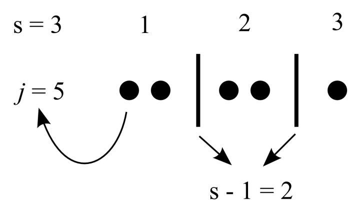
Dynamics and Kinetics. Exercises 10: Solutions

Problem 1

$$O_3 \longrightarrow O_2 + O$$

Recall: O_3 is non-linear $\Longrightarrow$ # of normal modes: s = $3N-6 = 3$
Total quanta: $j = 40$
Probability P to find $m = 10, 20, 30$ quanta in a particular mode?

We can approach this question as a problem of placing j balls (quanta) in s boxes (modes) in such a way that at least m balls are in the same box.



The first trick, illustrated in the figure, is to consider the $s-1$ partitions ("dividing sticks") as additional elements to be arranged, i.e., balls and partitions must both be arranged to define a single overall configuration. Thus, the number of ways w to distribute j quanta in s modes can be translated to the problem of choosing j elements (i.e., the balls) out of $j+s-1$ elements:

$$w = w_{\text{balls}} = \binom{j+s-1}{j} = \frac{(j+s-1)!}{j!(s-1)!} \tag{1}$$

or choosing s $-$ 1 elements (i.e., the partitions):

$$w = w_{\text{partitions}} = \binom{j+s-1}{s-1} = \frac{(j+s-1)!}{(s-1)!j!} = w_{\text{balls}}. \tag{2}$$

On the other hand, the number of ways w' to distribute j $-$m <u>remaining</u> quanta in s modes if <u>at least</u> m quanta are in a given mode is:

$$w' = \binom{j-m+s-1}{j-m} = \frac{(j-m+s-1)!}{(j-m)!(s-1)!}. \tag{3}$$

Finally, we need to know the fraction of times that situation (3) happens among (1) total possibilities:

$$P_{\text{exact}} = \frac{w'}{w} = \frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!} \tag{4}$$

which can be approximated to:

$$P_{\text{approx}} \approx \left(\frac{j-m}{j}\right)^{s-1} \tag{5}$$

If we use the Sterling approximation: $n! \approx \left(\frac{n}{e}\right)^n$, and the fact that $j - m \gg s - 1$

Plugging in the numbers in Eqs. (4) and (5) gives:

	$m = 10$	$m = 20$	$m = 30$
P_{exact}	0.576	0.268	0.0767
P_{approx}	0.563	0.250	0.0625

Problem 2

Background:

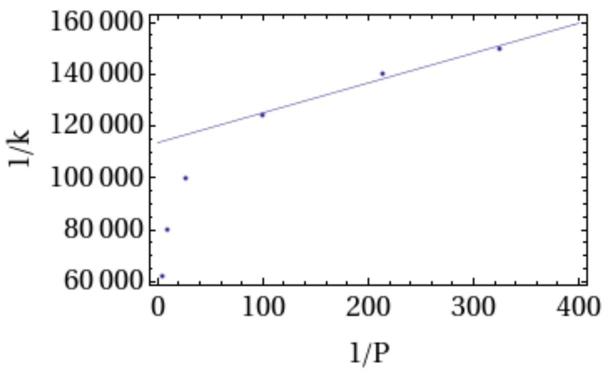
We start with the following equation:

$$k^1 = \frac{k^1_\infty}{1 + \frac{k_2}{k_{-1}[A]}} \tag{6}$$

Inverting Eq. (6) and considering the ideal gas law, i.e., $\frac{n}{V} = \frac{P}{RT}$, we obtain:

$$\frac{1}{k^1} = \frac{1}{k^1_\infty} + \frac{1}{k_1^{\text{conc}}[A]} = \frac{1}{k^1_\infty} + \frac{RT}{k_1^{\text{conc}} P_A} \tag{7}$$

a) According to Eq. (7), if we can plot $\frac{1}{k1}$ vs. $\frac{1}{P}$ we should obtain a straight line:



We observe linear behavior at low pressures, but deviation from theory at high pressures.

b) The energization step:

$$A + A \xrightarrow{k_1} A + A^*$$

Using the data for the three lower pressures that do not deviate from the linear regression we obtain a slope = 115.15 Torr · s.

The rate constants k_1 expressed from pressure and concentration are related due to the ideal gas law:

$$k_1^{\text{press}} = \frac{k_1^{\text{conc}}}{RT} = \frac{1}{\text{slope}} = 8.7 \times 10^{-3} \text{Torr}^{-1}\text{s}^{-1}$$

From collision theory:

$$k_1^{\rm coll} = \frac{1}{2} N_{\rm Av} \langle u \rangle \sigma e^{-\frac{\rm E^0}{RT}}$$

Computing the different "ingredients":

- $\langle u \rangle = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = \left(\frac{8RT}{\pi\frac{M}{2}}\right)^{1/2} = 749\mathrm{m}\cdot\mathrm{s}^{-1}$
- $\sigma = \pi d^2 = 7.85\times10^{-19}\mathrm{m}^2$
- $\frac{\rm E^0}{RT} = 42.5$

$$k_1^{\rm coll} = 5.9\times10^{-11}\mathrm{m^3s^{-1}mol^{-1}} \overset{\times\frac{1}{RT}}{=} 9.6\times10^{-15}\mathrm{Pa^{-1}s^{-1}} \overset{133.33\mathrm{Pa}=1\mathrm{Torr}}{=} 1.28\times10^{-12}\mathrm{Torr^{-1}s^{-1}}$$

which is much smaller than the constant found experimentally!

c) Rate constant for the Hinshelwood theory (k_1^H):

$$k_1^H = k_1^{\rm coll}\cdot r \quad \Rightarrow \quad r = \frac{1}{(s-1)!}\left(\frac{\rm E^0}{RT}\right)^{s-1}$$

For but-2-ene:

$N = 12;\text{non-linear} \Rightarrow \quad s = 3N-6 = 30 \Rightarrow \quad r = 1.95\times10^{16} \Rightarrow \quad k_1^H = 4.98\times10^4\mathrm{Torr^{-1}s^{-1}}$

which is too large!