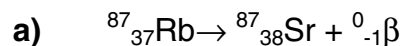


## Theoretical problems

### Problem 1 Dating moon rock



b)  ${}^{87}\text{Sr}_{\text{now}} = {}^{87}\text{Sr}_{t=0} + {}^{87}\text{Rb}_{t=0} - {}^{87}\text{Rb}_{\text{now}}$

$${}^{87}\text{Rb}_{\text{now}} = {}^{87}\text{Rb}_{t=0} \exp(-\lambda t)$$

$$({}^{87}\text{Rb}_{t=0} / {}^{87}\text{Rb}_{\text{now}}) = \exp(\lambda t)$$

$${}^{87}\text{Sr}_{\text{now}} = {}^{87}\text{Sr}_{t=0} + {}^{87}\text{Rb}_{\text{now}} (\exp(\lambda t) - 1)$$

$$({}^{87}\text{Sr}_{\text{now}} / {}^{86}\text{Sr}) = ({}^{87}\text{Sr}_{t=0} / {}^{86}\text{Sr}) + ({}^{87}\text{Rb}_{\text{now}} / {}^{86}\text{Sr}) (\exp(\lambda t) - 1)$$

$$y = c + x(m)$$

$({}^{87}\text{Sr}_{t=0} / {}^{86}\text{Sr})$  same for A and B using assumption given in question

$$m = (0.709 - 0.699) / (0.180 - 0.004) = 0.0568 = (\exp(\lambda t) - 1)$$

$$\lambda t = \ln(2) t / t_{1/2}$$

$$t_{1/2} = 4.8 \times 10^{10} \text{ years}$$

$$t = (4.8 \times 10^{10}) \ln(1.0568) / \ln(2) = 3.8 \times 10^9 \text{ years}$$

### Problem 2 Snorkelling

a)  $m = 0.79 \times M_{\text{N}_2} + 0.21 \times M_{\text{O}_2} = 0.79 \times 28.02 \text{ g mol}^{-1} + 0.21 \times 32.00 \text{ g mol}^{-1} =$   
 $= 28.86 \text{ g mol}^{-1} = 4.79 \times 10^{-26} \text{ kg}$

b)  $Z = \frac{p}{\sqrt{2\pi m k T}} \times t = \frac{101300 \text{ N m}^{-2}}{\sqrt{2\pi \times 4.79 \times 10^{-26} \text{ kg} \times 1.3806 \times 10^{-23} \text{ J K}^{-1} \times 287 \text{ K}}} \times 5 \text{ s} = 1.47 \times 10^{28}$

c)  $m = \rho V = \rho A d$

$$F = mg = \rho A d g$$

d) 
$$\Delta p = \frac{F}{A} = \rho d g$$

$$d_{\max} = \frac{\Delta p}{\rho g}$$

$$\rho = 1000 \text{ kg m}^{-3}$$

e) 
$$g = 9.8 \text{ m s}^{-2}$$

$$\Delta p = \frac{1}{20} \times p_{\text{atm}} = 5065 \text{ Pa}$$

$$d_{\max} = \frac{5065 \text{ Pa}}{1000 \text{ kg m}^{-3} \times 9.8 \text{ m s}^{-2}} = 0.52 \text{ m}$$

### Problem 3 Ideal and not-so-ideal gases

a) i) pressure would double    ii) pressure would halve

iii) pressure would double    iv) pressure would increase slightly

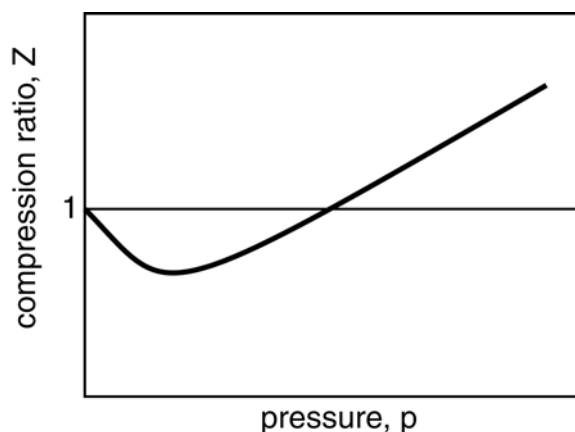
b) A – approximately zero    B – attractive

C – approximately zero    D – repulsive

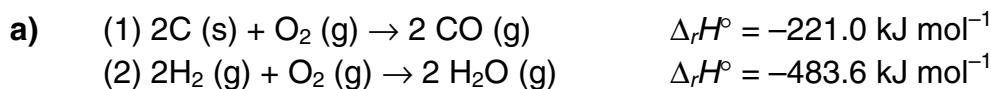
c)  $Z=1$     no intermolecular forces, ideal gas behaviour

$Z < 1$     attractive forces dominate                       $Z > 1$     repulsive forces dominate

d)

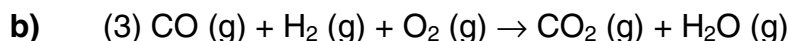


**Problem 4 Coal gasification**



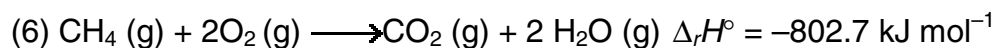
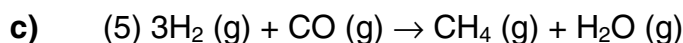
The overall reaction is  $\frac{1}{2}(\text{E1} - \text{E2})$

$$\Delta_r H^\circ = +131.3\text{ kJ mol}^{-1}.$$



$$\text{E3} = \text{E4} + \frac{1}{2}\text{E2} - \frac{1}{2}\text{E1}$$

$$\Delta_r H^\circ = -524.8\text{ kJ mol}^{-1}.$$



$$\text{E5} = 3\text{E2} - \frac{1}{2}\text{E1} - \text{E6}$$

$$\Delta_r H^\circ = -205.7\text{ kJ mol}^{-1}$$

**Problem 5 The industrial preparation of hydrogen**

a)

$$\Delta_r H^\circ = -110.5 - (-74.4) - (-241.8) = 205.7\text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = 197.7 + 3 \times 130.7 - 186.3 - 188.8 = 214.7\text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 205700 - 298 \times 214.7 = 141700\text{ J mol}^{-1} = 141.7\text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = -RT \ln K_p$$

$$K_p = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{141700}{8.314 \times 298}\right) = 1.44 \times 10^{-25}$$

b) As the reaction is endothermic increasing the temperature will result in shifting the equilibrium towards the products, i.e. increasing the equilibrium constant.

- c) For ideal gases, vol % is the same as the mole fraction

If 0.2 vol % CH<sub>4</sub> remains then there must be 0.2 vol % H<sub>2</sub>O as well.  
Remaining 99.6% corresponds to the products H<sub>2</sub> and CO in ratio 3 : 1.  
Therefore there is 24.9% CO and 74.7% H<sub>2</sub>.

$$K_p = \frac{a(\text{H}_2)^3 a(\text{CO})}{a(\text{H}_2\text{O}) a(\text{CH}_4)} = \frac{\left(\frac{p(\text{H}_2)}{p^\circ}\right)^3 \left(\frac{p(\text{CO})}{p^\circ}\right)}{\left(\frac{p(\text{H}_2\text{O})}{p^\circ}\right) \left(\frac{p(\text{CH}_4)}{p^\circ}\right)} = \frac{(x(\text{H}_2) \frac{P_{\text{tot}}}{p^\circ})^3 (x(\text{CO}) \frac{P_{\text{tot}}}{p^\circ})}{(x(\text{H}_2\text{O}) \frac{P_{\text{tot}}}{p^\circ}) (x(\text{CH}_4) \frac{P_{\text{tot}}}{p^\circ})}$$

$$= \frac{x(\text{H}_2)^3 x(\text{CO})}{x(\text{H}_2\text{O}) x(\text{CH}_4)} \times \left(\frac{P_{\text{tot}}}{p^\circ}\right)^2$$

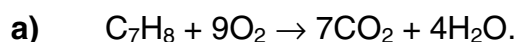
$$K_p = \frac{0.747^3 \times 0.249}{0.002 \times 0.002} \times \frac{101325^2}{100000^2} = 26640$$

- d) Van't Hoff isochore :

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$T_2 = \left( -\frac{R}{\Delta_r H^\circ} \ln \frac{K_2}{K_1} + \frac{1}{T_1} \right)^{-1} = 1580 \text{ K}$$

### Problem 6 The bonds in dibenzyl



- b) (all at 298 K)

i)  $\Delta_c H^\circ(\text{C}_7\text{H}_8, \text{l}) = 7\Delta_c H^\circ(\text{CO}_2, \text{g}) + 4\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\circ(\text{C}_7\text{H}_8, \text{l})$

$$\Rightarrow \Delta_f H^\circ(\text{C}_7\text{H}_8, \text{l}) = +12.2 \text{ kJ mol}^{-1}$$

ii)  $\Delta_f H^\circ(\text{Bz}, \text{g}) = \Delta_f H^\circ(\text{C}_7\text{H}_8, \text{l}) + \Delta_{\text{vap}} H^\circ(\text{C}_7\text{H}_8) + \Delta_{\text{bond}} H^\circ(\text{Bz} - \text{H}) - \frac{1}{2} \Delta_{\text{at}} H^\circ(\text{H}_2, \text{g})$

$$= 210.6 \text{ kJ mol}^{-1}$$

- b) i)  $\Delta_{\text{vap}} G^\circ = \Delta_{\text{vap}} H^\circ - T \Delta_{\text{vap}} S^\circ = +8.50 \text{ kJ mol}^{-1}$
- ii) liquid ( $\Delta_{\text{vap}} G^\circ > 0$ )
- iii)  $T_B = \frac{\Delta_{\text{vap}} H^\circ}{\Delta_{\text{vap}} S^\circ} = 384 \text{ K}$
- c)  $\Delta_{\text{bond}} H^\circ(\text{Bz}-\text{Bz}) = 2\Delta_f H^\circ(\text{Bz}, \text{g}) - \Delta_f H^\circ(\text{Bz}-\text{Bz}, \text{g}) = 277.3 \text{ kJ mol}^{-1}$ .

### Problem 7 Interstellar chemistry

- a) We can apply the SSA to  $\text{NH}^+$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3^+$  and  $\text{NH}_4^+$ .

$$\frac{d[\text{NH}^+]}{dt} = 0 = k_1[\text{N}^+][\text{H}_2] - k_2[\text{NH}^+][\text{H}_2]$$

$$[\text{NH}^+] = \frac{k_1[\text{N}^+]}{k_2}$$

$$\frac{d[\text{NH}_2^+]}{dt} = 0 = k_2[\text{NH}^+][\text{H}_2] - k_3[\text{NH}_2^+][\text{H}_2]$$

$$[\text{NH}_2^+] = \frac{k_2[\text{NH}^+]}{k_3} = \frac{k_2}{k_3} \frac{k_1}{k_2} [\text{N}^+] = \frac{k_1}{k_3} [\text{N}^+]$$

$$\frac{d[\text{NH}_3^+]}{dt} = 0 = k_3[\text{NH}_2^+][\text{H}_2] - k_4[\text{NH}_3^+][\text{H}_2]$$

$$[\text{NH}_3^+] = \frac{k_3[\text{NH}_2^+]}{k_4} = \frac{k_1}{k_4} [\text{N}^+]$$

$$\frac{d[\text{NH}_4^+]}{dt} = 0 = k_4[\text{NH}_3^+][\text{H}_2] - k_5[\text{NH}_4^+][e^-] - k_6[\text{NH}_4^+][e^-]$$

$$[\text{NH}_4^+] = \frac{k_4[\text{NH}_3^+][\text{H}_2]}{(k_5 + k_6)[e^-]} = \frac{k_1[\text{N}^+][\text{H}_2]}{(k_5 + k_6)[e^-]}$$

$$\text{b) } \frac{d[\text{NH}_3]}{dt} = k_5[\text{NH}_4^+][e^-] = \frac{k_1 k_5 [\text{N}^+][\text{H}_2]}{k_5 + k_6} = k_{2\text{nd}}[\text{N}^+][\text{H}_2]$$

where  $k_{2\text{nd}} = k_1 k_5 / (k_5 + k_6)$

- c) Chemical reactions involve the making and breaking of bonds. The activation energy is related to the energy required to break the initial bond or provide a sufficient rearrangement of the reactant geometries to initiate reaction.
- d) The temperature dependence of a rate constant  $k$  is described by the Arrhenius equation.

$$k(T) = A \exp(-E_a / RT)$$

Where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  the temperature. Virtually no temperature dependence therefore indicates that the activation energy is very close to zero.

- e) Temperatures in the interstellar medium are extremely low. Only reactions with very low activation energies can occur.

### **Problem 8      Simple collision theory**

- a) Assuming the reaction has an Arrhenius temperature dependence, a plot of  $\ln k$  vs  $1/T$  should be linear, with slope  $-E_a / R$  and intercept  $\ln A$ .

Plotting these data gives a straight line with a slope of  $-1042.9$  K and an intercept of  $-23.991$ . We therefore have:

$$E_a = -(R)(\text{slope}) = -8.314 \times -1042.9 = 8663.118 \text{ J mol}^{-1} = 8.66 \text{ kJ mol}^{-1}.$$

$$\ln A = \text{intercept} = -23.991$$

$$\text{so } A = \exp(-23.991) = 3.81 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

- c) i) Explanation for the simple collision theory expression for the rate constant:

$$k = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma \exp(-E_0/RT)$$

The rate of a chemical reaction must obviously be proportional to the number

of collisions between the reactants. The collision rate is given by

$$Z_{AB} = \sigma v_{\text{rel}} n_A n_B = \sigma \left( \frac{8kT}{\pi\mu} \right)^{1/2} n_A n_B$$

Here,  $v_{\text{rel}} = (8kT/\pi\mu)^{1/2}$  is the mean relative velocity of the collision partners and  $\sigma$  is the collision cross section (the effective size of one reactant as 'viewed' by the other). Often,  $\sigma$  is set equal to  $\pi(r_A + r_B)^2$ , where  $r_A$  and  $r_B$  are the radii of reactants A and B.  $n_A$  and  $n_B$  are the number densities of the two reactants.

The exponential term,  $\exp(-E_0/RT)$ , reflects the fact that a collision will only lead to reaction if the collision energy exceeds the activation barrier.

The overall rate is therefore

$$\text{rate} = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma \exp(-E_0/RT) n_A n_B$$

and we can identify the rate constant as

$$k = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma \exp(-E_0/RT)$$

- c) From part (a), we have  $A = 3.81 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We can identify  $A$  from the simple collision theory expression as

$$A = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma$$

so that  $\sigma = \left( \frac{\pi\mu}{8kT} \right)^{1/2} A$

The reduced mass of H + C<sub>2</sub>H<sub>4</sub> is

$$\mu = \frac{m(\text{H})m(\text{C}_2\text{H}_4)}{m(\text{H}) + m(\text{C}_2\text{H}_4)} = \frac{1 \times 28}{1 + 28} = 0.9655 \text{ g mol}^{-1} = 1.603 \times 10^{-27} \text{ kg}$$

giving

$$\sigma = 3.775 \times 10^{-17} \left( \frac{1.603 \times 10^{-27} \pi}{8k(400)} \right)^{1/2} = 1.275 \times 10^{-20} \text{ m}^2$$

- d) The calculated reaction cross section is around 30 times smaller than the collision cross section. This reflects the fact that not all collisions lead to reaction. Often the collision geometry and / or internal energy states of the collision partners are important in determining whether two molecules will react when they collide.

### Problem 9 Hinshelwood

b)

	Reactions
initiation	1
propagation	2, 3, 4, 5
termination	6

- c) (1)  $[\text{HCO}]' = k_1[\text{AcH}] - k_4[\text{HCO}] = 0 \Rightarrow [\text{HCO}] = \frac{k_1}{k_4}[\text{AcH}]$   
 (2)  $[\text{H}]' = k_4[\text{HCO}] - k_5[\text{H}][\text{AcH}] = 0 \Rightarrow [\text{H}] = \frac{k_4[\text{HCO}]}{k_5[\text{AcH}]} = \frac{k_1}{k_5}$  (from 1.)  
 (3)  $[\text{Me}]' = k_1[\text{AcH}] - k_2[\text{Me}][\text{AcH}] + k_3[\text{Ac}] - 2k_6[\text{Me}]^2 = 0$   
 (4)  $[\text{Ac}]' = k_2[\text{Me}][\text{AcH}] - k_3[\text{Ac}] + k_5[\text{H}][\text{AcH}] = 0$

Add (3) + (4), and substitute from (2) and then from (1).

$$0 = 2k_1[\text{AcH}] - 2k_6[\text{Me}]^2 \Rightarrow [\text{Me}] = \sqrt{\frac{k_1}{k_6}}[\text{AcH}]^{1/2}$$

$$[\text{Ac}] = \frac{k_2[\text{Me}] + k_5[\text{H}]}{k_3}[\text{AcH}] = \frac{k_2}{k_3} \sqrt{\frac{k_1}{k_6}}[\text{AcH}]^{3/2} + \frac{k_1}{k_3}[\text{AcH}]$$

Finally from (4).

d)

$$-[\text{Ac}]' = k_1[\text{AcH}] + k_2[\text{Me}][\text{AcH}] + k_5[\text{H}][\text{AcH}] = 2k_1[\text{AcH}] + k_2 \sqrt{\frac{k_1}{k_6}}[\text{AcH}]^{3/2}$$



$$[\text{CH}_4]' = k_2[\text{Me}][\text{AcH}] = k_2 \sqrt{\frac{k_1}{k_6}} [\text{AcH}]^{3/2}$$

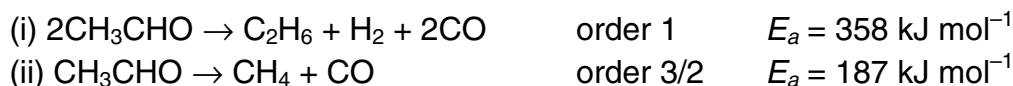
$$[\text{C}_2\text{H}_6]' = k_6[\text{Me}]^2 = k_1[\text{AcH}]$$

$$[\text{H}_2]' = k_5[\text{H}][\text{AcH}] = k_1[\text{AcH}]$$

$$[\text{CO}]' = k_3[\text{Ac}] + k_4[\text{HCO}] = 2k_1[\text{AcH}] + k_2 \sqrt{\frac{k_1}{k_6}} [\text{AcH}]^{3/2}$$

- e) Find this by analysing the rates of formation of the different products: the formation of ethane and hydrogen is first order in ethanal with equal rates, and the formation of methane is order 3/2. Both routes form CO. The first order route forms CO at twice the rate of ethane and hydrogen, and the order 3/2 rate forms it at the same rate as methane.

To get the activation energies use the Arrhenius equation. Because the activation energy is the exponent, when the effective rate constant is a product of elementary rate constants, their activation energies must be added (with related rules for division and powers).



### Problem 10 Enzyme kinetics

a) i)  $\frac{d[\text{ES}]}{dt} = k_1[\text{E}][\text{S}] - (k_{-1} + k_2)[\text{ES}]$

ii)  $\frac{d[\text{P}]}{dt} = k_2[\text{ES}]$

b)  $[\text{ES}] = \frac{[\text{S}][\text{E}]_0}{K_M + [\text{S}]}$

c)  $\frac{d[\text{P}]}{dt} = \frac{k_2[\text{E}]_0[\text{S}]}{K_M + [\text{S}]}$

d)  $\frac{d[\text{P}]}{dt} = \frac{V_{\text{max}}[\text{S}]}{K_M + [\text{S}]}$

- e) The extinction coefficient of the product is calculated to be  $9000 \text{ mol dm}^3\text{cm}^{-1}$

at 299 nm. The product concentrations at each time point and the initial rate of production at each concentration of GTP are given in the table below:

GTP concentration	200 $\mu\text{M}$	150 $\mu\text{M}$	100 $\mu\text{M}$	80 $\mu\text{M}$	60 $\mu\text{M}$	40 $\mu\text{M}$	20 $\mu\text{M}$
Time (s)	Product concentration ( $\mu\text{M}$ )						
6	0.571	0.521	0.494	0.437	0.419	0.288	0.219
7	0.648	0.608	0.530	0.504	0.431	0.281	0.274
8	0.787	0.710	0.631	0.562	0.502	0.343	0.281
9	0.776	0.781	0.710	0.657	0.579	0.361	0.328
10	0.909	0.889	0.788	0.717	0.638	0.430	0.336
11	1.00	0.982	0.836	0.780	0.709	0.494	0.391
12	1.14	1.02	0.943	0.857	0.786	0.550	0.429
	Initial rate ( $\mu\text{mol dm}^{-3} \text{s}^{-1}$ )						
	0.0910	0.0871	0.0755	0.0702	0.0640	0.0464	0.0328

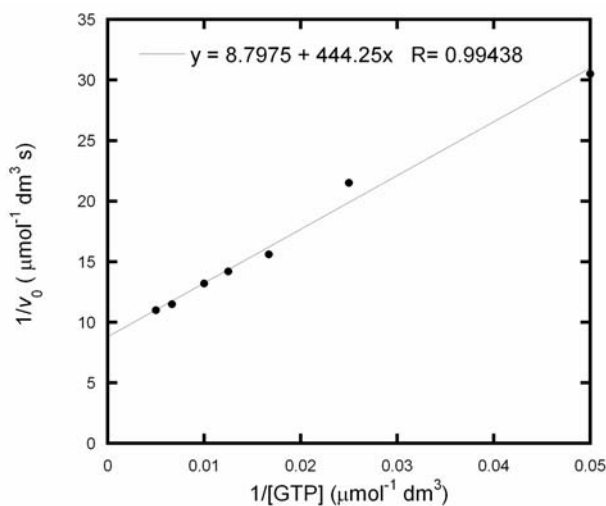
- f) There are a number of different linear forms for the equation obtained in part (d). Writing  $d[\text{P}]/dt$  as  $V$  The simplest form is:

$$\frac{1}{V} = \frac{K_M}{V_{\max} [S]} + \frac{1}{V_{\max}}$$

g)

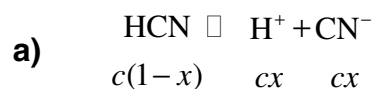
[GTP] ( $\mu\text{mol dm}^{-3}$ )	$V_0$ ( $\mu\text{mol dm}^{-3} \text{s}^{-1}$ )	$1/[\text{GTP}]$ ( $\mu\text{mol}^{-1} \text{dm}^3$ )	$1/V_0$ ( $\mu\text{mol}^{-1} \text{dm}^3 \text{s}$ )
20	0.0328	0.0500	30.5
40	0.0464	0.0250	21.5
60	0.0640	0.0167	15.6
80	0.0702	0.0125	14.2
100	0.0755	0.0100	13.2
150	0.0871	0.00667	11.5
200	0.0910	0.00500	11.0

Plotting  $1/V_0$  against  $1/[\text{GTP}]$  gives:



Therefore the value for  $V_{\max}$  is  $0.114 \mu\text{mol dm}^{-3} \text{s}^{-1}$  whilst that for  $K_M$  is  $50.5 \mu\text{mol dm}^{-3}$ .

**Problem 11 Hydrocyanic acid**



$$K_a = \frac{cx^2}{(1-x)} \Rightarrow cx^2 + K_a x - K_a = 0$$

$$\Rightarrow x = \frac{-K_a + \sqrt{K_a^2 + 4K_a c}}{2c}$$

$$[\text{H}^+] = cx = 2.22 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 4.65 \quad \text{Acceptable to ignore } [\text{OH}^-]$$

b)

(1)  $[\text{H}^+][\text{CN}^-] = K_a[\text{HCN}]$

(2)  $[\text{H}^+][\text{OH}^-] = K_w$

(3)  $[\text{H}^+] + [\text{Na}^+] = [\text{CN}^-] + [\text{OH}^-]$

(4)  $[\text{Na}^+] = [\text{CN}^-] + [\text{HCN}]$

(5)  $[\text{H}^+] = 3.98 \times 10^{-8} \text{ M}$

From (2)  $[\text{OH}^-] = 2.51 \times 10^{-7} \text{ M}$

From (1)  $[\text{HCN}] = \frac{[\text{H}^+][\text{CN}^-]}{K_a} = 80.8 [\text{CN}^-]$

From (3)  $[\text{Na}^+] = [\text{CN}^-] + 2.11 \times 10^{-7} \text{ M}$

From (4)  $[\text{HCN}] = 2.11 \times 10^{-7} \text{ M}$

Hence  $[\text{CN}^-] = 2.62 \times 10^{-9} \text{ M}$ ,  $[\text{Na}^+] = 2.14 \times 10^{-7} \text{ M}$

Hence 10 L contains  $2.14 \times 10^{-6} \text{ mol} = 0.105 \text{ mg}$

**Problem 12 Chlorine electrochemistry**

b) The difference between the alkaline and acidic perchlorate half cells is

	$E^\circ / \text{V}$	$\Delta G^\circ / \text{kJ mol}^{-1}$
$\text{ClO}_4^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	0.37	-71.4
$\text{ClO}_4^- + 2\text{H}^+ + 2e^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	1.20	-231.6
$2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^-$		+80.1

Hence  $K_w = 9.2 \times 10^{-15}$ .

ii) Alkaline conditions

	$E^\circ / \text{V}$	$\Delta G^\circ / \text{kJ mol}^{-1}$
$\frac{1}{2}\text{Cl}_2 + e^- \rightarrow \text{Cl}^-$	1.36	-131.2
$\text{ClO}^- + \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{Cl}_2 + 2\text{OH}^-$	0.42	-40.5
$\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$		-90.7

Hence  $K_c = 7.9 \times 10^{15}$ .

Acidic conditions

	$E^\circ / \text{V}$	$\Delta G^\circ / \text{kJ mol}^{-1}$
$\frac{1}{2}\text{Cl}_2 + e^- \rightarrow \text{Cl}^-$	1.36	-131.2
$\text{HOCl} + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$	1.63	-157.3
$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+$		+26.1

Hence  $K_c = 2.7 \times 10^{-5}$ .

iii) The  $\text{p}K_a$  value for HOCl.

	$\Delta G^\circ / \text{kJ mol}^{-1}$
$\text{HOCl} + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$	-157.3

$\text{ClO}^- + \text{H}_2\text{O} + e \rightarrow \frac{1}{2}\text{Cl}_2 + 2\text{OH}^-$	-40.5
$\text{HOCl} + \text{H}^+ + 2\text{OH}^- \rightarrow \text{ClO}^- + 2\text{H}_2\text{O}$	-116.8
$2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^-$	+160.2
$\text{HOCl} \rightarrow \text{H}^+ + \text{ClO}^-$	+43.4

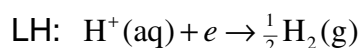
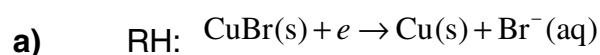
$$K_a = 2.4 \times 10^{-8} \text{ and } \text{p}K_a = 7.61$$

(iv) With this value of  $K_a$ , at pH 7.5 we have the ratio  $[\text{HOCl}]/[\text{OCl}^-] = 1.29$ , thus  $[\text{HOCl}] = 0.113 \text{ mM}$  and  $[\text{OCl}^-] = 0.087 \text{ mM}$ .

$$E = E^\circ - \frac{RT}{F} \ln \left( \frac{a_{\text{Cl}_2}^{1/2}}{[\text{HOCl}][\text{H}^+]} \right) \text{ or } E = E^\circ - \frac{RT}{F} \ln \left( \frac{a_{\text{Cl}_2}^{1/2} [\text{OH}^-]^2}{[\text{OCl}^-]} \right)$$

In either case, taking the activity of chlorine as 1, the result is 1.13 V.

### Problem 13 The solubility of CuBr



$$E = E^\circ - \frac{RT}{F} \ln \left( \frac{[\text{H}^+][\text{Br}^-]}{p_{\text{H}_2}^{1/2}} \right) \quad E^\circ = +0.086 \text{ V}$$



$$\Delta G^\circ(\text{CuBr(s)} + e \rightarrow \text{Cu(s)} + \text{Br}^-(\text{aq})) = -8.3 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ(\text{Cu}^+(\text{aq}) + e \rightarrow \text{Cu(s)}) = -50.4 \text{ kJ mol}^{-1}$$

Taking the difference

$$\Delta G^\circ(\text{CuBr}(s) + e \rightarrow \text{Cu}^+(\text{aq}) + \text{Br}^-(\text{aq})) = +42.1 \text{ kJ mol}^{-1}.$$

Using  $\Delta G^\circ = -RT \ln K_s$ ,  $K_s = 4.2 \times 10^{-8}$

b) Since  $[\text{Br}^-(\text{aq})] = 1.0 \times 10^{-4} \text{ M}$ ,  $[\text{Cu}^+] = 4.2 \times 10^{-4} \text{ M}$

c) Using the Nernst equation,  $E_2 - E_1 = \frac{RT}{F} \ln \left( \frac{p_2^{1/2}}{p_1^{1/2}} \right) = \frac{RT}{2F} \ln 2 = .0089 \text{ V}$

### Problem 14 Electrochemical equilibria

a)  $\text{Fe}^{3+}(\text{aq}) + e \rightarrow \text{Fe}^{2+}(\text{aq}); E^\circ = +0.770 \text{ V}; \Delta G^\circ = -74.3 \text{ kJ mol}^{-1}$

$$\text{Fe}^{3+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(\text{aq}); K_c = 7.9 \times 10^{43}; \Delta G^\circ = -250.4 \text{ kJ mol}^{-1}$$

$$\text{Fe}^{2+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(\text{aq}); K_c = 7.9 \times 10^{36}; \Delta G^\circ = -210.5 \text{ kJ mol}^{-1}$$

Hence, from the cycle:  $\text{Fe}(\text{CN})_6^{3-}(\text{aq}) + e \rightarrow \text{Fe}(\text{CN})_6^{4-}(\text{aq}); \Delta G^\circ = -34.4 \text{ kJ mol}^{-1};$   
 $E^\circ = +0.356 \text{ V}$

b) (1)  $\text{In}^+(\text{aq}) + e^- \rightleftharpoons \text{In}(s) \quad E^\circ = -0.13 \text{ V}, \Delta G^\circ = 12.5 \text{ kJ mol}^{-1}$

(2)  $\text{In}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{In}(s) \quad E^\circ = -0.34 \text{ V}, \Delta G^\circ = 98.4 \text{ kJ mol}^{-1}$

To balance  $3 \times (1) - (2)$ .

$$3\text{In}^+(\text{aq}) + 3e^- \rightleftharpoons 2\text{In}(s) + \text{In}^{3+}(\text{aq}) \quad \Delta G^\circ = -60.8 \text{ kJ mol}^{-1}$$

$$K_c = 4.5 \times 10^{10}$$

(1)  $\text{Tl}^+(\text{aq}) + e^- \rightleftharpoons \text{Tl}(s) \quad E^\circ = -0.34 \text{ V}, \Delta G^\circ = 32.8 \text{ kJ mol}^{-1}$

(2)  $\text{Tl}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Tl}(s) \quad E^\circ = +0.72 \text{ V}, \Delta G^\circ = -208.4 \text{ kJ mol}^{-1}$

$$3\text{Tl}^+(\text{aq}) + 3e^- \rightleftharpoons 2\text{Tl}(s) + \text{Tl}^{3+}(\text{aq}) \quad \Delta G^\circ = +306.8 \text{ kJ mol}^{-1}$$

### Problem 15 Photodissociation of $\text{Cl}_2$

a) the kinetic energy of the ions is  $eV = \frac{1}{2}mv^2$ ,

so  $v = (2eV/m)^{1/2} = 128\,600 \text{ m s}^{-1}$ .

The distance the ions fly is  $d = 0.4\text{m}$ , so the flight time is  $t = d/v = 3.11\ \mu\text{s}$ .

**b)** The atoms travel a radial distance of  $6.34\ \text{mm}$  in  $3.11\ \mu\text{s}$ , so their velocity is  $v_{\text{Cl}} = 2038\ \text{m s}^{-1}$ .

**c)** Conservation of energy requires that  $h\nu - D_0 = 2\ (\frac{1}{2} m_{\text{Cl}} v_{\text{Cl}}^2)$ .

From the data given,  $D_0 = 4.035 \times 10^{-19}\ \text{J}$  ( $2.519\ \text{eV}$ ),  $m_{\text{Cl}} = 5.812 \times 10^{-26}\ \text{kg}$ ,

$$v_{\text{Cl}} = 2038\ \text{m s}^{-1}.$$

The photon energy is therefore  $h\nu = 6.449 \times 10^{-19}\ \text{J}$  ( $4.026\ \text{eV}$ ), corresponding to a wavelength  $\lambda = hc/E$  of  $308\ \text{nm}$ .

### Problem 16 Laser Cooling

**a)**  $E = \frac{3}{2}kT = 1.81 \times 10^{-20}\ \text{J}$

$$p = \sqrt{2mE} = 4.90 \times 10^{-23}\ \text{kg m s}^{-1}$$

$$v = p/m = 738\ \text{m s}^{-1}$$

**b)**  $v = c/\lambda = 7.5522 \times 10^{14}\ \text{Hz}$

$$E = h\nu = 5.0042 \times 10^{-19}\ \text{J}$$

$$p = h/\lambda = 1.6692 \times 10^{-27}\ \text{kg m s}^{-1}$$

**c)** At each cycle the mean momentum of the ion is reduced by the momentum of the photon it has absorbed. The re-emission is isotropic and has no effect on the mean momentum.

$$\Delta p_{\text{atom}} = -1.6692 \times 10^{-27}\ \text{kg m s}^{-1}$$

$$\Delta v_{\text{atom}} = \Delta p_{\text{atom}}/m = -2.5156 \times 10^{-2}\ \text{m s}^{-1}$$

To slow the ion to rest therefore takes approximately  $2.93 \times 10^4$  photons.

**d)**  $\text{Ca}^+$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ .

$$l = 0, \text{ hence } \hbar\sqrt{l(l+1)} = 0$$



$$s = 1/2, \text{ hence } \hbar\sqrt{s(s+1)} = \hbar\frac{\sqrt{3}}{2}$$

e) For an electron in a p orbital,  $l = 1$ , hence  $\hbar\sqrt{l(l+1)} = \hbar\sqrt{2}$

$$s = 1/2, \text{ hence } \hbar\sqrt{s(s+1)} = \hbar\frac{\sqrt{3}}{2}$$

f)  $j = 1/2$  (antiparallel)

$j = 3/2$  (parallel)

g) The first transition was calculated in (b):  $E = h\nu = 5.0042 \times 10^{-19}$  J

The second transition is  $E = hc/\lambda = 5.0484 \times 10^{-19}$  J

The energy difference is  $\Delta E = 4.43 \times 10^{-21}$  J

### Problem 17 Hydrogen bond strength determination

a)  $\delta_{\text{obs}} = x_{\text{h}}\delta_{\text{h}} + x_{\text{f}}\delta_{\text{f}}$

where  $x_{\text{h}}$  and  $x_{\text{f}}$  are the mole fractions of the hydrogen bonded species and the free species respectively and so  $x_{\text{h}} + x_{\text{f}} = 1$ .

b)  $K = \frac{x_{\text{h}}}{x_{\text{f}}}$

$$\delta_{\text{obs}} = x_{\text{h}}\delta_{\text{h}} + x_{\text{f}}\delta_{\text{f}} = x_{\text{h}}\delta_{\text{h}} + (1 - x_{\text{h}})\delta_{\text{f}} \Rightarrow x_{\text{h}}(\delta_{\text{h}} - \delta_{\text{f}}) = \delta_{\text{obs}} - \delta_{\text{f}}$$

also

$$\delta_{\text{obs}} = (1 - x_{\text{f}})\delta_{\text{h}} + x_{\text{f}}\delta_{\text{f}} \Rightarrow x_{\text{f}}(\delta_{\text{f}} - \delta_{\text{h}}) = \delta_{\text{obs}} - \delta_{\text{h}}$$

$$\begin{aligned} K &= \frac{x_{\text{h}}}{x_{\text{f}}} = \frac{\delta_{\text{obs}} - \delta_{\text{f}}}{\delta_{\text{h}} - \delta_{\text{f}}} \times \frac{\delta_{\text{f}} - \delta_{\text{h}}}{\delta_{\text{obs}} - \delta_{\text{h}}} = \frac{\delta_{\text{obs}} - \delta_{\text{f}}}{\delta_{\text{h}} - \delta_{\text{f}}} \times \frac{\delta_{\text{h}} - \delta_{\text{f}}}{\delta_{\text{h}} - \delta_{\text{obs}}} \\ &= \frac{\delta_{\text{obs}} - \delta_{\text{f}}}{\delta_{\text{h}} - \delta_{\text{obs}}} \end{aligned}$$

c)

$T / \text{K}$	$\delta_{\text{obs}}$	$K$
220	6.67	0.5607
240	6.5	0.4211
260	6.37	0.3300
280	6.27	0.2676
300	6.19	0.2217

d) A plot of  $\ln K$  vs  $1/T$  gives a straight line with slope  $(= -\Delta_r H^\circ / R) = 764.1 \text{ K}$  [and intercept  $(= \Delta_r S^\circ / R) = -4.050$ ].

$$\Delta_r H^\circ = -764.1 \times 8.3145 \text{ J mol}^{-1} = -6.4 \text{ kJ mol}^{-1}$$

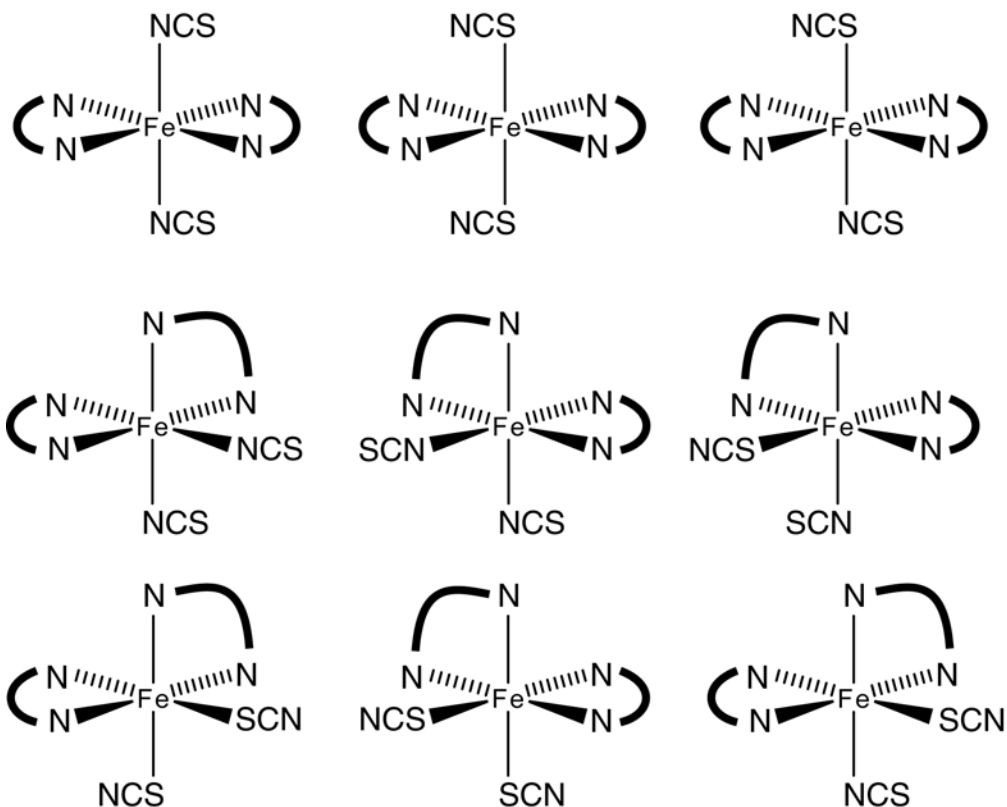
$$\Delta_r S^\circ_{(300)} = ((\Delta_r H^\circ - \Delta_r G^\circ_{(300)}) / 300) \text{ J K}^{-1} \text{ mol}^{-1} = -34 \text{ J K}^{-1} \text{ mol}^{-1}$$

e) The enthalpy change is exothermic, which is not surprising since a new bond is formed. However, the value is much smaller than that for forming a full covalent bond.

The entropy change is negative due to the loss of rotational freedom as the chain becomes a ring.

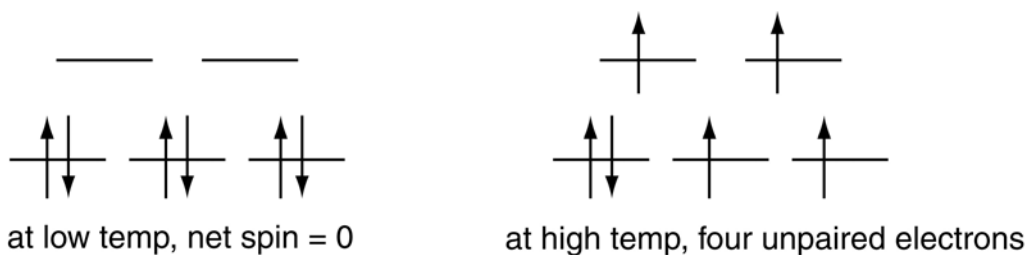
### Problem 18 Magnetic Complexes

a) The NCS ligand could bond either through the sulfur, or through the nitrogen. Representing the bidentate phenanthroline ligand as a line between two adjacent sites on the octahedral complex gives the following isomers.



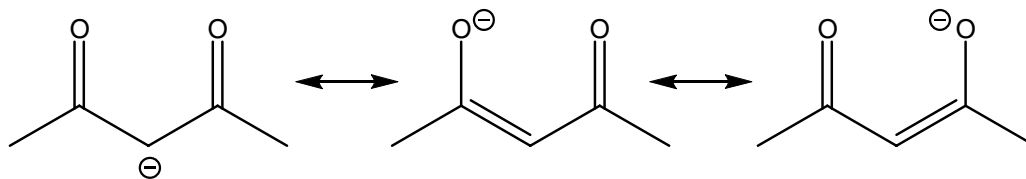
b) Since the iron is in the +2 state, the number of d electrons the Fe contributes is 6.

c)  $\mu_{\text{eff}} = 4.9 \text{ B.M.} = \sqrt{n(n+2)}$ . Solving gives  $n = 4$ .



d & e) Unfortunately, this question is rather vague. Hund's Rules of maximum multiplicity apply only to degenerate orbitals; the Pauli exclusion principle is always obeyed.

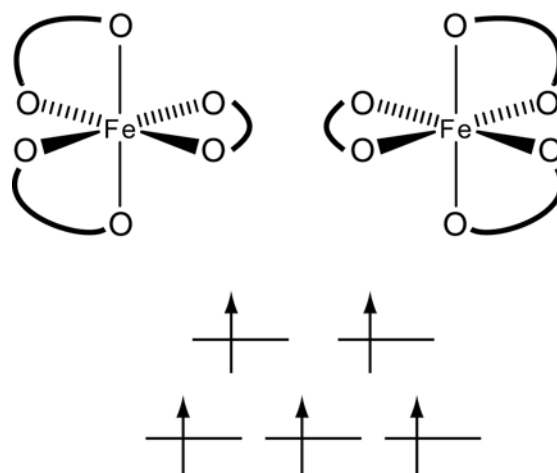
f)



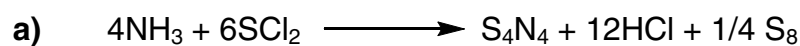
g)



h)  $\mu_{\text{eff}} = 5.9 \text{ B.M.} = \sqrt{n(n+2)}$ . Solving gives  $n = 5$ .



### Problem 19 Explosive $\text{S}_4\text{N}_4$



could also be written with the extra ammonia molecules needed to react with the product HCl. i.e.:



b) To form one mole of  $\text{S}_4\text{N}_4$  from the elements requires breaking 4 S–S bonds, two  $\text{N}\equiv\text{N}$  bonds and forming 4 S=N bonds and 4 S–N bonds:

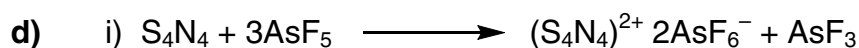
$$\Delta_f H^\circ = 4(226) + 2(946) - 4(328) - 4(273) = 392 \text{ kJ mol}^{-1}$$

(This value is somewhat out due to the imprecise nature of the bond strengths.)

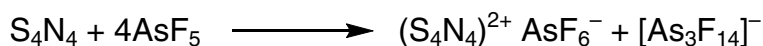
c) For the reaction as first written in a)

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{S}_4\text{N}_4) + 12\Delta_f H^\circ(\text{HCl}) + 1/4 \Delta_f H^\circ(\text{S}_8) - 4\Delta_f H^\circ(\text{NH}_3) - 6\Delta_f H^\circ(\text{SCl}_2)$$

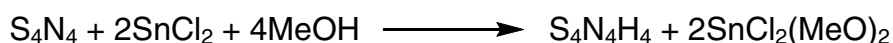
$$392 + 12(-92.3) + 0 - 4(-45.9) - 6(-50.0) = -232 \text{ kJ mol}^{-1}$$



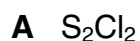
further complexation occurs with the  $\text{AsF}_3$  with  $\text{AsF}_5$  and  $\text{AsF}_6^-$  so the reaction may also be written:



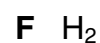
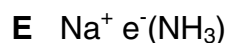
ii) During this reaction, the Sn(II) becomes oxidised to Sn(IV):



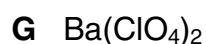
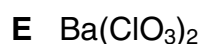
### Problem 20 Sulfur compounds

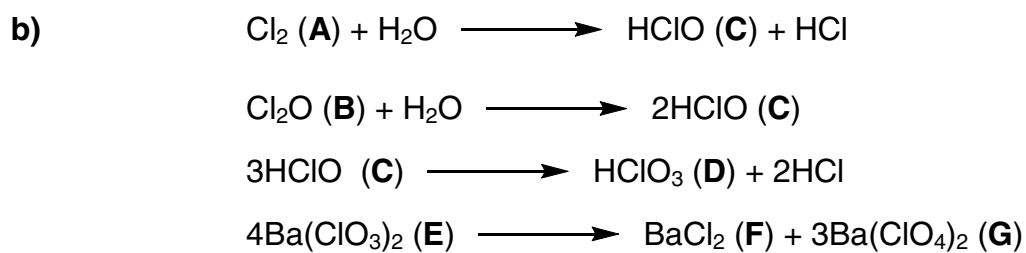


### Problem 21 Reactions of sodium



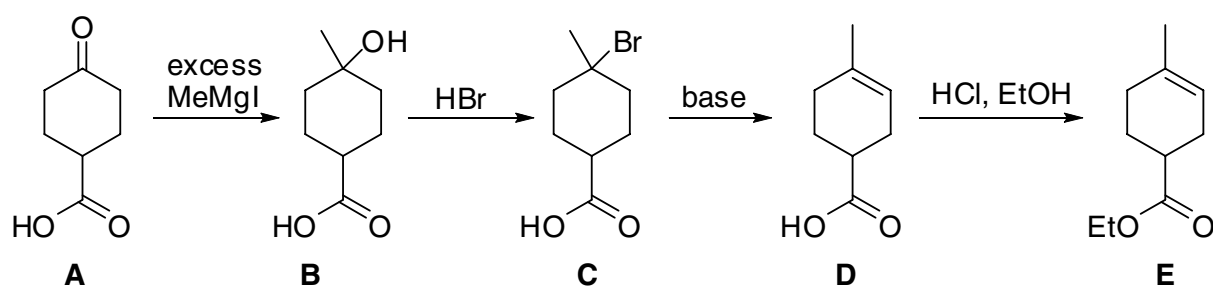
### Problem 22 Chlorine compounds



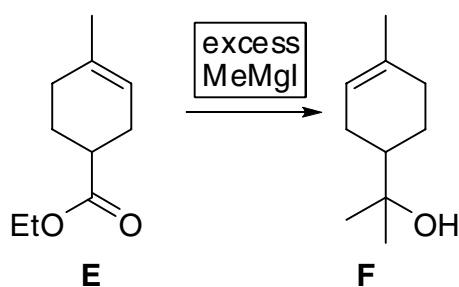


**Problem 23 Perkin Junior**

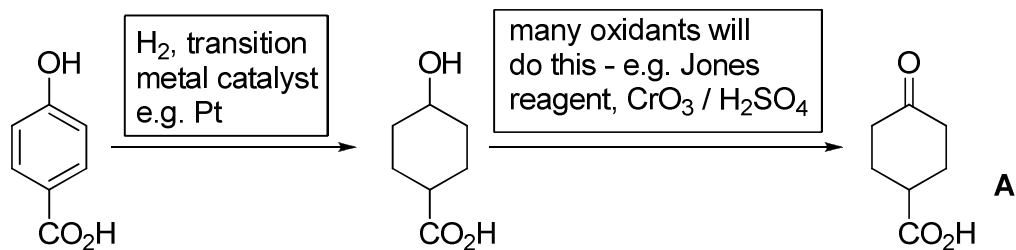
a)



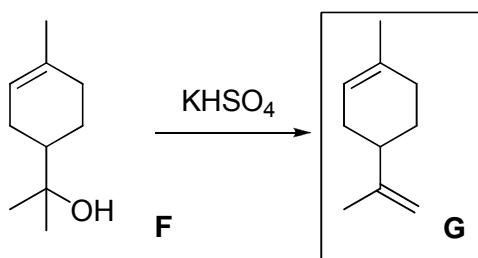
b)



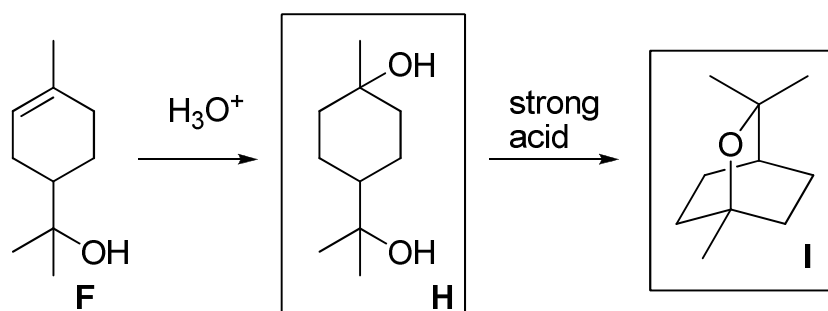
c)



d)

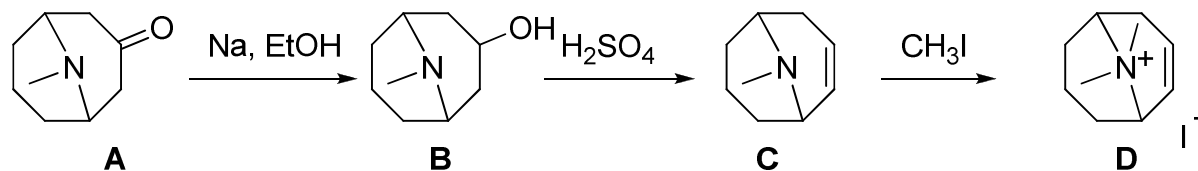


e)

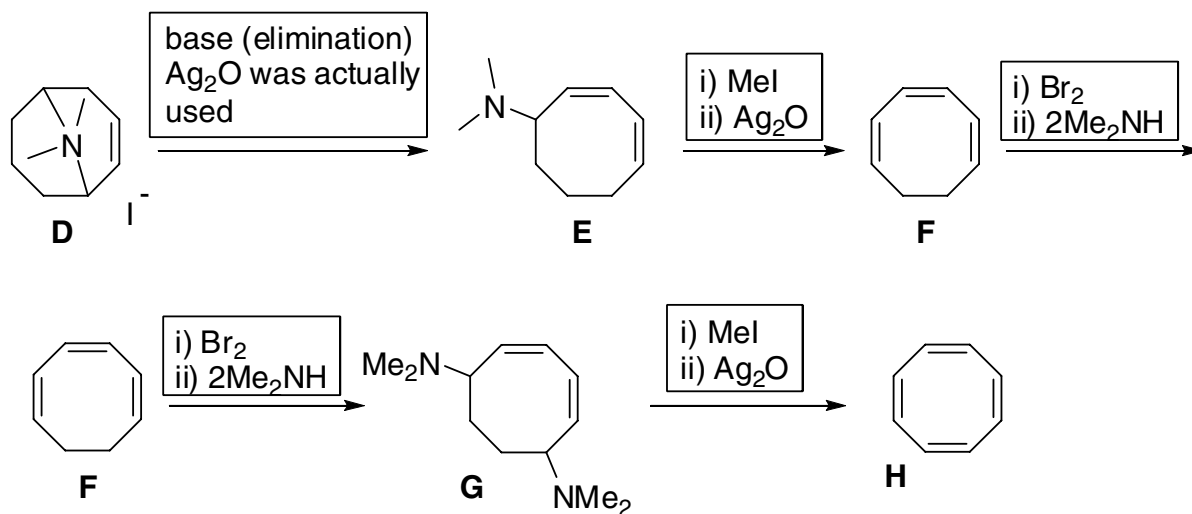


### Problem 24 Cyclooctatetraene

a)

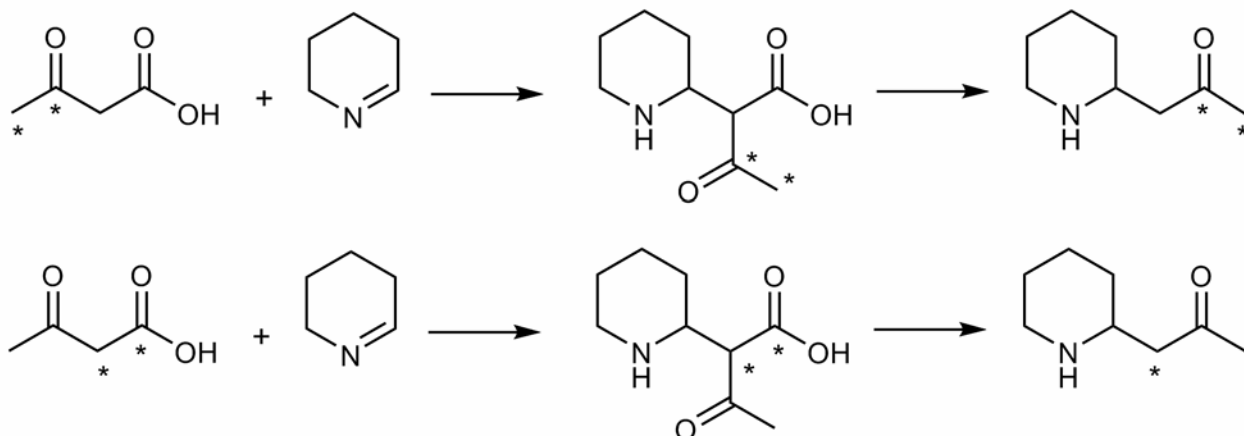


b)



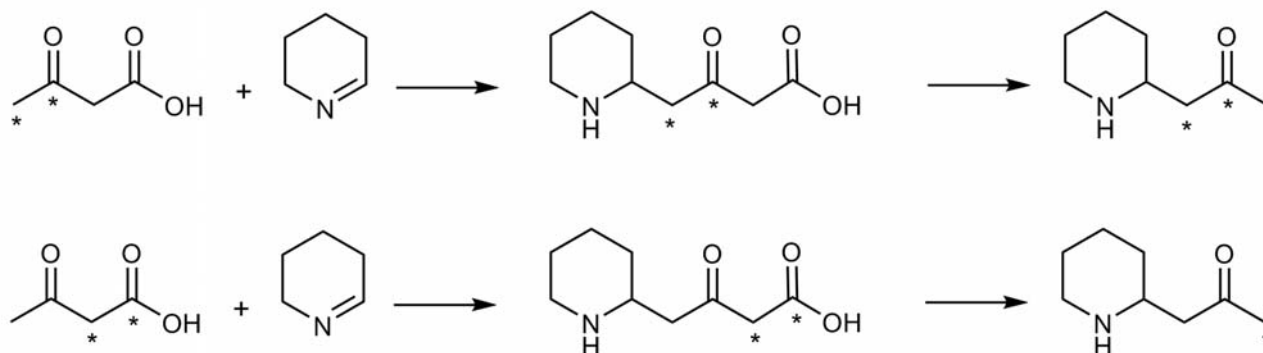
c) The positions at which  $^{13}\text{C}$  labels would appear if each of the biosynthetic routes were followed are indicated with an asterisk:

Route I

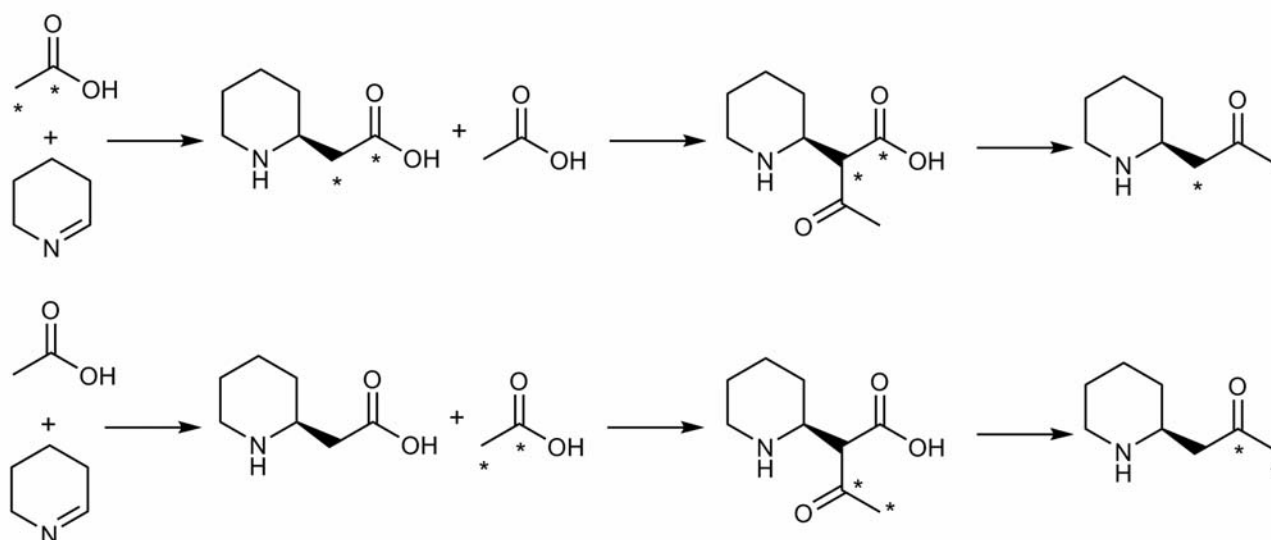




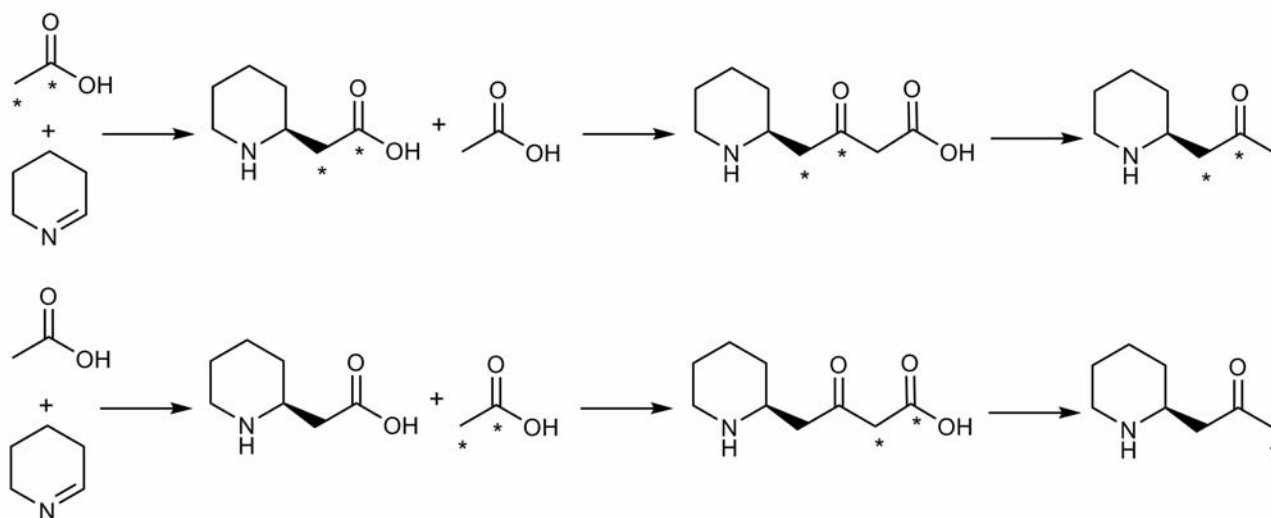
Route II



Route III



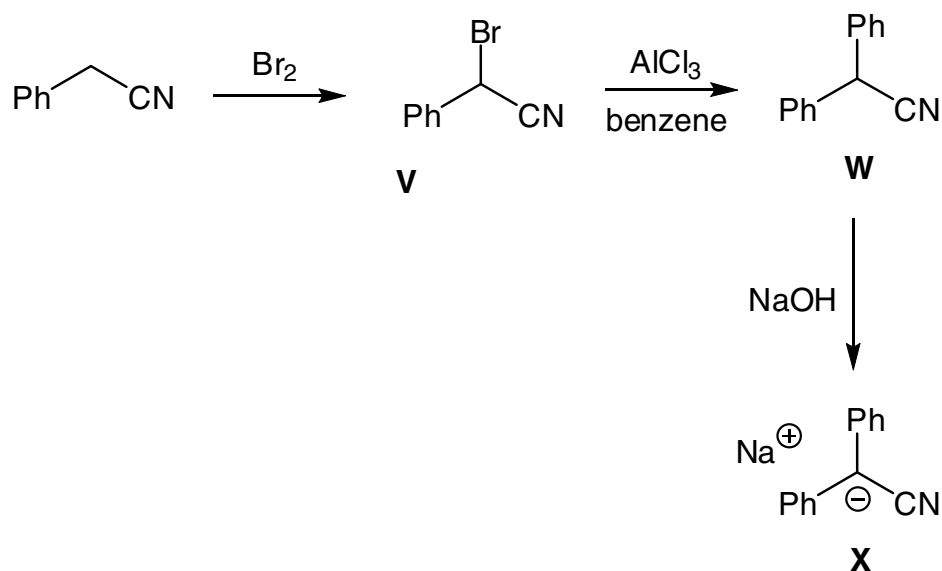
Route IV



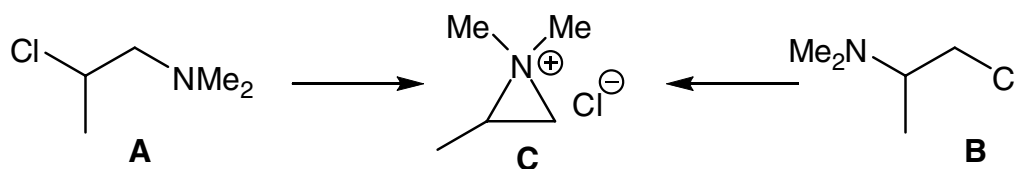
- d) Routes I & III can be distinguished from II & IV in this experiment.
- e) Routes I & II can be distinguished from III & IV in this experiment.
- f) The additional peaks in the NMR spectra from experiments 1 and 2 arise from coupling between  $^{13}\text{C}$  nuclei. Experiment 1 shows that carbon k and j are  $^{13}\text{C}$  labelled thus pelletierene must be synthesised via route I or route III. In experiment 2 a  $^{13}\text{C}$  label is seen at carbon j, k and l showing that the biosynthesis proceeds via route I.

**Problem 25 The synthesis of methadone**

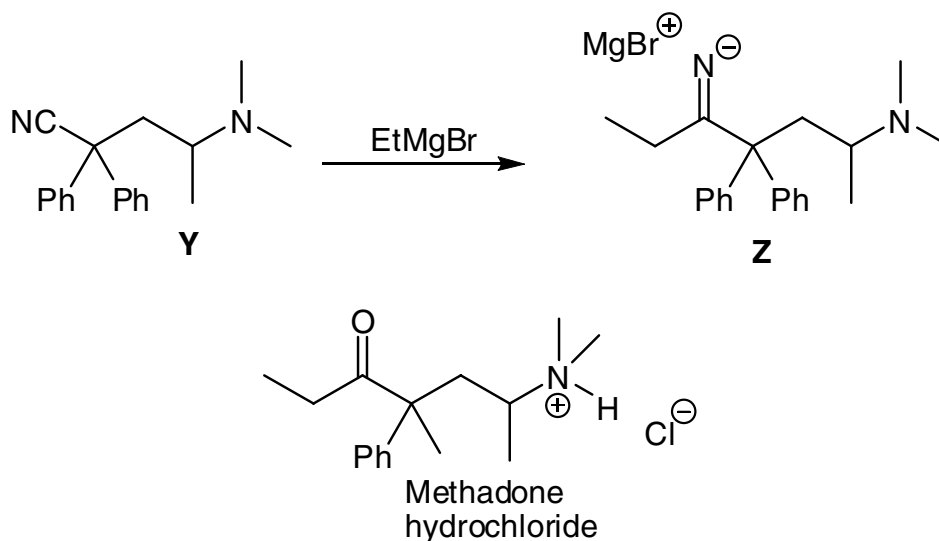
a)



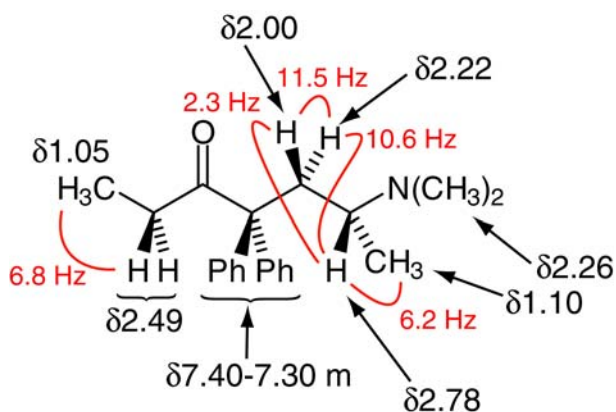
b)



c)

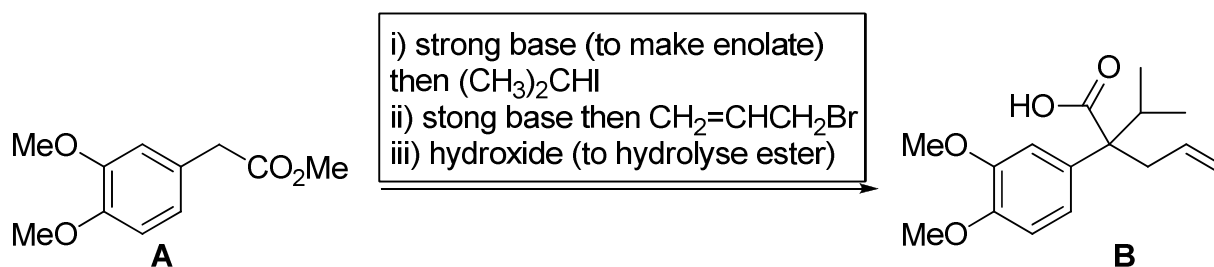


**d and e)** The structure and spectral assignment of *R*-methadone is shown below.

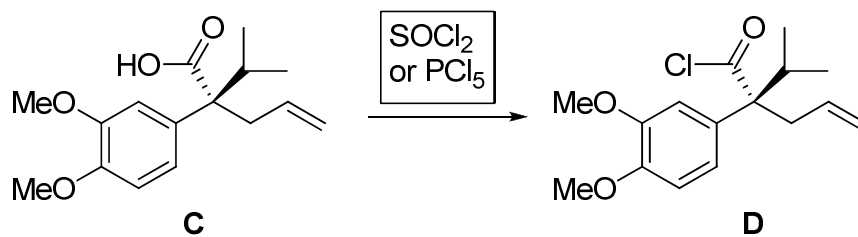


### Problem 26 Verapamil

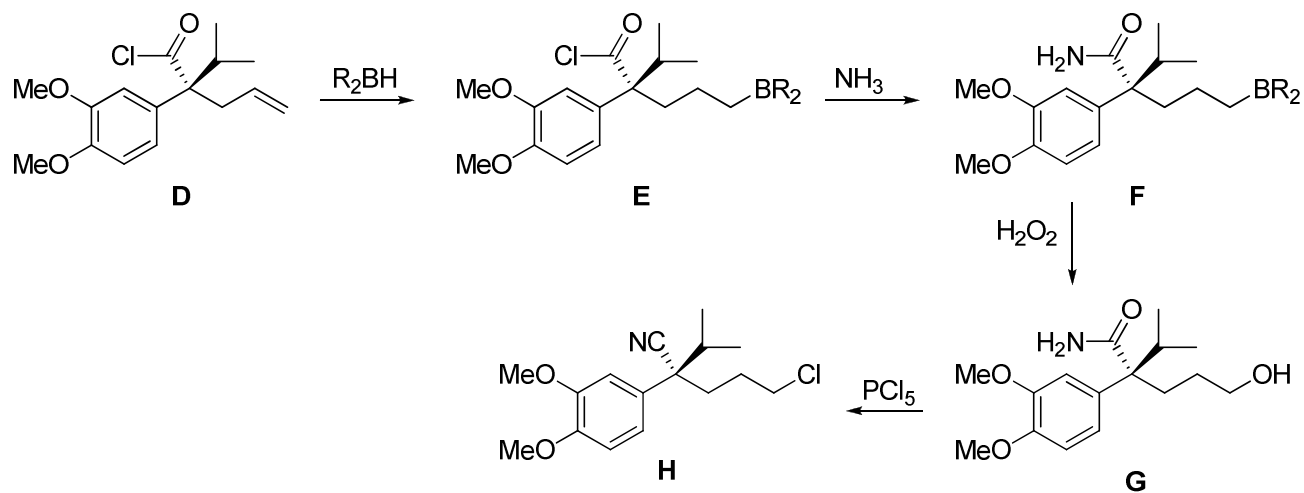
a)



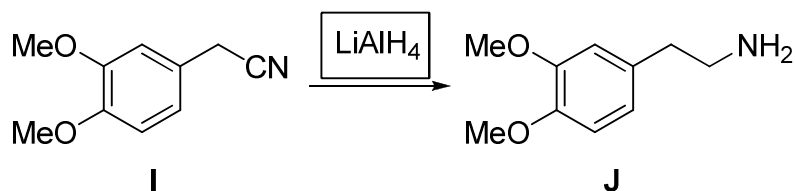
b)



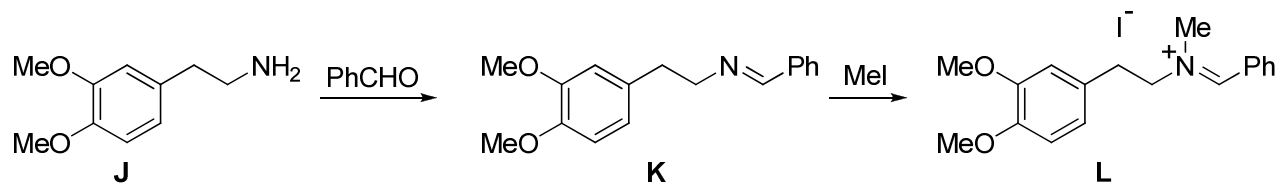
c)



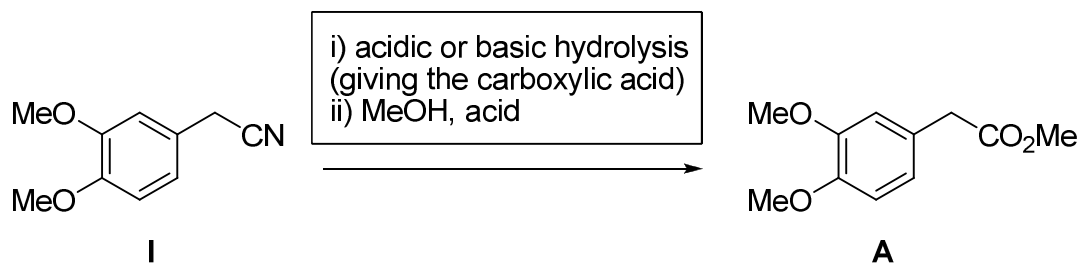
d)



e)



f)



**Problem 27** *Mass spectrometry of a peptide*

- a)
- i) If Glx are both the same amino acid then the number of unique sequences is given by  $10!/(4! \times 2!)$ . This gives 75600 sequences.
- ii) If Glx are two different amino acids then the number of unique sequences is given by  $10!/4!$ . This gives 151200 sequences.
- b) There are six possible peptides that could be formed depending upon the identity of Asx and Glx:

Amino Acids	Peptide mass	Amino Acids	Peptide Mass
Asn, Gln, Gln	1213	Asp, Gln, Gln	1214
Asn, Gln, Glu	1214	Asp, Gln, Glu	1215
Asn, Glu, Glu	1215	Asp, Glu, Glu	1216

- c) The mass of ion b1 can be used to determine the identity of the first amino acid in the polypeptide:

$$M_r(\text{amino acid 1}) = \text{mass}(b1) + M_r(\text{O}) + M_r(\text{H}) = 129.2.$$

This does not correspond to the mass of any of the 20 amino acids typically found in proteins, therefore amino acid 1 must be Mod.

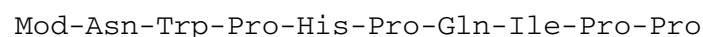
The identity of amino acids 2 to 9 can be determined using consecutive b-ions:

ion	m/z	Mass difference between b(n) and b(n-1)	Number of corresponding amino acid in sequence	Mass of amino acid
b9	1082.2	97.2	9	115.2
b8	985	113	8	131.0
b7	872	128.2	7	146.2
b6	743.8	97.1	6	115.1
b5	646.7	137	5	155.0
b4	509.7	97.2	4	115.2
b3	412.5	186.1	3	204.1
b2	226.4	114.2	2	132.2
b1	112.0			

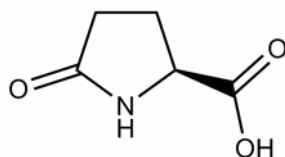
Finally the identity of amino acid 10 can be verified using the masses of the polypeptide X and ion b9:

$$M_r(\text{amino acid 1}) = M_r(\mathbf{X}) - \text{mass}(\text{b9}) + M_r(\text{H}) = 115.6.$$

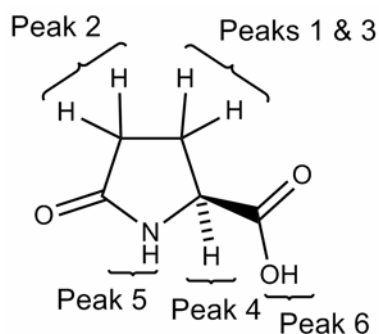
The sequence is therefore:



- d)** The mass of the modified amino acid is 129.2.
- e)** It is known from the amino acid composition that Mod must be based on Gln or Glu. The mass and NMR spectra are consistent with the cyclic amino acid usually referred to as pyroglutamic acid:



- f) If the peaks in the  $^1\text{H}$  NMR spectrum of mod in organic solvent are numbered 1 to 6 from low to high chemical shift then the assignment is as follows:



Candidates are not expected to be able to completely assign peaks 1 and 3.

### Problem 28 A fossilized peptide

- a) The mass of ion y1 can be used to determine the identity of the last amino acid in the polypeptide. The y1 ion is one mass unit larger in size than the corresponding amino acid; therefore the last amino acid must be Arg.

The y-series of ions is the most complete, comparison of the masses of consecutive y-ions can be used to determine the sequence:

ion	m/z	Mass difference between y(n) and y(n-1)	Corresponding amino acid	Mass of amino acid
y1	175.1			
y2	272.2	97.1	18	115.1
y3	401.2	129.0	17	147.0
y4				
y5	611.4			

y6	726.4	115.0	14	133.0
y7	823.4	97.1	13	115.1
y8	986.5	163.1	12	181.1
y9	1083.5	97.1	11	115.1
y10				
y11	1267.6			
y12	1338.7	71.0	8	89.0
y13	1395.7	57.0	7	75.0
y14	1508.8	113.1	6	131.1
y15	1694.9	186.1	5	204.1
y16	1831.9	137.1	4	155.1
y17	1946.9	115.0	3	133.0

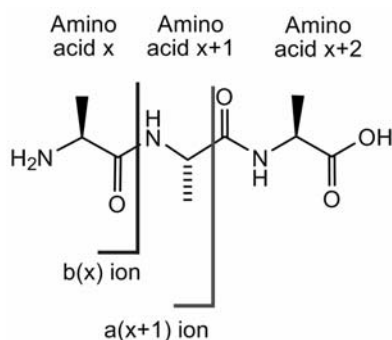
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From the y-series the sequence is:

Tyr-Leu-Asp-His-Trp-Leu/Ile/Hyp-Gly-Ala-xxx-xxx-Pro-Tyr-Pro-Asp-xxx-xxx-Glu-Pro-Arg

The identity of the 15<sup>th</sup> amino acid in the sequence can be determined from the difference in mass between b14 and a15:





$$M_r(\text{amino acid 15}) = \text{mass}(a_{15}) - \text{mass}(a_{14}) + M_r(\text{C}) + 2M_r(\text{O}) + 2M_r(\text{H}) = 115.0$$

Therefore amino acid 15 must be Pro.

The difference in mass between ions  $y_3$  and  $y_5$  gives the mass of the fragment corresponding to amino acids 15 and 16.

$$M_r(\text{15-16 dipeptide}) = \text{mass}(y_5) - \text{mass}(y_3) + M_r(\text{H}_2\text{O})$$

$$M_r(\text{amino acid 16}) = M_r(\text{15-16 dipeptide}) - M_r(\text{amino acid 15}) + M_r(\text{H}_2\text{O}) = 131.1$$

Amino acid 16 must therefore be Ile, Leu or Hyp.

The mass of amino acid 10 can be determined from the difference in mass between  $b_9$  and  $b_{10}$ :

$$M_r(\text{amino acid 10}) = \text{mass}(b_{10}) - \text{mass}(b_9) + M_r(\text{H}_2\text{O})$$

Amino acid 10 is Ala.

The difference in mass between ions  $y_{11}$  and  $y_9$  gives the mass of the fragment corresponding to amino acids 9 and 10.

$$M_r(\text{9-10 dipeptide}) = \text{mass}(y_{11}) - \text{mass}(y_9) + M_r(\text{H}_2\text{O})$$

$$M_r(\text{amino acid 9}) = M_r(\text{9-10 dipeptide}) - M_r(\text{amino acid 10}) + M_r(\text{H}_2\text{O})$$

Amino acid 9 has a mass of 131.1, so must be Ile, Leu or Hyp.

The sequence of the polypeptide is therefore:

Tyr-Leu-Asp-His-Trp-Leu/Ile/Hyp-Gly-Ala-Leu/Ile/Hyp-Ala-Pro-Tyr-Pro-Asp-Pro-Leu/Ile/Hyp-Glu-Pro-Arg

**b)** The sequence is most similar to that of the horse.

**Problem 29 Creatine kinase**

- a) Let  $n_0$  be the initial number of moles of ATP and  $x$  the number of moles that of ATP that have formed ATP at equilibrium

	ATP	ADP	Pi	Total
Initial	$n_0$	0	0	$n_0$
Equilibrium	$n_0 - x$	$x$	$x$	$n_0 + x$

Therefore:

$$K' = \frac{\left( \frac{x^2}{(n_0 + x)^2} \right)}{\left( \frac{n_0 - x}{n_0 + x} \right)}$$

Which rearranges to give:

$$x = \sqrt{\frac{Kn_0^2}{K+1}}$$

Hence  $[\text{ADP}] = [\text{P}_i] = 9.99996377 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{ATP}] = 3.62 \times 10^{-8} \text{ mol dm}^{-3}$

- b)  $-30.503 \text{ kJ mol}^{-1}$ .

**c & d)**

In order to calculate the  $[\text{ADP}]$ , the  $[\text{creatine}]$  is first calculated from the  $[\text{phosphocreatine}]$  measured in the  $^{31}\text{P}$  NMR spectrum and the total concentration of creatine and phosphocreatine in the cell.

The equilibrium constant for the creatine kinase reaction is then used in conjunction with  $[\text{creatine}]$ ,  $[\text{ATP}]$  and  $[\text{phosphocreatine}]$  to determine  $[\text{ADP}]$ .

Finally these concentrations and the value for  $\Delta_r G^{\circ}(\text{ATP})$  calculated in part b) are used to determine  $\Delta_r G'(\text{ATP})$ :

Condition	[phosphocreatine] mol dm <sup>-3</sup>	[ATP] mol dm <sup>-3</sup>	[Pi] mol dm <sup>-3</sup>	[creatine] mol dm <sup>-3</sup>	[ADP] mol dm <sup>-3</sup>	$\Delta_r G'$ (ATP) kJ mol <sup>-1</sup>
Rest	$3.82 \times 10^{-2}$	$8.20 \times 10^{-3}$	$4.00 \times 10^{-3}$	$4.30 \times 10^{-3}$	$5.54 \times 10^{-6}$	-63.5
Light exercise	$2.00 \times 10^{-2}$	$8.50 \times 10^{-3}$	$2.20 \times 10^{-2}$	$2.25 \times 10^{-2}$	$5.74 \times 10^{-5}$	-53.2
Heavy exercise	$1.00 \times 10^{-2}$	$7.70 \times 10^{-3}$	$3.50 \times 10^{-2}$	$3.25 \times 10^{-2}$	$1.50 \times 10^{-4}$	-49.3

- e) The data show an increase in the value of  $\Delta_r G'$ (ATP) when subjects undertake both light and heavy exercise, and the increase is greater after heavy exercise which would appear to support the hypothesis. However the increase in  $\Delta_r G'$ (ATP) is similar for both intensities of exercise, and in both cases the value of  $\Delta_r G'$ (ATP) is large and negative, so it is difficult to draw a firm conclusion from this limited data set. In fact, in the cell there is a large pH change after exercise and when this is taken into account the values of  $\Delta_r G'$ (ATP) are within error after both light and heavy exercise. Further experiments suggest that the rate of recovery of the concentration of metabolites such as creatine to resting levels plays an important role in exercise induced exhaustion.