]^{-1}$$

The average energy of one such system is

$$\begin{aligned} \langle E \rangle &= \sum_{i=1}^M E_i P(E_i) \\ &= \frac{\sum_{i=1}^M E_i \exp[-E_i/RT]}{\sum_{i=1}^M \exp[-E_i/RT]} \end{aligned}$$

(b) let there be N systems

let the systems be in the respective energy states $E_a, E_b, E_c, E_d, \dots, E_w$

so that

$$E_{TOT} = E_a + E_b + E_c + E_d + \dots + E_w$$

The combined probability of this situation is

$$P_{TOT} = P(E_a) \cdot P(E_b) \cdot P(E_c) \cdot P(E_d) \cdot \dots \cdot P(E_w)$$

$$\langle E_{TOT} \rangle = \sum_{\text{situations}} P_{TOT} \cdot E_{TOT} = \sum_{a=1}^{M \text{ states}} \sum_{b=1}^M \sum_{c=1}^M \dots \sum_{w=1}^M$$

$$\begin{aligned} & [E_a + E_b + E_c + E_d + \dots + E_w] P(E_a) P(E_b) \dots \\ &= \left[\sum_{a=1}^M E_a \cdot P(E_a) \right] \times \left[\sum_{b=1}^M P(E_b) \right] \times \left[\sum_{c=1}^M P(E_c) \right] \times \dots \times \left[\sum_{w=1}^M P(E_w) \right] \\ &+ \left[\sum_{a=1}^M P(E_a) \right] \times \left[\sum_{b=1}^M E_b \cdot P(E_b) \right] \times \left[\sum_{c=1}^M P(E_c) \right] \times \dots \times \left[\sum_{w=1}^M P(E_w) \right] \end{aligned}$$

$$\begin{aligned}
& + \left[\sum_{a=1}^M P(E_a) \right] \left[\sum_{b=1}^M P(E_b) \right] \left[\sum_{c=1}^M E_c \cdot P(E_c) \right] \times \dots \times \left[\sum_{w=1}^M P(E_w) \right] \\
& + \dots \\
& + \left[\sum_{a=1}^M P(E_a) \right] \times \left[\sum_{b=1}^M P(E_b) \right] \times \left[\sum_{c=1}^M P(E_c) \right] \times \dots \times \left[\sum_{w=1}^M E_w \cdot P(E_w) \right]
\end{aligned}$$

but we know $\sum_{a=1}^M P(E_a) = 1$ for all, a or b or c, ... or w

Probability normalized to 1

Therefore, all of the factors in each of the N terms equal 1 except for the one containing E_i

$$\begin{aligned}
\langle E \rangle_{TOT} &= \left[\sum_{a=1}^M E_a \cdot P(E_a) \right] \cdot 1 \cdot 1 \cdot 1 \cdot 1 \cdot \dots \\
&+ 1 \cdot \left[\sum_{b=1}^M E_b \cdot P(E_b) \right] \cdot 1 \cdot 1 \cdot 1 \cdot 1 \cdot \dots \\
&+ 1 \cdot 1 \cdot \left[\sum_{c=1}^M E_c \cdot P(E_c) \right] \cdot 1 \cdot 1 \cdot 1 \cdot 1 \cdot \dots \\
&+ \dots \dots \dots + 1 \cdot 1 \cdot 1 \cdot 1 \cdot \dots \cdot 1 \cdot \left[\sum_{w=1}^M E_w \cdot P(E_w) \right]
\end{aligned}$$

But $\sum_{a=1}^M E_a \cdot P(E_a) = \langle E \rangle_1 = \sum_{b=1}^M E_b \cdot P(E_b) = \dots$

average for one energy system

$$\langle E \rangle_{TOT} = N \langle E \rangle_1$$

(3) Given At the classical turning points $x = x_t$, all of the energy is in the form of potential energy

$$E = E_{\text{vib}} = \overbrace{\left(v + \frac{1}{2} \right) h \nu_e}^{\text{all of the energy}} = \overbrace{\frac{k x_t^2}{2}}^{\text{potential energy}}$$

For the ground state $v=0$

$$\left(0 + \frac{1}{2} \right) h \nu_e = \frac{k}{2} x_t^2$$

Substitute given expression
 $\nu_e = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$

$$x_t = \pm \left(\frac{h \nu_e}{k} \right)^{1/2} = \pm \frac{h^{1/2} \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{k}{\mu} \right)^{1/4}}{k^{1/2}}$$

$$x_t = \pm \frac{1}{\sqrt{\alpha}}$$

Forbidden regions:

Probability that the quantum oscillation will lie in the range $x \leq -\frac{1}{\sqrt{\alpha}}$ to $-\infty$ is

$$\int_{x=-\infty}^{x=-\frac{1}{\sqrt{\alpha}}} \Psi_0^*(x) \Psi_0(x) dx$$

Probability that it will lie in the range

$x \geq +\frac{1}{\sqrt{\alpha}}$ to $+\infty$ is

$$\int_{x=+\frac{1}{\sqrt{\alpha}}}^{x=+\infty} \Psi_0^*(x) \Psi_0(x) dx$$

Probability that H_2 will be found in the classical region is the sum of these two integrals which are equal because $\Psi_0(x)$ is only a function of x^2 .

Answer:

$$\begin{aligned} \text{Probability} &= 2 \int_{x=+\frac{1}{\sqrt{\alpha}}}^{\infty} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \exp^{-\frac{\alpha x^2}{2}} \cdot \exp^{-\frac{\alpha x^2}{2}} dx \\ &= 2 \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{x=+\frac{1}{\sqrt{\alpha}}}^{\infty} \exp^{-\alpha x^2} dx \end{aligned}$$

Let $y = \sqrt{\alpha} x$ $dy = \sqrt{\alpha} dx$

$$\begin{aligned} \text{Probability} &= 2 \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{1}{\sqrt{\alpha}} \int_{y=1}^{\infty} \exp^{-y^2} dy \\ &= \frac{2}{\sqrt{\pi}} \int_1^{\infty} \exp^{-y^2} dy \end{aligned}$$