

Q1)

T_1 / K	T_2 / K	$E_a / \text{kJ mol}^{-1}$	E_a / R	$1/T_2 - 1/T_1$	k_2/k_1
298.15	308.15	52.9	6362	-0.0001088	2.00
100	110	52.9	6362	-0.0009091	325
500	510	52.9	6362	-3.922E-05	1.28
298.15	308.15	26.4	3181	-0.0001088	1.41
298.15	308.15	105.8	12724	-0.0001088	3.99

a) 52.9 kJ mol^{-1}

2 points in total
if get 4 out of 5 that would be full
mark

b) The rate constant ratio is very sensitive to temperature.

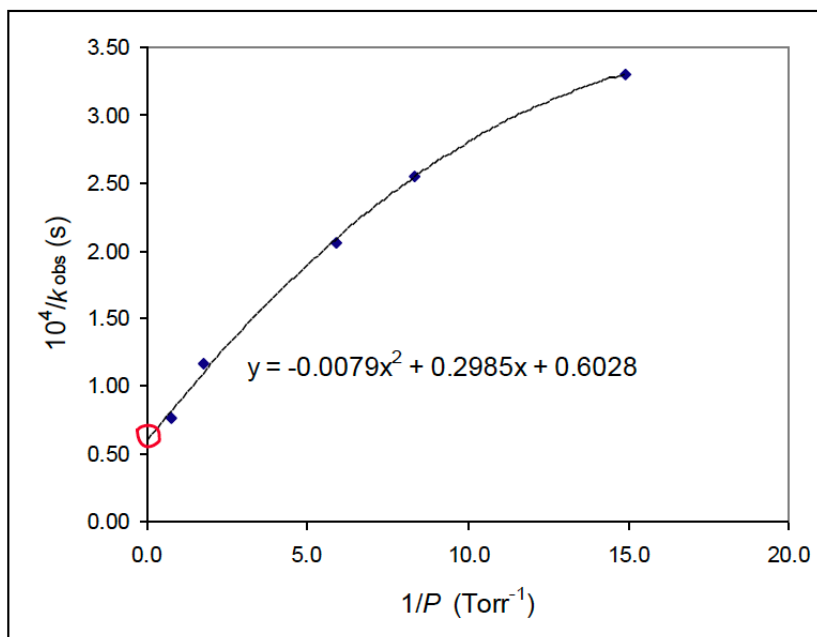
c) The rate constant ratio also depends on the activation energy.

d) For thermally activated reactions with an activation energy of about 50 kJ mol^{-1} , the reaction rate roughly doubles for every 10 K increase in temperature close to room temperature.

e) The “typical” reaction which fits this rule of thumb must involve making as well as breaking bonds, so that the energy maximum at the transition state is above the reactants by only a fraction of a bond energy.

Q2)

1 point plot



Not a straight line; therefore not Lindemann.

A parabola seems to fit reasonable well.

From the intercept (inverse), $k_{\infty} = 1.66 \times 10^4 \text{ s}^{-1}$

1 point

Q3)

[S] /mM	$\rho / 10^{-5} \text{ M s}^{-1}$	$[\text{S}]^{-1} / \text{mM}^{-1}$	$\rho^{-1} / 10^5 \text{ M}^{-1} \text{ s}$
1.5	2.18	0.667	0.459
2.0	2.52	0.500	0.397
3.0	3.15	0.333	0.317
6.0	4.02	0.167	0.249
16.0	4.85	0.063	0.206

$$\frac{1}{\rho} = \frac{1}{\rho_{\max}} + \frac{K_M}{\rho_{\max}} \cdot \frac{1}{[\text{S}]}$$

From intercept,

$$\rho_{\max} = 5.59 \times 10^{-5} \text{ M s}^{-1}$$

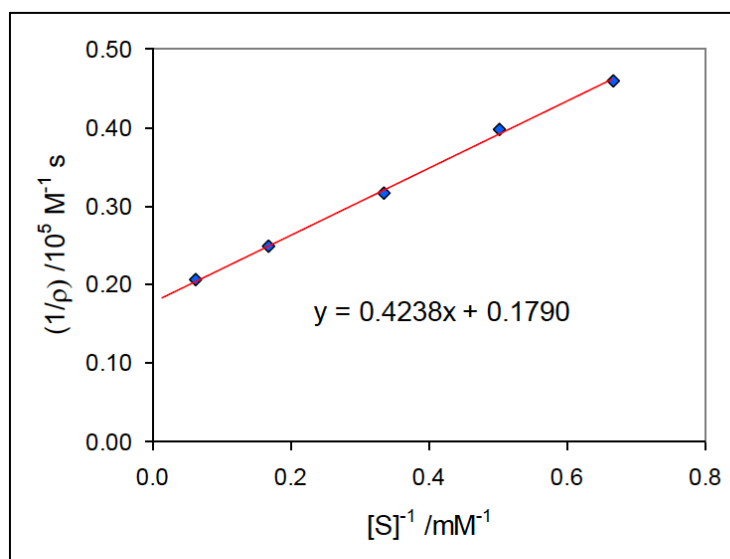
0.5 point

From slope,

$$K_M = 2.37 \times 10^{-3} \text{ M}$$

0.5 point

1 point plot



Q4)

- (a) Estimate the diffusion-limited rate constants at 25°C and 200°C. The viscosity of water is 8.9×10^{-4} Pa s at 25°C and 1.4×10^{-4} Pa s at 200°C.

$$k_D = 4000\pi N_{Av} r_{AB} (D_{Mu} + D_{HQ}) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The diffusion constants scale with viscosity/ T .

$$\text{At } 200^\circ\text{C } (D_{Mu} + D_{HQ}) = (14 + 1) \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \times (1.4/473)(298/8.9)$$

$$\underline{k_D = 2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C} ; \quad \underline{25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 200^\circ\text{C}}$$

1 point (do not miss units)

- (b) If the experimental values for the rate constants are $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and $6.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 200°C, determine the activated rate constants at these temperatures and thence find the activation energy for the reaction.

$$\frac{1}{k_{\text{exp}}} = \frac{1}{k_D} + \frac{1}{k_{\text{act}}}$$

$$\underline{k_{\text{act}} = 3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C} ; \quad \underline{8.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 200^\circ\text{C}}$$

1 point

$$\underline{E_a = 6.9 \text{ kJ mol}^{-1}}$$

Q5)

0.5 point

(a) The collision rates depend on the relative velocity of the reactants, which depends on their masses – lighter atoms will move faster at a given temperature. Thus the rates will increase in the order $D < H < Mu$.

0.5 point

(b) The tunnelling probability depends strongly on mass and increases in the order $D < H < Mu$.

(c) Since the reactions have a common molecule as reactant, the rate constants are only affected through zero-point vibrational contributions to the transition state (X-H-H). These are greatest for the lightest isotope (Mu) so the rate constants will increase in the order $Mu < H < D$.

1 point

This question will be marked based on your understanding of the question. Do not need to mention the exact answers.