Dynamics and Kinetics. Solutions to training problems

Problem 1

a) True.

b) True.

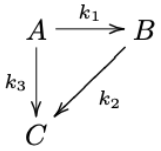
c) False. This is only true for an elementary step.

d) False. This is only true for an elementary step.

e) True. The rate constant has units of $(time)^{-1}(concentration)^{-(n-1)}$ where n is the order of the reaction.

Problem 2

(a)



$$\frac{da}{dt} = -(k_1 + k_3)a$$

$$\frac{db}{dt} = +k_1 a - k_2 b$$

$$\frac{dc}{dt} = +k_3 a + k_2 b$$

(b) Sequential method:

(1) $[A]$: $a(t) = a_0\, e^{-(k1 + k3)t}$ (1st order)

(2) $[B : \frac{db}{dt} + k_2 b = k_1 a$

1) Homogeneous eq.

$$\frac{db}{dt} + k_2 b = 0$$

Solution :

$$b(t) = \tilde{b} e^{-k_2 t}$$

2) Variation of constants:

$$\tilde{b} \equiv \tilde{b}(t)$$

$$\frac{db}{dt} + k_2 b = (\frac{d\tilde{b}}{dt} - k_2\tilde{b} + k_2\tilde{b})e^{-k_2 t} = k_1 a_0 e^{-(k_1+k_3)t}$$

$$\frac{d\tilde{b}}{dt} = k_1 a_0 e^{-(k_1+k_3-k_2)t}$$

$$\tilde{b}(t) = \tilde{\tilde{b}} - \frac{a_0 k_1}{k_1 + k_3 - k_2} e^{-(k_1+k_3-k_2)t}$$

At $t = 0, b = 0 \Rightarrow \tilde{b} = 0$:

$$\tilde{b}(t) = \frac{a_0 k_1}{k_1 + k_3 - k_2}(1 - e^{-(k_1+k_3-k_2)t})$$

$$b(t) = \frac{a_0 k_1}{k_1 + k_3 - k_2}(e^{-k_2 t} - e^{-(k_1+k_3)t})$$

3) Since $b_0 = c_0 = 0$, conservation of mass gives
$c(t) = a_0 + b_0 + c_0 - a(t) - b(t) = a_0 - a(t) - b(t)$
After simplification,

$$c(t) = a_0 \left\{ 1 - \frac{1}{k_1 + k_3 - k_2} \left[k_1 e^{-k_2 t} + (k_3 - k_2)\, e^{-(k_1+k_3)t} \right] \right\}.$$

Problem 3

Consider the reaction

$$A + B \rightleftharpoons E + F,$$

which occurs in two steps. At equilibrium, the processes are occurring at equal rates in the forward and reverse directions:

(1) $A + B \rightleftharpoons C + D$
(2) $C + D \rightleftharpoons E + F$

Thus, at equilibrium:

$$k_1[A][B] = k_{-1}[C][D],$$

$$k_2[C][D] = k_{-2}[E][F].$$

The equilibrium constant for each reaction is thus:

$$K_1 := \left(\frac{[C][D]}{[A][B]}\right)_{\text{eq}} = \frac{k_1}{k_{-1}}$$

$$K_2 := \left(\frac{[E][F]}{[C][D]}\right)_{\text{eq}} = \frac{k_2}{k_{-2}}$$

The equilibrium constant for the overall reaction is

$$K := \left(\frac{[E][F]}{[A][B]}\right)_{\text{eq}} = K_1 K_2 = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

Example:

$$\mathrm{H_2 + 2ICl \rightleftharpoons I_2 + 2HCl},$$

which occurs in two steps. At equilibrium the following processes are occurring at equal rates in the forward and reverse directions:

(1) $\mathrm{H_2 + ICl \rightleftharpoons HI + HCl}$,

(2) $\mathrm{HI + ICl \rightleftharpoons HCl + I_2}$.

Thus, at equilibrium:

$$k_1[\mathrm{H_2}][\mathrm{ICl}] = k_{-1}[\mathrm{HI}][\mathrm{HCl}],$$

$$k_2[\mathrm{HI}][\mathrm{ICl}] = k_{-2}[\mathrm{HCl}][\mathrm{I_2}].$$

The equilibrium constant for each reaction is thus:

$$K_1 = \left(\frac{[\mathrm{HI}][\mathrm{HCl}]}{[\mathrm{H_2}][\mathrm{ICl}]}\right)_{\text{eq}} = \frac{k_1}{k_{-1}},$$

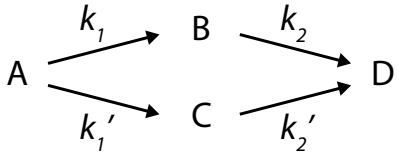
$$K_2 = \left(\frac{[\mathrm{HCl}][\mathrm{I_2}]}{[\mathrm{HI}][\mathrm{ICl}]}\right)_{\text{eq}} = \frac{k_2}{k_{-2}}.$$

The overall equilibrium constant is

$$K := \left(\frac{[\mathrm{HCl}]^2[\mathrm{I_2}]}{[\mathrm{H_2}][\mathrm{ICl}]^2}\right)_{\text{eq}} = K_1 K_2 = \frac{k_1 k_2}{k_{-1} k_{-2}}.$$

Problem 4

Given is the following reaction sequence.



a) Derive the time-dependent concentrations of A, B, and C, assuming that all initial concentrations are zero apart from that of A.

For species A,

$$\frac{d[\mathrm{A}]}{dt} = -(k_1 + k_1')[\mathrm{A}]$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_1')t}$$

For species B,

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

We substitute [A] to obtain

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-(k_1+k_1')t} - k_2[\mathrm{B}]$$

The solution of the homogeneous differential equation is

$$[\mathrm{B}]_h = b_0 e^{-k_2 t}$$

and the general solution of the inhomogeneous differential equation therefore

$$[\mathrm{B}] = c(t) e^{-k_2 t}$$

Substitution into the differential equation yields

$$\dot{c}(t) e^{-k_2 t} = k_1[\mathrm{A}]_0 e^{-(k_1+k_1')t}$$

$$\dot{c}(t) = k_1[\mathrm{A}]_0 e^{-(k_1+k_1'-k_2)t}$$

and upon integration

$$c(t) = c_0 + \frac{k_1[\mathrm{A}]_0}{k_2 - (k_1 + k_1')} e^{-(k_1+k_1'-k_2)t}$$

so that

$$[\mathrm{B}] = c_0 e^{-k_2 t} + \frac{k_1[\mathrm{A}]_0}{k_2 - (k_1 + k_1')} e^{-(k_1+k_1')t}$$

With $[\mathrm{B}]_0 = 0$, we find

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_2 - (k_1 + k_1')} \left(e^{-(k_1+k_1')t} - e^{-k_2 t} \right)$$

By analogy,

$$[\mathrm{C}] = \frac{k_1'[\mathrm{A}]_0}{k_2' - (k_1 + k_1')} \left(e^{-(k_1+k_1')t} - e^{-k_2' t} \right)$$

b) Explain how one can simply calculate the time-dependent concentration of D from the results obtained above. Just describe the approach without actually calculating it.

$$[\mathrm{D}] = [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] - [\mathrm{C}]$$

X Problem 5

Steps to find $[A]_t$ and $[B]_t$:

1. Rate equations (for simplicity $[A] = a$ and $[B] = b$):
$$\begin{array}{ll} \frac{da}{dt} = -k_1 a + k_{-1} b & x_1 \equiv a \\ \frac{db}{dt} = k_1 a - k_{-1} b & x_2 \equiv b \end{array} \quad \Rightarrow \quad X = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

2. Put in matrix form:
$$\frac{d}{dt} X = M \cdot X \qquad \text{where} \qquad M = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -k_{-1} \end{pmatrix}$$

3. Find eigenvalues:
$$0 = \det(M - \lambda \mathrm{Id}) = (k_1 + \lambda)(k_{-1} + \lambda) - k_1 k_{-1} = \lambda^2 + (k_1 + k_{-1})\lambda$$
$$\lambda_1 = 0; \qquad \lambda_2 = -(k_1 + k_{-1})$$

4. Find eigenvectors $\mathbf{v_1}$ and $\mathbf{v_2}$ for λ_1 and λ_2 respectively:

For $\lambda_1 = 0$: $\quad (M - \lambda \mathrm{Id}) \cdot \mathbf{v_1} = (M - \lambda \mathrm{Id}) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$

$$\text{choose } v_2 = 1: \quad -k_1 v_1 + k_{-1} = 0 \quad \Rightarrow \quad v_1 = \frac{k_{-1}}{k_1} \quad \Rightarrow \quad \mathbf{v_1} = \begin{pmatrix} \frac{k_{-1}}{k_1} \\ 1 \end{pmatrix}$$

For $\lambda_2 = -(k_1 + k_{-1})$:

$$(M - \lambda \mathrm{Id}) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} k_{-1} & k_{-1} \\ k_1 & k_1 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0 \quad \Rightarrow \quad \mathbf{v_2} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

5. General solution:

$$X(t) = c_1 \mathbf{v_1} e^{\lambda_1 t} + c_2 \mathbf{v_2} e^{\lambda_2 t} = c_1 \begin{pmatrix} \frac{k_{-1}}{k_1} \\ 1 \end{pmatrix} + c_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_1 + k_{-1})t}$$

6. Considering initial conditions:

$$\text{For } t = 0 \quad \Rightarrow \quad X(0) = \begin{pmatrix} a_0 \\ 0 \end{pmatrix}$$

$$\begin{array}{c} c_1 \left(\frac{k_{-1}}{k_1} \right) + c_2 = a_0 \\ c_1 + (-c_2) = 0 \end{array} \qquad \Longrightarrow \qquad c_1 = c_2 = \frac{a_0 k_1}{k_1 + k_{-1}}$$

7. Final result:

$$a(t) = \frac{a_0 \left(k_{-1} + k_1 e^{-(k_1 + k_{-1})t} \right)}{k_1 + k_{-1}}$$
$$b(t) = \frac{a_0 k_1 \left(1 - e^{-(k_1 + k_{-1})t} \right)}{k_1 + k_{-1}}$$

8. Check at $t \to \infty$:

$$a_{\mathrm{eq}} = a(t = \infty) = \frac{a_0 k_{-1}}{k_1 + k_{-1}}$$
$$b_{\mathrm{eq}} = b(t = \infty) = \frac{a_0 k_1}{k_1 + k_{-1}}$$

X Problem 6

Describe an algorithm (no need to write proper code) to simulate the reaction 2A → products with the stochastic method.

We know that reactions between two A molecules out of a total of n occur at the rate

$$R = -kn^2$$

In fact, we have made a small mistake here when we did not consider that a molecule cannot react with itself. Therefore, more accurately,

$$R = -kn(n-1)$$

The probability for a reaction to occur in a short time interval $\Delta\tau$ is therefore

$$kn(n-1)\Delta\tau$$

and the probability for no reaction is

$$1 - kn(n-1)\Delta\tau$$

We calculate the probability $P_n(\tau + \Delta\tau)$ that at time $\tau + \Delta\tau$, all n molecules have not reacted. This is the product of the probability $P_n(\tau)$ that at time τ, none had reacted and the probability that no reaction occurs in the time interval $\Delta\tau$.

$$P_n(\tau + \Delta\tau) = P_n(\tau)(1 - kn(n-1)\Delta\tau)$$

We thus obtain a differential equation for P_n

$$\frac{dP_n}{d\tau} = -kn(n-1)P_n$$

which upon integration gives an expression for the probability that for n molecules of A, none have reacted after a given time τ

$$P_n = e^{-kn(n-1)\tau}$$

We initially set the number of molecules to $n = n_0$ and the time to $t = 0$. We then have the computer calculate a random number r in the interval between 0 and 1 and set

$$r = P_n = e^{-kn(n-1)\tau}$$

so that

$$\tau = -\frac{\ln(r)}{kn(n-1)}$$

This way, we randomly determine the time interval τ at which the next reaction occurs. We increment the time by this value τ and reduce the number of molecules n by two. Then we repeat.

The following matlab code will do the trick.

```
% stochastic method for solving second order rate equation

for l = 1:6
    set(figure(l) ,'WindowStyle','docked'); clf;
end
clc; clearvars;

n0 = 1e3; % number of molecules at t0
k = 1; % bimolecular rate constant

t = 0; % vector of time steps
```

```
n = n0; % vector of corresponding number of molecules n
while n > 0 % repeat until all molecules have reacted
   % calculate next time step dt from random number 'rand'
   dt = -log(rand)/k/(n(end)*(n(end)-1));
   t = [t; t(end) + dt]; % add new time step to vector t
   n = [n; n(end) - 2]; % add new number of molecules to vector n
end

figure(1); hold on
plot(t, n); % plot result of simulation
xlabel('time'); ylabel('number of molecules')

% for comparison, plot analytical solutions for second order rate equation (just for fun)
t = linspace(0, t(end), 1e4);
plot(t, n0./(1 + 2*n0*k*t))
plot(t, n0./(n0 + (1-n0)*exp(-2*k*t)))
```

Problem 7

Use Arrhenius formula

$$
\begin{aligned}
k_1 &= Ae^{-E_a/RT_1}, \qquad k_2 = Ae^{-E_a/RT_2} \\
\frac{k_1}{k_2} &= e^{-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \\
\ln\frac{k_1}{k_2} &= \frac{1}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)E_a \\
E_a &= \frac{R}{\frac{1}{T_2}-\frac{1}{T_1}}\ln\frac{k_1}{k_2} = \frac{8.314}{\frac{1}{277}-\frac{1}{298}}\ln 40\ \mathrm{J\cdot mol^{-1}} = 121\ \mathrm{kJ\cdot mol^{-1}}
\end{aligned}
$$

Problem 8

(a) Following solution of problem 1, we have that

$$
E_a = \frac{R}{\frac{1}{T_2}-\frac{1}{T_1}}\ln\frac{k_1}{k_2} = \frac{8.314}{\frac{1}{323.15}-\frac{1}{303.15}}\ln\left(\frac{2.8\times10^{-3}}{1.38\times10^{-2}}\right)\ \mathrm{J\cdot mol^{-1}} = 65\ \mathrm{kJ\cdot mol^{-1}}.
$$

(b) From the Arrhenius equation it straightforwardly follows that

$$
k_j = Ae^{-E_a/RT_j} \Rightarrow A = k_j e^{E_a/RT_j}, \qquad j = 1, 2.
$$

Let us compute A from k_1, T_1:

$$
A = 2.8\times10^{-3}\ \mathrm{M^{-1}s^{-1}}\exp\left(\frac{65000\ \mathrm{J\cdot mol^{-1}}}{8.314\ \mathrm{J\cdot K^{-1}mol^{-1}}303.15K}\right) = 4.44\times10^{8}\ \mathrm{M^{-1}s^{-1}}. \tag{1}
$$

As a check we can also compute A from k_2, T_2

$$
A = 1.38\times10^{-2}\ \mathrm{M^{-1}s^{-1}}\exp\left(\frac{65000\ \mathrm{J\cdot mol^{-1}}}{8.314\ \mathrm{J\cdot K^{-1}mol^{-1}}323.15K}\right) = 4.44\times10^{8}\ \mathrm{M^{-1}s^{-1}}, \tag{2}
$$

which of course has to agree.

Problem 9

Michaelis-Menten equation:

$$v = \frac{v_{max}}{1 + \frac{K_M}{[S]}}$$

Equation for the Lineweaver-Burk plot:

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \frac{1}{[S]}$$

From the original data:

1/[S] (M^{-1})	20	60	100	200	500
1/v (min/mm^3)	0.06	0.08	0.10	0.15	0.30

By eye:

$$\frac{1}{v_{max}} = 0.05 \text{ min} \cdot \text{mm}^{-3}$$
$$\frac{K_M}{v_{max}} = \frac{0.05}{100} \text{ min} \cdot \text{mm}^{-3} \cdot \text{M}$$

Therefore:

$$K_M = \frac{0.05/100}{0.05}\text{M} = 0.01\text{M}$$

More generally: Use linear regression, e.g. in Mathematica or Matlab.

Problem 10

The only "hard part" about this problem is: "What is the standard temperature?" Using the IUPAC standard, $T = 0^\circ\text{C} = 273.15\text{K}$, and

$$\text{N}_2 : v_{\text{rms}} = \sqrt{\frac{3RT}{M_{\text{N}_2}}} = \sqrt{\frac{3 \times 8.314 \times 273}{0.02802}}\ \text{ms}^{-1} = 493\text{ms}^{-1},$$
$$\text{H}_2 : v_{\text{rms}} = \sqrt{\frac{3RT}{M_{\text{H}_2}}} = \sqrt{\frac{3 \times 8.314 \times 273}{0.002016}}\ \text{ms}^{-1} = 1838\text{ms}^{-1}.$$

If we used the NIST standard instead, $T = 20^\circ\text{C} = 293.15\text{K}$, and

$$\text{N2} : v\text{rms} = 511\text{ms}^{-1},$$
$$\text{H2} : v\text{rms} = 1904\text{ms}^{-1}.$$

Problem 11

Recall from lecture:

$$\text{rate of escape} = Z_S \cdot S_0 = \frac{1}{4} c\langle v \rangle S_0 = \frac{p\langle v \rangle}{4 k_B T} S_0 = \frac{p}{\sqrt{2\pi m k_B T}} S_0$$

(a) Loss of mass per unit time: $\frac{\Delta \text{mass}}{\Delta t} = m Z_S \cdot S_0 = m \frac{p S_0}{\sqrt{2\pi m k_B T}}$

Pressure:

$$p = \sqrt{\frac{2\pi k_B T}{m}} \frac{\Delta \text{mass}}{\Delta t} \frac{1}{S_0} = \sqrt{\frac{2RT}{\pi M}} \frac{\Delta \text{mass}}{\Delta t} \frac{1}{r^2}$$

(b) $T = 1273\text{K}$

$$p = \sqrt{\frac{2 \times 8.314 \times 1,273}{3.14 \times 73 \times 10^{-3}}} \frac{\text{m}}{\text{s}} \frac{4.3 \times 10^{-8}\text{kg}}{7200\ \text{s}} \frac{1}{(5 \times 10^{-4}\text{m})^2} = 7.3 \times 10^{-3}\text{Pa}$$

Problem 13

The mechanism is:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A^*$$
$$A^* \xrightarrow{k_2} P$$

Recall from lecture:

$$k^1 := \frac{k_2 k_1 / k_{-1}}{1 + \frac{k_2}{k_{-1}[A]}} \tag{6}$$

$$k^1_\infty = \frac{k_2 k_1}{k_{-1}} \tag{7}$$

Substituting the expression (7) in (6):

$$k^1 = \frac{k^1_\infty}{1 + \frac{k_2}{k_{-1}[A]}} \tag{8}$$

Rearranging:

$$\frac{k^1_\infty}{k^1} = 1 + \frac{k_2}{k_{-1}[A]} \quad \Rightarrow \quad \frac{k_2}{k_{-1}} = \left(\frac{k^1_\infty}{k^1} - 1\right)[A]$$

and since $\frac{k^1}{k^1_\infty}$ 0.8 when $[A]$ = 10^{-4}M:

$$\frac{k_2}{k_{-1}} = \left(\frac{1}{0.8} - 1\right) 10^{-4}\text{M}$$
$$= 2.5 \times 10^{-5}\text{M}$$

Problem 14

$k^I = 2.5 \times 10^{-4}\ s^{-1}$ at 1.3 kPa
$k^I = 2.1 \times 10^{-5}\ s^{-1}$ at 12 Pa

Inverting Eq. (8) from problem 2 and considering $\frac{n}{V} = \frac{P}{RT}$

$$\frac{1}{k^1} = \frac{1}{k_\infty^1} + \frac{1}{k_1^{\text{conc}}[A]} = \frac{1}{k_\infty^1} + \frac{RT}{k_1^{\text{conc}} P_A} \tag{9}$$

For two different pressures:

$$\Delta\frac{1}{k^1} = \frac{1}{k_1^{\text{conc}}} RT \Delta\frac{1}{P_A} \quad \Rightarrow \quad k_1^{\text{conc}} = RT\frac{\Delta\frac{1}{P_A}}{\Delta\frac{1}{k^1}} = RTk_1^{\text{press}}$$

And we can compute k_1^{press} as:

$$k_1^{\text{press}} = \frac{\frac{1}{1300\text{Pa}} - \frac{1}{12\text{Pa}}}{\frac{1}{2.5\times10^{-4}\text{s}^{-1}} - \frac{1}{2.1\times10^{-5}\text{s}^{-1}}} = 1.9 \times 10^{-6}\ \text{Pa}^{-1}\text{s}^{-1}$$

Problem 15

The RRK rate constant is given by

$$k(E) = \nu\left(\frac{E - E_0}{E}\right)^{s-1}$$

where $\nu = \nu_{\text{vib}} = 5.19 \cdot 10^{12}$ Hz is the frequency of the critical mode, $E = h\nu_{\text{laser}} \cdot N_A = 44.7\ \text{kJ/mol}$ is the internal energy of the molecule, which we can equate to the photon energy, and $E_0 = 13.2\ \text{kJ/mol}$ is the dissociation energy of the molecule. Water dimer has $s = 3N - 6 = 12$ vibrational degrees of freedom.

We obtain

$$k(E) = 5.19 \cdot 10^{12} \cdot \left(\frac{44.7 - 13.2}{44.7}\right)^{11} = 1.10 \cdot 10^{11}$$

and a lifetime of

$$\tau = \frac{1}{k(E)} = 9.05\ \text{ps}$$

X Problem 16

The partition function of a spin in a magnetic field B is given by

$$q = e^{-\epsilon_0/k_\mathrm{B}T} + e^{-\epsilon_1/k_\mathrm{B}T} = \underbrace{e^{+\mu_\mathrm{B}B/k_\mathrm{B}T}}_{x_0} + \underbrace{e^{-\mu_\mathrm{B}B/k_\mathrm{B}T}}_{x_1}.$$

The populations of the two states (i.e., the probabilities to be in the two states) can be expressed in terms of x_0 and x_1 as

$$P_0 = \langle n_0 \rangle = \frac{x_0}{q} = \frac{x_0}{x_0 + x_1},$$
$$P_1 = \langle n_1 \rangle = \frac{x_1}{q} = \frac{x_1}{x_0 + x_1},$$

from which it follows, as it should, that $P_0 + P_1 = 1$.

(If one considered N spins, the total populations of the two states would be $\langle \mathrm{n}_0 \rangle = NP_0$ and $\langle n_1 \rangle = NP_1$).

The populations of the two states in a magnetic field of 1 T at temperatures 4 K and 298 K are summarized in the following table

	T = 4K	T = 298K
q	2.028	2.00001
P_0	0.583	0.501
P_1	0.417	0.499

X Problem 17

We know from the class that the translational partition function is given by

$$q_\mathrm{tr} = \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V.$$

In order to compute the isotope effect on it for molecules H_2 and D_2 we just evaluate the following ratio (conventionally, the quantity for H is in the numerator)

$$\mathrm{IE}_{q_\mathrm{tr}} = \frac{q_\mathrm{tr}(\mathrm{H_2})}{q_\mathrm{tr}(\mathrm{D_2})} = \left(\frac{m_{\mathrm{H_2}}}{m_{\mathrm{D_2}}}\right)^{3/2} \approx (1/2)^{3/2} \approx 0.354.$$

X Problem 18

(a) O_2 is a symmetric molecule so the symmetry number $s = 2$. In SI units, $B = 145\text{m}^{-1}$. The number of thermally accessible rotational states is

$$q_{\text{rot}} = \frac{1}{s}\frac{k_{\text{B}}T}{hcB} = \frac{k_{\text{B}}T}{2hcB} = \frac{1}{2}\frac{1.38 \times 10^{-23} \times 298\ \text{J}}{6.63 \times 10^{-34} \times 3 \times 10^{8} \times 145\ \text{J}} = 71.3.$$

(b) Recall that the vibrational partition function is

$$q_{tvib} = \frac{e^{-x/2}}{1 - e^{-x}},$$

where

$$x = \frac{h\nu}{k_{\text{B}}T} = \frac{h\tilde{\nu}c}{k_{\text{B}}T} = \frac{6.626 \times 10^{-34} \times 1.58 \times 10^{5} \times 3 \times 10^{8}\ \text{J}}{1.38 \times 10^{-23} \times 298\ \text{J}} \approx 7.64.$$

In our case $q_{\text{vib}} = 0.0219$. However, the number of thermally accessible vibrational states is obtained as a par $\tilde{q}_{\text{vib}}$ function in which the zero point energy is subtracted from each $\tilde{\varepsilon}_n := \varepsilon_n - \varepsilon_0$.

Hence the number of thermally accessible vibrational states is

$$\tilde{q}_{\text{vib}} = \frac{1}{1 - e^{-x}} = 1.0005.$$

X Problem 19

$q_{\text{tr,V}}$ for H_2 at 25°C:

$$q_{\text{tr,V}} = \left(\frac{2\pi m_{\text{H}_2} k_{\text{B}} T}{h^2}\right)^{3/2} = \left(\frac{2\pi \times 2 \times 1.67 \times 10^{-27} \times 1.38 \times 10^{-23} \times 298}{(6.63 \times 10^{-34})^2}\right)^{3/2} \text{m}^{-3} = 2.75 \times 10^{30}\text{m}^{-3}$$

q_{rot} for $H^{35}Cl$ at 25°C: $r_{\text{bond}} = 127.4$ pm

$$q_{\text{rot}} = \frac{1}{s}\frac{k_{\text{B}}T}{hcB} = \frac{1}{s}\frac{2Ik_{\text{B}}T}{\hbar^2}$$

symmetry number $s = 1$, moment of inertia $I = \mu r^2$, $\hbar = \frac{h}{2\pi}$

reduced mass:

$$\mu = \frac{M_{r,\text{H}} M_{r,\text{Cl}}}{M_{r,\text{H}} + M_{r,\text{Cl}}} m_u \approx \frac{1 \times 35}{1 + 35} m_u = \frac{35}{36} m_u$$

$$q_{\text{rot}} = \frac{8\pi^2 \mu r^2 k_{\text{B}} T}{h^2} = \frac{8\pi^2 \times \frac{35}{36} \times 1.66 \times 10^{-27} \times \left(1.274 \times 10^{-10}\right)^2 \times 1.38 \times 10^{-23} \times 298}{(6.63 \times 10^{-34})^2} = 19.3$$

q_{vib} of I_2 at 25°C:

$$q_{\text{vib}} = \frac{e^{-x/2}}{1 - e^{-x}}$$

$$x := \beta hc\tilde{\nu} = \frac{hc\tilde{\nu}}{k_{\text{B}}T} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8} \times 214.6 \times 10^{2}\text{J}}{1.38 \times 10^{-23} \times 298\text{J}} = 1.038$$

$$q_{\text{vib}} = \frac{e^{-x/2}}{1 - e^{-x}} = 0.922$$

Number of thermally accessible vibrational states (as in Problem 18):

$$\tilde{q}_{\text{vib}} = \frac{1}{1 - e^{-x}} = 1.55$$