

Worked Solutions to Problems

1. Water

A. Phase diagram

- a. The three phases of water coexist in equilibrium at a unique temperature and pressure (called the triple point):

$$T_{\text{tr}} = 273.16 \text{ K} = 0.01 \text{ }^{\circ}\text{C} \quad P_{\text{tr}} = 6.11 \times 10^{-3} \text{ bar}$$

- b. If pressure decreases, boiling point decreases, but melting point increases (slightly).
- c. Beyond this point, there is no distinction between liquid and vapour phases of water. Put alternatively, it is possible to have liquid to vapour transition by a continuous path going around the critical point. (In contrast, solid-liquid transition is discontinuous.)
- d. $T = 300\text{K}$, $P = 12.0 \text{ bar}$: liquid phase
 $T = 270\text{K}$, $P = 1.00 \text{ bar}$: solid phase
- e. Below $P = 6.11 \times 10^{-3} \text{ bar}$, ice heated isobarically will sublime to vapour.
- f. If x_l and x_v are the mole fractions of water in liquid and vapour phases,

$$V = x_l \bar{V}_l + x_v \bar{V}_v = x_l \bar{V}_l + (1 - x_l) \bar{V}_v$$

$$\therefore x_l = \frac{\bar{V}_v - V}{\bar{V}_v - \bar{V}_l} = 4.6 \times 10^{-1}$$

$$\frac{V_l}{V} = \frac{x_l \bar{V}_l}{V} = 0.140$$

$$\frac{V_v}{V} = 1 - 0.14 = 0.860$$

B. Clausius – Clapeyron equation

$$\text{a. } \frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

$\Delta\bar{H}$ = molar enthalpy change in phase transition

$\Delta\bar{V}$ = molar change in volume in phase transition.

For ice-liquid water transition :

$\Delta\bar{H} > 0$ $\Delta\bar{V} < 0$, since ice is less dense than water.

$$\therefore \frac{dP}{dT} < 0$$

Since $|\Delta\bar{V}|$ is not large, the P-T curve for this transition is steep, with a negative slope. Thus decrease of pressure increases the melting point slightly.

For liquid water - vapour transition

$\Delta\bar{H} > 0$ $\Delta < 0$

$$\therefore \frac{dP}{dT} > 0$$

Decrease of pressure decreases the boiling point.

b. Clausius - Clapeyron equation for (solid) liquid - vapour transition is

$$\frac{dP}{dT} = \frac{P \Delta\bar{H}_{\text{vap}}}{RT^2}$$

This equation follows from the Clapeyron equation under the assumptions:

1. Vapour follows ideal gas law.
2. Molar volume of the condensed phase is negligible compared to molar volume of vapour phase.
3. If further $\Delta\bar{H}_{\text{vap}}$ is assumed to be constant (no variation with T), the eq. is integrated to give

$$\ln \frac{P_2}{P_1} = \frac{\Delta\bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\begin{aligned} \text{Here } P_1 &= 1.01 \text{ bar}, & T_1 &= 373.15 \text{ K} \\ T_2 &= 393.15 \text{ K} & \Delta \bar{H}_{\text{vap}} &= 40.66 \text{ kJ mol}^{-1} \\ R &= 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \\ \therefore P_2 &= 2.01 \text{ bar} \end{aligned}$$

The estimate is based on assumptions 1, 2 and 3.

c. For ice - liquid water equilibrium, use Clapeyron equation

At $T_1 = 273.15 \text{ K}$, $P_1 = 1.01 \text{ bar}$

1. Assume that for a small change in T , $\frac{\Delta \bar{H}}{\Delta \bar{V}}$ is constant.

Integrating the Clapeyron equation above

$$P_2 - P_1 = \frac{\Delta \bar{H}}{\Delta \bar{V}} \ln \left(\frac{T_2}{T_1} \right)$$

$$T_2 = 272.95 \text{ K}, \quad \Delta \bar{H}_{(\text{fusion})} = 6008 \text{ J mol}^{-1}$$

$$\Delta \bar{V} = \left(\frac{1}{1.00} - \frac{1}{0.917} \right) \times 18.015 = -1.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$P_2 - P_1 = 28.39 \times 10^3 \text{ J m}^{-3} = 0.284 \text{ bar}$$

$$P_2 = 1.30 \text{ bar}$$

The estimate is based on assumption 1.

C. Irreversible condensation

a. On the P-T plane, this equilibrium state is a solid phase (ice). Water in liquid phase at this temperature and pressure is not an equilibrium state - it is a supercooled state that does not lie on the given P-T plane.

b. Treating the metastable state as equilibrium state, we can go from the supercooled liquid state to the solid state at the same temperature and pressure by a sequence of 3 reversible steps.

1. Supercooled liquid at -12.0°C to liquid at 0°C

$$q_1 = \text{number of moles} \times \bar{C}_p (\text{liquid water}) \times \text{change of temperature}$$

$$\frac{28.5\text{g}}{18.015\text{ g mol}^{-1}} \times 76.1\text{ J K}^{-1}\text{ mol}^{-1} \times 12.0\text{ K} = 1445\text{ J}$$

2. *liquid at 0°C to ice at 0°C*

$$q_2 = 28.5\text{ g} \times (-333.5)\text{ J g}^{-1} = -9505\text{ J}$$

3. *Ice at 0°C to ice at -12.0°C*

$$q_3 = \text{number of moles} \times \bar{C}_p (\text{liquid water}) \times \text{change of temp.}$$

$$= \frac{28.5}{18.015\text{ g mol}^{-1}} \times 37.15\text{ J K}^{-1}\text{ mol}^{-1} \times (-12.0\text{ K})$$

$$= -705.3\text{ J}$$

$$\therefore q = q_1 + q_2 + q_3 = -8765\text{ J}$$

Since all the steps are at the constant pressure of 1.00 bar,

$$q = \Delta H$$

But ΔH is independent of the path, i.e., it depends only on the end points.

Thus for the irreversible condensation of supercooled liquid to ice

$$q = \Delta H = -8765\text{ J}$$

- c. The actual irreversible path between the two end states of the system is replaced by the sequence of three reversible steps, as above. For each reversible step, ΔS can be calculated.

$$\Delta S_1 = n \int_{T_1}^{T_2} \frac{\bar{C}_p}{T} dT = n \bar{C}_p \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = \frac{28.5\text{ g}}{18.015\text{ g mol}^{-1}} \times 76.1\text{ J K}^{-1}\text{ mol}^{-1} \times \ln \frac{273.15}{261.15}$$

$$= 5.41\text{ J K}^{-1}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-9505}{273.15} = -34.79 \text{ JK}^{-1}$$

$$\Delta S_3 = \frac{28.5 \text{ g}}{18.015 \text{ g mol}^{-1}} 37.15 \text{ J K}^{-1} \text{ mol}^{-1} \ln \frac{261.15}{273.15}$$

$$= -2.64 \text{ J K}^{-1}$$

$$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -32.02 \text{ J K}^{-1}$$

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} = \frac{8765}{261.15} = 33.56 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{sur}} = 1.54 \text{ JK}^{-1}$$

The entropy of the universe increases in the irreversible process, as expected by the Second Law of Thermodynamics.

2. van der Waals gases

a. For a van der Waals gas

$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT} - \frac{na}{VRT} + \frac{n^2 ab}{V^2 RT}$$

The ratio of the magnitudes of the second and third terms on the right side is :

$$\frac{b}{na} PV \approx \frac{b}{a} RT, \quad \text{taking } PV = nRT \text{ up to zeroth order.}$$

The ratio of the magnitudes of the fourth and third terms on the right side is :

$$\frac{nb}{V} \approx \frac{bP}{RT}$$

i. From the ratios above, it follows that at sufficiently high temperature for any given pressure, the second term dominates the third and fourth terms. Therefore,

$$Z \cong 1 + \frac{bP}{RT} > 1$$

For small P, Z nearly equals unity.

ii. At lower temperatures, the third term can be greater (in magnitude) than the second term. It may be greater (in magnitude) than the fourth term also, provided P is not too large. Since the third term has a negative sign, this implies that Z can be less than unity.

iii. For $a = 0$

$$Z = 1 + \frac{bP}{RT}$$

which shows that Z increases linearly with P .

b. Helium has negligible value of a . Graph (1) corresponds to He and (2) corresponds to N_2 .

c. Above $T > T_c$, only one phase (the gaseous phase) exists, that is the cubic equation in V has only one real root. Thus isotherm (2) corresponds to $T < T_c$.

d. At $T = T_c$, the three roots coincide at $V = V_c$. This is an inflexion point.

$$\left. \frac{dP}{dV} \right|_{V_c} = \left. \frac{d^2P}{dV^2} \right|_{V_c} = 0$$

The first condition gives

$$\frac{RT_c}{(V_c - nb)^2} = \frac{2na}{V_c^3} \quad (1)$$

The second condition gives

$$\frac{RT_c}{(V_c - nb)^3} = \frac{3na}{V_c^4} \quad (2)$$

These equations give

$$V_c = 3nb \text{ and } T_c = \frac{8a}{27bR}$$

$$\text{For He, } T_c = 5.2\text{K}$$

$$\text{For } N_2, T_c = 128\text{K}$$

Since, $T_c(N_2)$ is greater than $T_c(\text{He})$, N_2 is liquefied more readily than He.

e.

$$W = \int_{V_1}^{V_2} P dV$$

$$= \int_{V_1}^{V_2} \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV$$

$$= RT \ln \left(\frac{V_2-b}{V_1-b} \right) + a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$= 56.7 \text{ L bar mol}^{-1}$$

3. Rates and reaction mechanisms

a. Mechanism 1 :

$$\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_1 [\text{I}]^2 [\text{H}_2]$$

Since the first step is fast, there is a pre - equilibrium :

$$K = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$\therefore \frac{d[\text{HI}]}{dt} = 2k_1 K [\text{I}_2][\text{H}_2] = k [\text{H}_2][\text{I}_2]$$

Mechanism 2 :

$$\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_2 [\text{I}_2]_d [\text{H}_2]$$

$$K' = \frac{[\text{I}_2]_d}{[\text{I}_2]}$$

$$\therefore \frac{d[\text{HI}]}{dt} = 2k_2 K' [\text{I}_2][\text{H}_2] = k [\text{H}_2][\text{I}_2]$$

Both mechanisms are consistent with the observed rate law.

b. i. $k = A e^{-E_a/RT}$

$$E_a \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = R \ln \frac{k_2}{k_1}$$

With the given numerical values,

$$E_a = 170 \text{ kJ mol}^{-1}$$

- ii. The activation energy is greater than the bond dissociation energy of I_2 . Hence the second step is rate determining in both the mechanisms.
- c. The activation energy E_a' for the reverse reaction is

$$\begin{aligned} E_a' &= E_a - \Delta U \\ &= 170 + 8.2 = 178.2 \text{ kJ mol}^{-1} \end{aligned}$$

- d. i.

$$\begin{aligned} \frac{d[I_2]}{dt} &= k_3 [IAr][I] \\ K'' &= \frac{[IAr][Ar]}{[I][Ar]^2} \\ \therefore \frac{d[I_2]}{dt} &= K'' k_3 [I]^2 [Ar] \\ &= k [I]^2 [Ar] \end{aligned}$$

- ii. A possible reason why this is negative is that E_{a3} is positive and less in magnitude than $|\Delta H^\circ|$, while ΔH° is negative.

$$\begin{aligned} k &= k_3 K'' \\ &= A_3 e^{-E_{a3}/RT} e^{-\Delta G^\circ/RT} \\ \text{we know } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \therefore k &= A_3 e^{\frac{\Delta S^\circ}{R}} e^{-(E_{a3} + \Delta H^\circ)/RT} \end{aligned}$$

The activation energy for the overall reaction is $E_{a3} + \Delta H^\circ$

4. Enzyme catalysis

- a. i. The differential rate equations for the Michaelis-Menten mechanism are

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_1' [ES] - k_2 [ES] \quad (1)$$

$$\frac{d[P]}{dt} = k_2 [ES] \quad (2)$$

In the steady-state approximation, $\frac{d[ES]}{dt} = 0$ (3)

Eq. (1) then gives $[ES] = \frac{k_1 [E][S]}{k_1 + k_2}$ (4)

Now $[E]_0 = [E] + [ES]$ (5)

where $[E]_0$ is the total enzyme concentration. Eqs. (4) and (5) gives

$$[ES] = \frac{[E]_0[S]}{K_m + [S]} \quad (6)$$

where $K_m = \frac{k_1 + k_2}{k_1}$ is the Michaelis-Menten constant.

From eq. (2), $\frac{d[P]}{dt} = \frac{k_2 [E]_0 [S]}{K_m + [S]}$ (7)

Since the backward rate is ignored, our analysis applies to the initial rate of formation of P and not close to equilibrium. Further, since the enzyme concentration is generally much smaller than the substrate concentration, [S] is nearly equal to $[S]_0$ in the initial stage of the reaction.

Thus, according to the Michaelis-Menten mechanism, the initial rate versus substrate concentration is described by eq. (7), where [S] is replaced by $[S]_0$.

For $[S] \ll K_m$,

$$\text{Initial rate} = \frac{k_2}{K_m} [E]_0 [S] \quad (8)$$

i.e., initial rate varies linearly with [S].

For $[S] \gg K_m$,

$$\text{Initial rate} = k_2 [E]_0 \quad (9)$$

i.e., for large substrate concentration, initial rate approaches a constant value $k_2 [E]_0$.

Thus the indicated features of the graph are consistent with Michaelis-Menten mechanism.

- ii. The asymptotic value of initial rate is $k_2 [E]_0$

From the graph,

$$k_2 [E]_0 = 3.0 \times 10^{-6} \text{ M s}^{-1}$$

With $[E]_0 = 1.5 \times 10^{-9} \text{ M}$

we get $k_2 = 2.0 \times 10^3 \text{ s}^{-1}$

- iii. From eq. (7), for $[S] = K_m$, the initial rate is half the asymptotic value. From the graph, therefore,

$$K_m = 5.0 \times 10^{-5} \text{ M}$$

For $[S] = 1.0 \times 10^{-4} \text{ M}$, using eq. (7) again,

$$\text{Initial rate} = \frac{[2.0 \times 10^3 \text{ s}^{-1}] \times [1.5 \times 10^{-9} \text{ M}] \times [1.0 \times 10^{-4} \text{ M}]}{[5.0 \times 10^{-5} \text{ M}] + [1.0 \times 10^{-4} \text{ M}]}$$

$$= 2.0 \times 10^{-6} \text{ M s}^{-1}$$

- iv. We have $K_m = \frac{k_1^{\dagger} + k_2}{k_1} = 5.0 \times 10^{-5} \text{ M}$

The enzyme equilibrates with the substrate quickly, that is the first step of equilibration between E, S and [ES] is very fast. This means that k_1^{\dagger} is much greater than k_2 . Therefore, neglecting k_2 above,

$$\frac{k_1^{\dagger}}{k_1} = 5.0 \times 10^{-5} \text{ M}$$

The equilibrium constant K for the formation of ES from E and S is,

$$\frac{K}{1\text{M}} = \frac{k_1}{k_1^{\dagger}} = 2.0 \times 10^{-5}$$

- b. From the graph at the new temperature, $k_2 [E]_0 = 6.0 \times 10^{-6} \text{ M s}^{-1}$

i.e., $k_2 = \frac{6.0 \times 10^{-6} \text{ M s}^{-1}}{1.5 \times 10^{-9} \text{ M}} = 4.0 \times 10^3 \text{ s}^{-1}$

Using Arrhenius relation for temperature dependence of rate constant :

$$k = A e^{-\frac{E_a}{RT}} \quad (10)$$

where E_a is the molar activation energy.

$$\frac{k(T_1)}{k(T_2)} = e^{-\frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]}$$

$$\text{i.e.} \quad E_a = R \frac{\ln \frac{k(T_2)}{k(T_1)}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (11)$$

$$\text{Now} \quad \frac{k_2(310)}{k_1(285)} = 2.0, \quad R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore E_a = 20.4 \text{ kJ mol}^{-1}$$

- c. i.** The fraction of the enzyme that binds with the substrate is, from eq. (6):

$$\frac{[ES]}{[E]_0} = \frac{[S]}{K_m + [S]} \quad (12)$$

where $[S]$ is nearly equal to $[S]_0$ in the initial stage of the reaction.

$$\text{Now} \quad [S]_0 = \frac{3.0 \times 10^{-6} \text{ mol}}{1 \times 10^{-3} \text{ L}} = 3.0 \times 10^{-3} \text{ M}$$

$$\text{and} \quad K_m = 5.0 \times 10^{-5} \text{ M}$$

$$\therefore \frac{[ES]}{[E]_0} = \frac{3.0 \times 10^{-3} \text{ M}}{(5.0 \times 10^{-5} + 3.0 \times 10^{-3}) \text{ M}} = 0.98$$

Nearly the whole of the enzyme is bound with the substrate.

- ii.** From eq. (7),

Integrating the equation gives,

$$\frac{d[S]}{dt} = -\frac{k_2 [E]_0 [S]}{K_m + [S]}$$

$$K_m \ln \frac{[S]}{[S]_0} + [S] - [S]_0 = -k_2 [E]_0 t \quad (13)$$

If at $t = T$, $[S] = 1/2[S]_0$,

$$T k_2 [E]_0 = K_m \ln 2 + \frac{1}{2} [S]_0 \quad (14)$$

$$\text{Here } [E]_0 = \frac{2.0 \times 10^{-12} \text{ mol}}{1.0 \times 10^{-3} \text{ L}} = 2.0 \times 10^{-9} \text{ M}$$

$$k_2 = 2.0 \times 10^3 \text{ s}^{-1}, \quad K_m = 5.0 \times 10^{-5} \text{ M},$$

$$[S]_0 = 3.0 \times 10^{-3} \text{ M}$$

Substituting these values in eq. (14) gives

$$T = 384 \text{ s}$$

Thus 50% of the antibiotic dose is inactivated in 384 s.

d. i. The differential rate equations for the situation are :

$$\frac{d}{dt} [ES] = k_1 [E][S] - k_1^l [ES] - k_2 [ES] \quad (15)$$

$$\frac{d}{dt} [EI] = k_3 [E][I] - k_3^l [EI] \quad (16)$$

$$\frac{d}{dt} [P] = k_2 [ES] \quad (17)$$

where k_3 and k_3^l are the forward and backward rate constants for the enzyme-inhibitor reaction.

Applying steady-state approximation to [ES] and [EI],

$$[ES] = \frac{k_1 [E][S]}{k_1^l + k_2} \quad (18)$$

$$\text{and } [EI] = \frac{k_3 [E][I]}{k_3^l} \quad (19)$$

$$\text{Now } [E]_0 = [E] + [ES] + [EI] \quad (20)$$

Eliminating [E] and [EI] from eqs. (18) to (20) gives :

$$[\text{ES}] = \frac{[\text{E}]_0 [\text{S}]}{[\text{S}] + K_m \left(1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (21)$$

$$\frac{d[\text{P}]}{dt} = \frac{k_2 [\text{E}]_0 [\text{S}]}{[\text{S}] + K_m \left(1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (22)$$

Here, $K_i(1\text{M}) = \frac{k_3^l}{k_3}$ is the equilibrium constant for the dissociation of EI to E and I.

The degree of inhibition is $i = 1 - \frac{r}{r_0}$

$$\text{Using eq. (22), } i = \frac{\frac{K_m}{K_i} \frac{[\text{I}]}{(1\text{M})}}{[\text{S}] + K_m \left(1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (23)$$

For fixed [I], i decreases with increase in [S] (*competitive inhibition*).

and for large [S], $i \rightarrow 0$, i.e., the inhibitor ceases to play any role.

ii. For small [S] $i = \frac{[\text{I}]}{K_i (1\text{M}) + [\text{I}]}$

$$\text{If } r = \frac{1}{4} r_0, \quad i = \frac{3}{4}$$

$$\text{i.e., } [\text{I}] = 3 K_i \times (1\text{M}) = 1.5 \times 10^{-4} \text{ M}$$

The inhibitor concentration required to reduce the rate of inactivation by a factor of 4 is $1.5 \times 10^{-4} \text{ M}$; i.e., $0.15 \mu\text{mol}$ in a volume of 1.00 mL .

5. Schrödinger equation

a.

i. One-dimensional Schrödinger equation for a free particle of mass m :

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \hbar = \frac{h}{2\pi}$$

where E stands for the energy of the particle and ψ its wave function.

ii. The boundary conditions are :

$$\psi(0) = \psi(L) = 0$$

Only $\psi_n(x) = \sin \frac{n\pi x}{L}$ satisfies the required boundary conditions.

Other functions are not possible wave functions of the electron in a one-dimensional rigid box.

iii.

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sin \frac{n\pi x}{L} = \frac{\hbar^2\pi^2}{2mL^2} n^2 \sin \frac{n\pi x}{L}$$

$$\therefore E_n = \frac{\hbar^2\pi^2}{2mL^2} n^2 = \frac{h^2n^2}{8mL^2}$$

iv. Ground state ($n = 1$)

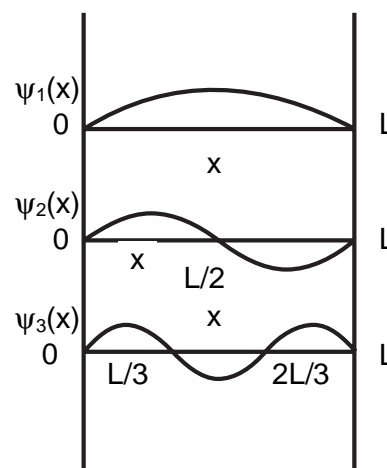
$$\psi_1(x) = \sin \frac{\pi x}{L}$$

First excited state ($n = 2$)

$$\psi_2(x) = \sin \frac{2\pi x}{L}$$

Second excited state ($n = 3$)

$$\psi_3(x) = \sin \frac{3\pi x}{L}$$



Number of nodes in $\psi_n = n - 1$, apart from the nodes at the end points.

v.

$$\begin{aligned}\psi_1^N(x) &= N \sin \frac{\pi x}{L} \\ 1 &= \int_{-\infty}^{\infty} |\psi_1^N(x)|^2 dx \\ &= N^2 \int_0^L \sin^2 \frac{\pi x}{L} dx = \frac{N^2}{2} \int_0^L \left(1 - \cos \frac{2\pi x}{L}\right) dx \\ &= N^2 \frac{L}{2} \\ \therefore N &= \sqrt{\frac{2}{L}} \quad (\text{N is chosen to be real}) \\ \psi_1^N(x) &= \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}\end{aligned}$$

b. In the example

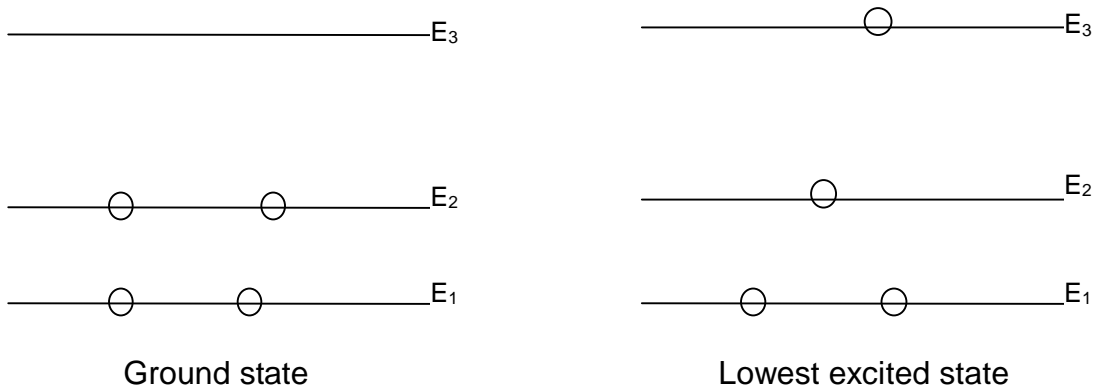
$$L = 5 \times 1.4 \times 10^{-10} \text{ m} = 7.0 \times 10^{-10} \text{ m}$$

The first three energy levels are:

$$E_1 = \frac{h^2}{8mL^2} = 1.22 \times 10^{-19} \text{ J}$$

$$E_2 = 4 E_1 = 4.88 \times 10^{-19} \text{ J}$$

$$E_3 = 9 E_1 = 10.98 \times 10^{-19} \text{ J}$$

In the ground state, the four electrons will occupy the levels E_1 and E_2 , each with two electrons.

The lowest excitation energy

$$E_3 - E_2 = 6.10 \times 10^{-19} \text{ J}$$

c. The condition that $\psi(\phi)$ is single valued demands that

$$\Psi(\phi) = \Psi(\phi + 2\pi)$$

$$e^{i\lambda\phi} = e^{i\lambda(\phi+2\pi)}$$

$$e^{i2\pi\lambda} = 1$$

i.e. $\lambda = m$, where $m = 0, \pm 1, \pm 2, \pm 3, \dots$

This shows that angular momentum projection (L_z) cannot be an arbitrary real number but can have only discrete values: $m\hbar$, where m is a positive or negative integer (including zero).

6. Atomic and molecular orbitals

A. Atomic orbitals

a.

$$\begin{aligned} \text{i. } \psi_{1s}^N &= N e^{-\frac{r}{a_0}} \\ 1 &= \int |\psi_{1s}^N|^2 dv = 4\pi a_0^3 N^2 \\ &= 4\pi N^2 \times \frac{a_0^3}{4} = \pi a_0^3 N^2 \quad (\text{N chosen to be real}) \end{aligned}$$

$$\therefore N = [\pi a_0^3]^{-\frac{1}{2}}$$

$$\psi_{1s}^N = [\pi a_0^3]^{-\frac{1}{2}} e^{-\frac{r}{a_0}}$$

ii. Probability of finding an electron between r and $r + dr$

$$= 4\pi r^2 \times [\pi a_0^3]^{-1} e^{-\frac{2r}{a_0}} dr$$

This is a maximum at $r = r_{\max}$, given by

$$\frac{d}{dr} \left(r^2 e^{-\frac{2r}{a_0}} \right)_{r=r_{\max}} = 0$$

This gives

$$r_{\max} = a_0$$

The 1s electron is most likely to be found in the neighborhood of $r = a_0$.

b. $\Psi_{2s} = 0$ at $r = 2a_0$

Nodal surface is a sphere of radius $2a_0$

$$\Psi_{2p_z} = 0 \quad \text{at } \theta = \frac{\pi}{2}$$

Nodal surface is the xy plane.

$$\Psi_{3d_{z^2}} = 0 \quad \text{at } 3\cos^2\theta - 1 = 0, \quad \text{i.e., } \theta = \cos^{-1}\left(\pm \frac{1}{\sqrt{3}}\right)$$

Nodal surfaces are cones with these values of half-angle, one above the xy plane and the other below it.

(Note: all three wave functions vanish as $r \rightarrow \infty$. At $r = 0$, ψ_{1s} does not vanish, but the other two wave functions vanish.)

c. Each electron in $n = 1$ shell of helium atom has energy $-Z_{\text{eff}}^2 \times 13.6 \text{ eV}$

$$\text{Helium ground state energy} = -Z_{\text{eff}}^2 \times 27.2 \text{ eV}$$

$$\text{Energy of He}^+ \text{ ground state} = -4 \times 13.6 = -54.4 \text{ eV}$$

$$\text{Ionization energy} = (-54.4 + Z_{\text{eff}}^2 \times 27.2) \text{ eV} = 24.46 \text{ eV}$$

$$\text{This gives } Z_{\text{eff}} = 1.70$$

B. Molecular orbitals

a. ψ_1 and ψ_2 are bonding orbitals

$$\tilde{\psi}_1 \text{ and } \tilde{\psi}_2 \text{ are antibonding orbitals}$$

Bonding orbital

No nodal surface between the nuclei. Electronic energy has a minimum at a certain internuclear distance. Qualitative reason: electron has considerable probability of being between the nuclei and thus has attractive potential energy due to both the nuclei.

Antibonding orbital

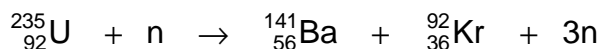
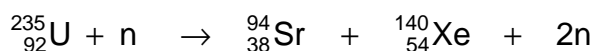
Nodal surface between the nuclei. Electronic energy decreases monotonically with internuclear distance. Hence bound state is not possible.

- b. $R_e = 1.32 \times 10^{-10} \text{ m}$
 $D = -1.36 - (-15.36) = 1.76 \text{ eV}$
- c. It will dissociate to a hydrogen atom in 2s state and a bare hydrogen nucleus (proton).
- d. The two electrons occupy the same molecular orbital with the lowest energy. By Pauli's principle, their spins must be antiparallel. Hence the total electronic spin is zero.
- e. In the first excited state of H_2 , one electron is in ψ_1 (bonding orbital) and the other in ψ_2 (antibonding orbital). It will dissociate into two hydrogen atoms.
- f. Using the aufbau principle, in the ground state two electrons of He_2 are in ψ_1 (bonding orbital) and two in ψ_2 (antibonding orbital). The bond order is $\frac{1}{2} (2 - 2) = 0$

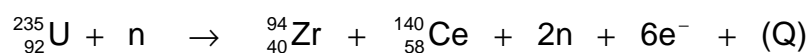
Therefore, bound He_2 is unstable and difficult to detect. However, if one or more electrons are elevated from the antibonding orbital to (higher energy) bonding orbitals, the bond order becomes greater than zero. This is why it is possible to observe He_2 in excited states.

7. Fission

a.



b. The net nuclear reaction is



The energy released is

$$Q = [m_{\text{N}}({}^{235}\text{U}) - m_{\text{N}}({}^{94}\text{Zr}) - m_{\text{N}}({}^{140}\text{Ce}) - m_{\text{n}} - 6m_{\text{e}}] c^2$$