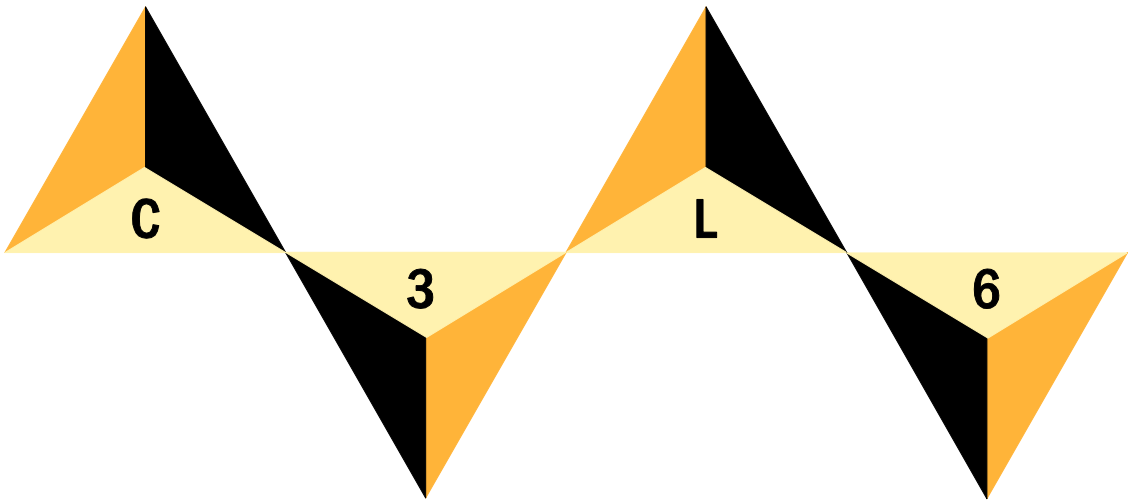


Cambridge Chemistry Challenge Lower 6th

December 2025

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical A-level papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 minutes under exam conditions.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block			d-block										p-block					
1	**H** 1 1.008																		**He** 2 4.003
2	**Li** 3 6.94	**Be** 4 9.01												**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
3	**Na** 11 22.99	**Mg** 12 24.31												**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
4	**K** 19 39.10	**Ca** 20 40.08		**Sc** 21 44.96	**Ti** 22 47.87	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.69	**Cu** 29 63.55	**Zn** 30 65.38	**Ga** 31 69.72	**Ge** 32 72.63	**As** 33 74.92	**Se** 34 78.97	**Br** 35 79.90	**Kr** 36 83.80
5	**Rb** 37 85.47	**Sr** 38 87.62		**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.95	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.42	**Ag** 47 107.87	**Cd** 48 112.41	**In** 49 114.82	**Sn** 50 118.71	**Sb** 51 121.76	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.29
6	**Cs** 55 132.91	**Ba** 56 137.34	*	**Lu** 71 174.97	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.84	**Re** 75 186.21	**Os** 76 190.23	**Ir** 77 192.22	**Pt** 78 195.08	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.38	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	+	**Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

Group Number

Symbol
atomic number
mean atomic mass

f-block

Lanthanoids:	*	**La** 57 138.91	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.36	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.05
Actinoids:	+	**Ac** 89	**Th** 90 232.04	**Pa** 91 231.04	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102

The Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1}

1. This question is about compounds of osmium

Osmium, symbol Os, is a remarkable metal in that it readily forms compounds with high oxidation states, but even more so since one of its oxides, osmium tetroxide, OsO_4, is extremely volatile (and toxic!). In fact, this oxide even gave the element its name because it has a peculiar smell (the Greek *osme* means 'smell'). Some of its compounds are known as *osmates*.



Different sort of osmates!

(a) **(i)** How many valence electrons does osmium have that could potentially be used in bonding?

(ii) What is the oxidation state of the osmium in OsO_4?

(iii) In the structure of OsO_4, all the oxygen atoms are in equivalent environments. Suggest TWO possible structures consistent with this.

(iv) In the actual structure of OsO_4, the separation between every oxygen atom is the same. What is the oxygen–osmium–oxygen bond angle?

(b) Osmium tetroxide reacts with potassium hydroxide to form a compound $K_x[OsO_4(OH)_x]$ which can be isolated as dark red crystals. Analysis found the compound to contain 22.1% K (by mass) and 51.5% Os (these are real experimental values, with errors).

(i) What is the oxidation state of the osmium in $K_x[OsO_4(OH)_x]$?

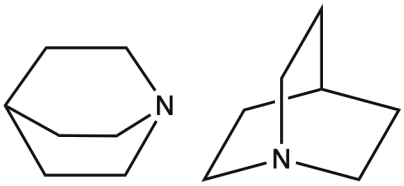
(ii) Determine the value of x in this compound.

(c) In aqueous potassium hydroxide, osmium tetroxide reacts with ethanol to form ethanoic acid and the dark purple compound potassium osmate, $K_2[OsO_2(OH)_4]$.

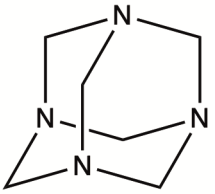
(i) What is the oxidation state of the osmium in $K_2[OsO_2(OH)_4]$?

(ii) What is the change in the oxidation state of the alcohol-carbon in ethanol during this reaction?

(iii) Give the balanced equation for the overall reaction forming $K_2[OsO_2(OH)_4]$ from osmium tetroxide, potassium hydroxide, and ethanol.



Two different views of quinuclidine



Amine **A**

Osmium tetroxide readily reacts with amine nucleophiles to form adducts which are often much safer than OsO_4 itself since they are not volatile. The amine *quinuclidine* reacts to form an orange 1:1 adduct formed which has three oxygen atoms in one environment, and one in a unique environment. The tricyclic amine **A** has four different nitrogens that could potentially react. When reacting with excess OsO_4 the only adduct that forms is found to contain (by mass) C 11.3%; H 1.6%; N 8.7% (these are real experimental values, with errors).

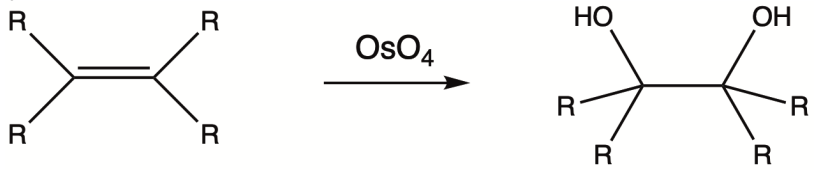
(d) (i) Suggest a structure for the adduct formed between quinuclidine and OsO_4 indicating the approximate bond angles around the osmium atom.

(ii) How many unique carbon environments are there in amine **A**?

(iii) Determine the formula of the adduct formed between OsO_4 and amine **A**.

(iv) With aqueous ammonia, OsO_4 forms a salt (X^+ Y^-) with overall formula $N_2H_4O_3Os$. The structure of anion Y^- shows that all the oxygen atoms are in the same environment. Suggest a structure for anion Y^-.

By far the most useful application of osmium is its use (as OsO_4) to oxidise alkenes to diols. The overall reaction may be written:



where the groups R in the alkene might all be the same or different.

During this reaction the oxidation state of the osmium decreases and, initially, so-called osmate esters are formed which contain 5-membered rings with an osmium in the +VI oxidation state. It is often found that the rate of reaction is faster when amine-OsO_4 adducts are used in place of OsO_4. When the adduct formed between OsO_4 and amine **A** reacts with 2,3-dimethylbutene, two osmate ester products are formed: the main one has the formula $C_6H_{12}OsO_4$**A** and the minor product has the formula $C_{12}H_{24}Os_2O_8$. In the latter compound, the alkene-carbons are in equivalent environments and there is no Os–Os bond.

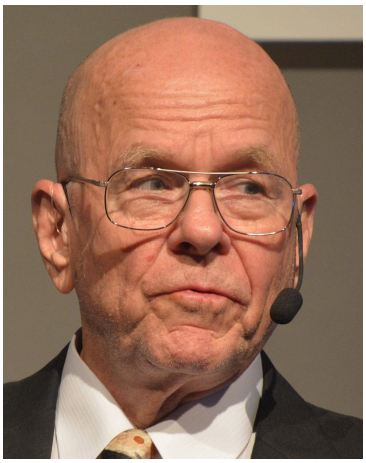
The osmate esters may be hydrolysed in aqueous alkali. This step does not affect the geometry around the carbon atoms and the net result is that the two oxygen atoms in the final diol add to the alkene from the same face. Because of the great expense of osmium, after hydrolysis of the osmate ester, it is common to re-oxidise the osmium species in the aqueous alkaline medium using a cheaper oxidising agent such as $K_3Fe(CN)_6$. In this way, only a tiny quantity of osmium-species is required as a catalyst.

(e) (i) Suggest a structure for the compound with formula $C_6H_{12}OsO_4$**A** (you do not need to draw the full structure for amine **A**).

(ii) Suggest a structure for the compound with formula $C_{12}H_{24}Os_2O_8$.

(iii) Give an equation for the oxidation of $K_2[OsO_2(OH)_4]$ to $K_x[OsO_4(OH)_x]$ with $K_3Fe(CN)_6$ in aqueous KOH. [Your expression should be in terms of x rather than a particular value.]

Professor Karl Barry Sharpless won his first Nobel Prize in Chemistry in 2001 “for his work on chirally catalysed oxidation reactions”. This included the development of a system based on OsO_4 that could product single enantiomer diols from alkenes in a process called Sharpless Asymmetric Dihydroxylation (SAD) ☹.

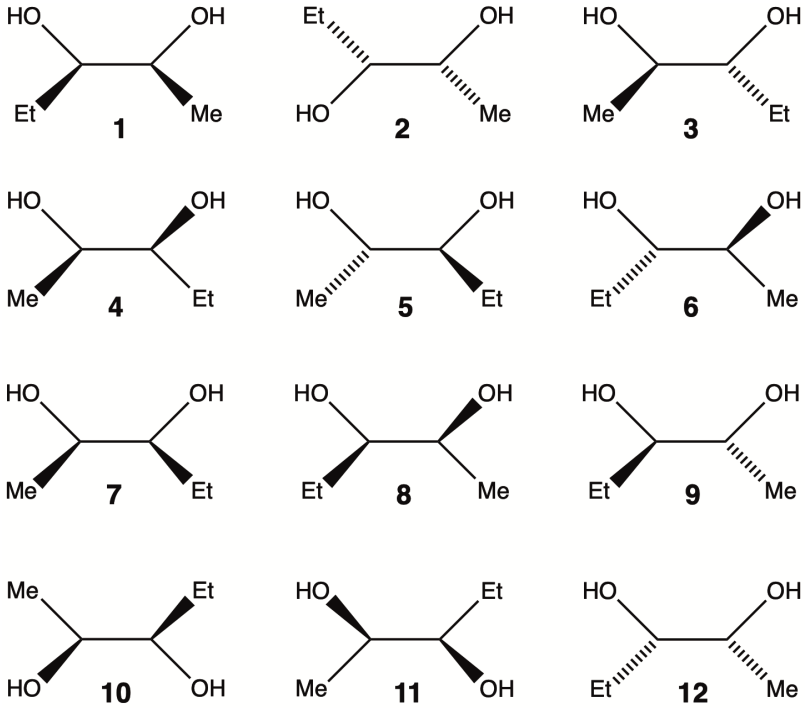


Karl Barry Sharpless
(taken from Wikipedia)

Enantiomers are isomers which cannot be superimposed on their mirror images (i.e. if a mould was made from one isomer so that isomer fitted into the space exactly, then the mirror image isomer could not fit into that space).

All the diols shown on the right can be made by the dihydroxylation of the appropriate isomer (either *cis* or *trans*) of pent-2-ene using OsO_4.

[Some of the diols shown are the same molecule after rotating about single bonds, or rotating the molecule as a whole (or both).]

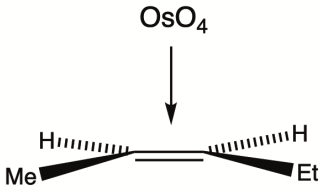


(f) **(i)** Which (if any) of the structures **2**-**12** are the same as structure **1**?

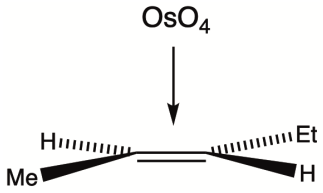
(ii) Which (if any) of the structures **2**-**12** are the enantiomer of structure **1**?

(iii) Which (if any) of the structures **1**-**12** could be made from the reaction between OsO_4 and cis-pentene.

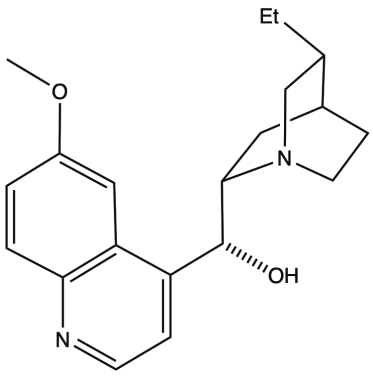
(iv) Which (if any) of the structures **1**-**12** could be made by the reaction between OsO4 and *cis*-pent-2-ene with the initial attack orientated as shown on the right?



(v) Which (if any) of the structures **1**-**12** could be made by the reaction between OsO4 and *trans*-pent-2-ene with the initial attack orientated as shown on the right?

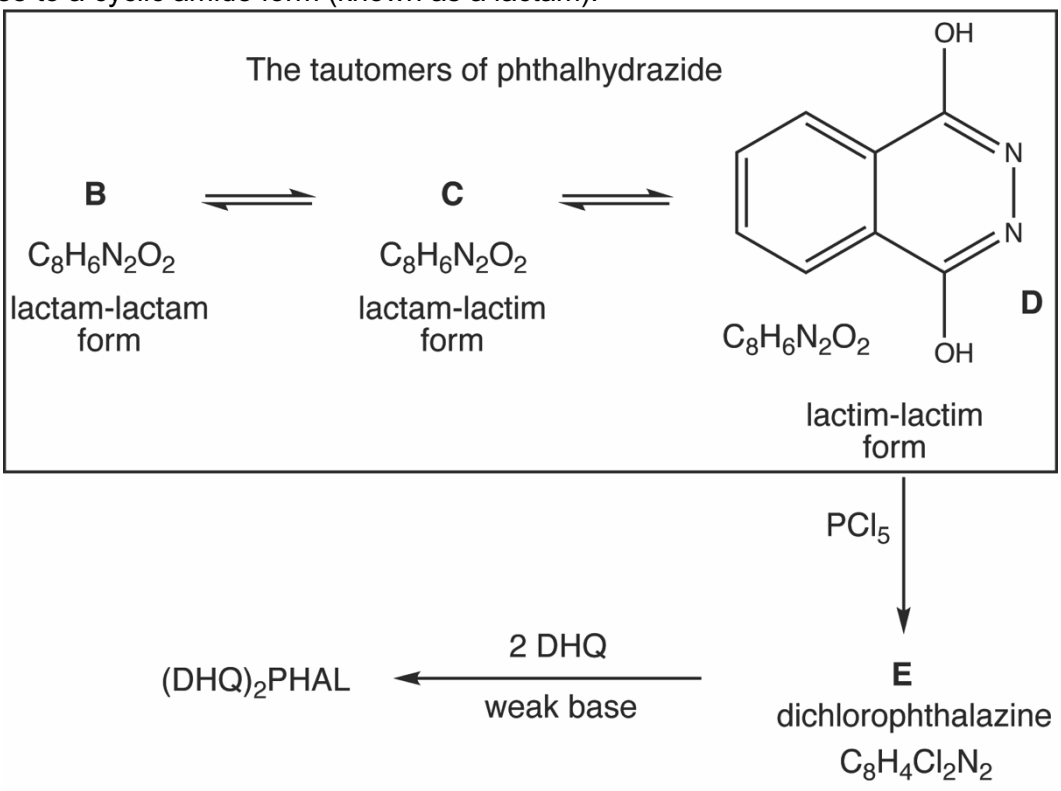


Crucial to the SAD reaction is the design of the amine-containing ligand to which the OsO_4 coordinates. Sharpless used dihydroquinine (DHQ), shown on the right. Two of these amines are joined (via their oxygens) to a phthalazine unit (PHAL) which acts as a spacer and creates a compound called $(DHQ)_2PHAL$ which forms a U-shaped pocket into which a single OsO_4 molecule binds to one of the nitrogen atoms. Alkenes fit snugly into the pocket of $(DHQ)_2PHAL$ allowing the osmate ester to form only on one face of the alkene.



(g) (i) How many chiral centres are there in DHQ? (For these purposes, a chiral centre is a carbon atom with 4 different substituents attached.)

To join the DHQ units to the phthalazine, dichlorophthalazine, **E**, is used. This is made from phthalhydrazide which itself is interesting since it can exist as three different tautomers. (Tautomers are isomers which can be interconverted by simply moving a proton from one atom to another.) Structure **D** below is the so-called 'lactim-lactim' form but each lactim functional group can tautomerise to a cyclic amide form (known as a lactam).



(h) (i) Give the structure of **E**, dichlorophthalazine.

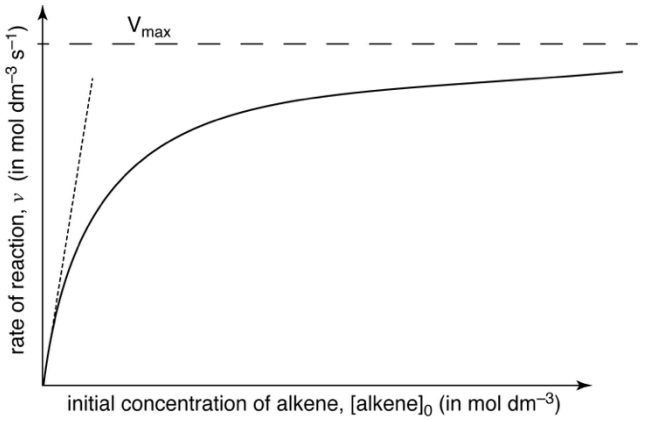
(ii) Suggest a structure for the lactam-lactam form of phthalhydrazide, **B**.

(iii) Suggest a structure for the lactam-lactim form of phthalhydrazide, **C**.

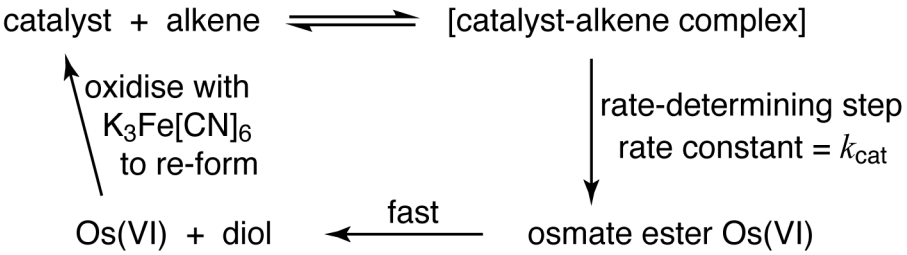
In the right solvent system, the lactam-lactim isomer **C** can self-assemble into a hydrogen-bonded trimer, $\mathbf{C_3}$.

(iv) On the template in your answer booklet, suggest a structure for the trimer $\mathbf{C_3}$. You will need to add in the missing atoms and bonds. Use dotted lines to show each hydrogen bond.

For the SAD reaction, how the initial rate of reaction varies with the initial concentration of alkene, $[\text{alkene}]_0$, shows a similar form to that of an enzyme-catalysed reaction. For a small concentration of the catalyst, as $[\text{alkene}]_0$ increases, at first there is a linear relationship (as shown by the dotted line) but eventually the rate approaches a maximum value, V_{max}, shown by the horizontal dashed line.



The (simplified) general reaction scheme is:



and the rate of reaction is given by the expression:

$$\text{rate of reaction, } v = \frac{k_{cat}\,[\text{catalyst}]_{tot}\,[\text{alkene}]}{[\text{alkene}] + K_M}$$

where $[\text{catalyst}]_{tot}$ is the total concentration of the catalyst (bound or unbound) in the reaction mixture, and K_M is a constant known as the Michaelis constant.

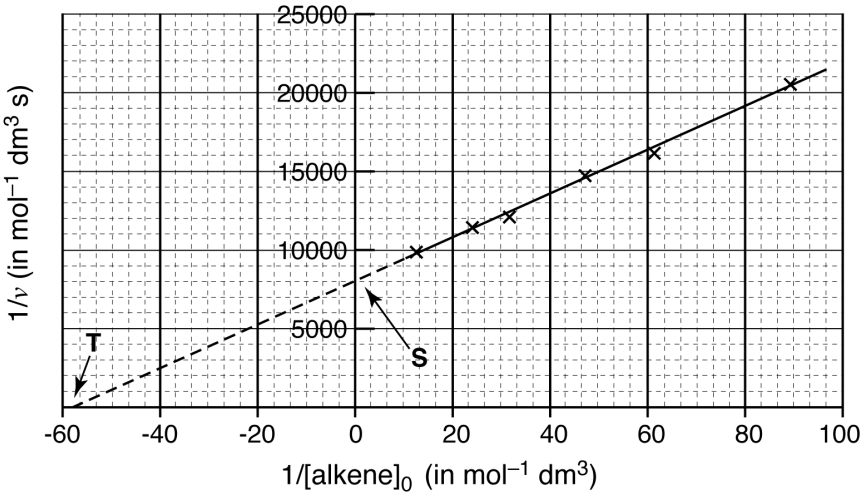
(j) **(i)** What must be the units for the constant K_M?

(ii) What are the units of k_{cat}?

(iii) Find an expression in terms of k_{cat}, K_M, and $[\text{catalyst}]_{tot}$ (as appropriate) for the initial rate of reaction for small initial concentrations of alkene, $[\text{alkene}]_0$.

(iv) Find an expression in terms of k_{cat}, K_M, and $[\text{catalyst}]_{tot}$ (as appropriate) for the maximum rate of reaction, V_{max}.

A graph designed to find the values of V_{max}, k_{cat}, and K_M is shown on the right. The data are for the reaction of the alkene styrene, at 0 °C, with $[\text{catalyst}]_{tot}$ = 0.5 mM.



(k) **(i)** Find an expression in terms of k_{cat}, K_M, and $[\text{catalyst}]_{tot}$ (as appropriate) for the slope of this plot.

(ii) Find an expression in terms of k_{cat}, K_M, and $[\text{catalyst}]_{tot}$ (as appropriate) for intercept **S**.

(iii) Find an expression in terms of k_{cat}, K_M, and $[\text{catalyst}]_{tot}$ (as appropriate) for intercept **T**.

(iv) From the graph, determine the numerical values of k_{cat}, K_M, and V_{max}.

(v) What will be the value of V_{max} for the reaction if $[\text{catalyst}]_{tot}$ = 2 mM?

Acknowledgements

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