

## AUSTRALIAN CHEMISTRY OLYMPIAD

### QUALIFYING EXAMINATION

1991

#### General Instructions

- (1) This paper is in **two** sections and you must answer each section according to the instructions. *ie.* Answer **ALL** questions in section A and **any three** (3) in section B.
- (2) All answers must be written in the space provided in the answer book.
- (3) **Use blue or black pen to write your answers**, pencil is not acceptable.
- (4) Rough working must be done only in the indicated areas of the answer book.
- (5) You are not permitted to refer to books or periodic tables and the only permitted aid is a non-programmable electronic calculator.
- (6) You are permitted **15 minutes** to read the paper and supply the requested information on the cover of the answer book, followed by **120 minutes** to work the questions.
- (7) Relevant data that may be required for a question will be found on page 2.

**DATA**

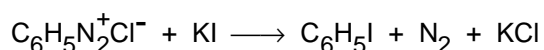
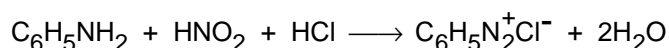
Avogadro constant	$6 \times 10^{23} \text{ mol}^{-1}$			
1 faraday	96,486 coulombs			
1 coulomb	1 amp sec			
Universal gas constant (R)	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$			
Standard temperature and pressure (STP)	$0^\circ\text{C}$ and 101.3 kPa $0^\circ\text{C}$ and 1 atm			
Molar volume of ideal gas at STP	22.4 L			
Relative atomic masses:	C 12.01	H 1.008	N 14.01	
	I 126.90	Cl 35.45	K 39.10	
	O 16.00	Cr 52.00	Cu 63.55	
	Br 79.90	S 32.06	V 50.94	
	Hg 200.59	Pb 207.2	Mn 54.94	
	As 74.92			

**SECTION A**

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake, **correct it clearly** so that the examiners can read your answer.

- Q1** In an experiment to determine the formula of a non-metallic bromide of known relative molecular mass, 0.1 mole of the bromide was dissolved in 500 mL of water, 50 mL of this solution reacted exactly with 300 mL of 0.1 M  $\text{AgNO}_3(\text{aq})$ . If the other element present is denoted by the letter Z, the most probable formula for the bromide is
- A  $\text{Z}_3\text{Br}$
  - B  $\text{Z}_2\text{Br}_6$
  - C  $\text{ZBr}$
  - D  $\text{ZBr}_3$
  - E  $\text{ZBr}_6$

- Q2** Iodobenzene ( $\text{C}_6\text{H}_5\text{I}$ ) is prepared from aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) in a two step process as shown below



In an actual preparation 9.30 g of aniline was converted to 16.32 g of iodobenzene. The percentage yield of iodobenzene is

- A 8%
  - B 50%
  - C 75%
  - D 80%
  - E 100%
- Q3** The following substances have approximately the same relative molecular mass. Which is likely to have the highest boiling point?
- A  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - B  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
  - C  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$
  - D  $(\text{CH}_3)_2\text{NC}_2\text{H}_5$
  - E  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- Q4** If a certain metal chloride is added to cold water, the solution becomes very hot and may even boil. This solution is found to conduct electricity.

Which of the following is most likely to be responsible for the evolution of the heat?

- A Dissociation
- B Sublimation
- C Hydration
- D Ionisation
- E Ionisation and dissociation together

**Q5** The reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  is exothermic.

Which of the following lines (A, B, C, D or E) correctly states the changes in the equilibrium yield of ammonia ( $\text{NH}_3$ ) when the reaction conditions are altered as indicated.

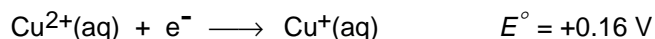
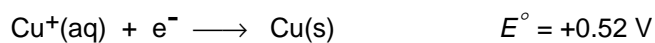
	An increase in temperature	An increase in pressure	Use of a catalyst
<b>A</b>	more $\text{NH}_3$	less $\text{NH}_3$	no change
<b>B</b>	less $\text{NH}_3$	more $\text{NH}_3$	no change
<b>C</b>	more $\text{NH}_3$	less $\text{NH}_3$	more $\text{NH}_3$
<b>D</b>	less $\text{NH}_3$	more $\text{NH}_3$	less $\text{NH}_3$
<b>E</b>	more $\text{NH}_3$	more $\text{NH}_3$	no change

**Q6** If a solution which is 0.0001 M with respect to carbonate ions,  $\text{CO}_3^{2-}$ , is mixed with an equal volume of a 0.0001 M solution of ions of a Group II metal, which of the following carbonates would be precipitated?

	Carbonates	$K_{\text{sp}}$ (298 K)/ $\text{mol}^2\text{L}^{-2}$
1	$\text{MgCO}_3$	$1.1 \times 10^{-5}$
2	$\text{CaCO}_3$	$5.0 \times 10^{-9}$
3	$\text{SrCO}_3$	$1.1 \times 10^{-10}$
4	$\text{BaCO}_3$	$5.5 \times 10^{-10}$

- A** 1, 2 and 3  
**B** 3 and 4  
**C** 1 and 3  
**D** 2 and 4  
**E** 1

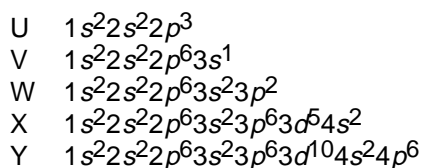
**Q7** Standard electrode potentials for the gain of one electron by the ions  $\text{Cu}^+(\text{aq})$  and  $\text{Cu}^{2+}(\text{aq})$  are as follows:



The standard potential for the disproportionation,  $2\text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ , would be

- A** -0.68 V  
**B** -0.36 V  
**C** +0.36 V  
**D** +0.68 V  
**E** +0.88 V

**Q8** The ground state electron configurations of the elements U, V, W, X, Y and Z (these symbols do not have any chemical significance) are as follows:



Determine which sequence of elements best fits the following statements

- (i) element - forms a carbonate which is not decomposed by heating  
 (ii) element - is most likely to form coloured ionic compounds  
 (iii) element - is a monatomic gas

	(i)	(ii)	(iii)
A	V	X	Y
B	V	Y	U
C	U	Y	X
D	W	X	Y
E	V	X	W

**Q9** In which compound does vanadium have an oxidation number of +4?

- A  $\text{NH}_4\text{VO}_2$   
 B  $\text{K}_4[\text{V}(\text{CN})_6]$   
 C  $\text{VSO}_4$   
 D  $\text{VOSO}_4$   
 E  $\text{VCl}_3$

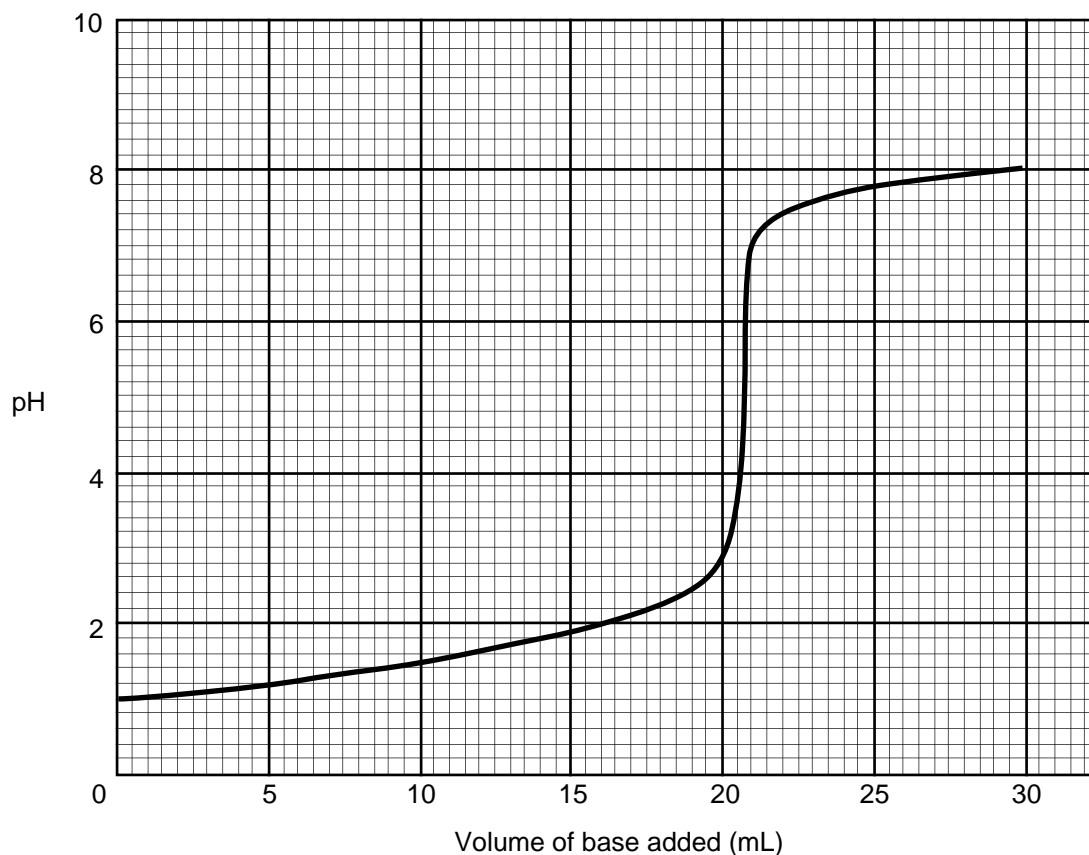
**Q10** The compound  $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$  is correctly named

- A 2-methylbutan-2-ol  
 B 2-ethylpropan-2-ol  
 C 4-methylbutan-3-ol  
 D pentan-3-ol  
 E 3-methylbutan-3-ol

**Q11** The solubility product for mercury(II)sulfide in aqueous solution at  $25^\circ\text{C}$  is given in data books as  $1.60 \times 10^{-52} \text{ mol}^2 \text{ L}^{-2}$ . Suppose the substance exists in solution as  $\text{Hg}^{2+}(\text{aq})$  and  $\text{S}^{2-}(\text{aq})$  ions, of what order of magnitude is the number of individual  $\text{Hg}^{2+}(\text{aq})$  ions per L of saturated solution at  $25^\circ\text{C}$ ?

- A  $10^{-28}$   
 B  $10^{-26}$   
 C  $10^{-2}$   
 D  $10^2$   
 E  $10^{26}$

## Q12



A solution of a base was added from a burette to 25 mL of acid and the pH of the mixture noted at intervals during the addition. The graph shows the changes in pH during addition of base to 25 mL of acid.

Which of the following was the acid used?

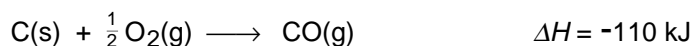
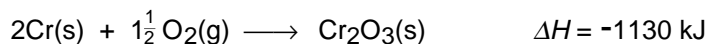
- A 0.1 M  $\text{CH}_3\text{CO}_2\text{H}$
- B 1 M  $\text{CH}_3\text{CO}_2\text{H}$
- C 0.1 M HCl
- D 1 M HCl
- E 1 M  $\text{H}_2\text{SO}_4$

**Q13** The unstable nucleus  $^{212}_{82}\text{Pb}$  decays with  $\beta$  particle emission, having a half life of 10 hours. From this it follows that the

1. mass number of the product is 212.
2. atomic number of the product is 81.
3. fraction of the original isotope remaining after 20 hours is  $\frac{1}{4}$ .
4. nucleus formed is stable.

- A 1, 2 and 3
- B 1 and 3
- C 2 and 4
- D 4
- E 2

**Q14** The enthalpy changes for two reactions are given by the equations



What is the enthalpy change, in kJ, for the reaction  $3\text{C(s)} + \text{Cr}_2\text{O}_3\text{(s)} \longrightarrow 2\text{Cr(s)} + 3\text{CO(g)}$  ?

- A -1460
- B -800
- C +800
- D +1020
- E +1460

**Q15** When a dilute, aqueous solution of potassium permanganate is run from a burette into a flask containing dilute, aqueous oxalic acid and dilute sulfuric acid, the rate of the reaction suddenly increases considerably as more potassium permanganate is added. The reason for this is that

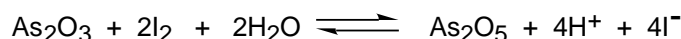
- A the manganese(II) ions produced catalyse the reaction.
- B the pH of the solution in the flask increases.
- C a definite minimum concentration of permanganate ions is necessary before the reaction will proceed.
- D the reaction is exothermic and the heat energy liberated affects the rate.
- E the sulfuric acid removes water and so causes the reaction to proceed more rapidly to completion.

**SECTION B**

Candidates should answer **any three** (3) of the four questions in this section. Be sure that **ALL** relevant working is shown in your answers to numerical questions. You should devote 90 minutes to this section.

**Q16** The amount of sulfur present in steel samples can be determined by conversion of the sulfur to hydrogen sulfide which is subsequently estimated by titration with iodine. In this latter process the  $\text{H}_2\text{S}$  is converted to elemental sulfur and the iodine reduced to iodide ion.

- (a) Write half equations for the oxidation of hydrogen sulfide and the reduction of iodine.
- (b) Iodine solutions used in volumetric analysis must be standardised prior to use as iodine is volatile and the solutions decrease in concentration with storage. One way of standardising iodine solutions is by titrating against a known mass of arsenic(III)oxide. One representation of this reaction is as follows



In using this standardisation method it is important to add sodium hydrogen carbonate (in excess) to the solution of arsenic(III)oxide.

Can you suggest why this is so?

- (c) Using a balanced chemical equation show why the sodium hydrogen carbonate can not be replaced with sodium hydroxide.
- (d) In an analysis of sulfur a chemist standardising an iodine solution finds that 10.00 mL of iodine solution reacts with exactly 0.04945 g of  $\text{As}_2\text{O}_3$ .

What is the molarity of the iodine solution?

- (e) Continuing the analysis the chemist finds that the  $\text{H}_2\text{S}$  liberated from a 5.00 g sample of steel requires 1.90 mL of the iodine solution to reach an end point in the titration.

What is the percentage of sulfur in the steel sample?

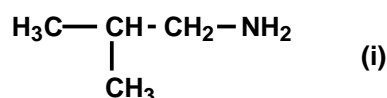
- (f) Can you suggest how the accuracy of this experiment might be improved?

**Q17** *Modern Organic chemists make extensive use of spectroscopy in determining molecular structures. In particular ultraviolet (UV) and infra-red (IR) spectroscopy can tell the chemist about functional groups present in a molecule. The following example shows how spectroscopy can combine with chemistry to solve a structural problem. However before proceeding further you should be aware that **additional information** is available at the end of the problem.*

- (a) The bark of the southern prickly ash contains an insecticidal substance neoherculin, which is shown by combustion analysis to contain C 77.73%, H 10.12%, N 5.66% and to have a relative molecular mass of 247.

What is the molecular formula of neoherculin?

- (b) Neoherculin reacts with hydrogen in the presence of a platinum catalyst to afford an octahydro derivative which is shown by infra-red spectroscopy to contain a secondary amide. Hydrolysis of octahydroneoherculin affords, n-dodecanoic acid and 2-methylpropylamine **(i)**.



What is the structure of octahydroneoherculin?

- (c) What is the minimum number of carbon-carbon double bonds that neoherculin can contain?
- (d) Careful examination of the ultraviolet spectrum of neoherculin suggests the presence of a conjugated triene. Whilst the infra-red spectrum suggests the presence of an amide carbonyl group conjugated with one double bond.

From this data give three possible structural formulae for neoherculin.



- (e) The choice of a unique structure for neoherculin can be made from the observation that ethanal (acetaldehyde) is formed as one of the products from the cleavage of neoherculin with ozone followed by a reduction.

What is the structure of neoherculin, (ignore *cis/trans* isomerism)?

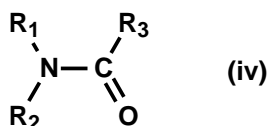
- (f) How many possible isomers of this structure exist if one considers the possibility of *cis/trans* isomerism?
- (g) Draw the structure of the all *trans* isomer being careful to show the correct disposition of groups about the carbon-carbon double bonds, remembering the bond angle is  $120^\circ$  for bonds joined directly to the double bond.

**Additional information:**

- (i) A conjugated system is one made up of alternating single and multiple bonds. For example 1,3-butadiene **(ii)** is referred to as a conjugated diene and propenoic acid **(iii)** is an example of a conjugated carboxylic acid.



- (ii) Amides have the general structure, **(iv)**, and when one of the groups  $R_1$  or  $R_2$  is hydrogen the amide is referred to as a secondary amide. Amides can be hydrolysed, usually with acid, to afford the related carboxylic acid and amine. This process is similar to the hydrolysis of esters.



- (iii) The term octahydro-derivative implies the additional presence of eight (8) atoms of hydrogen per molecule in comparison with the parent molecule.

**Q18**

Shown below are the first three rows of the periodic table:

1 H							2 He	1st row
I      II		III    IV    V    VI    VII    VIII						
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne	2nd row
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3rd row

- (a) The elements 3-18 are arranged in groups labelled I-VIII. The significance of the group number is that it gives the number of **valence** electrons the element has available to participate in bond formation in molecules. Thus, boron has 3 valence electrons and phosphorus has 5 valence electrons.

How many valence electrons do each of the following species have?

- (i) C  
 (ii) S  
 (iii)  $\text{Mg}^{2+}$   
 (iv)  $\text{Cl}^-$

- (b) The arrangement of valence electrons in atoms in molecules can be represented using **Lewis** structures, a dot being used to represent each valence electron. Lewis structures of molecules are constructed by using the following basic rules:

- (1) Sum the valence electrons from **all** the atoms.
- (2) Use a pair of electrons to form a bond between each pair of bound atoms.
- (3) Arrange the remaining electrons such that each atom achieves a **noble gas configuration** of valence electrons as, in general, the most stable compounds are those in which the atoms have such a configuration.

Some representative examples of Lewis structures of molecules are shown below:

Molecule	Total number of valence electrons	Lewis structure *
H <sub>2</sub>	2	H : H or H — H
He	2	He:
F <sub>2</sub>	14	:F : F: or :F — F:
H <sub>2</sub> O	8	H — O — H
CO <sub>2</sub>	16	O = C = O

\* A line is normally used to represent a bonding pair of electrons.

Note that the H atoms in H<sub>2</sub> 'share' the bonding pair of electrons and hence both atoms have access to two valence electrons, the noble gas configuration of helium. The F atoms in F<sub>2</sub> have access to eight valence electrons, the noble gas configuration of valence electrons for neon. Second and third row elements, in general, have access to eight valence electrons in molecules and are said to obey the **octet rule**.

Write Lewis structures for each of the following species:

- (i) Br<sub>2</sub>
- (ii) H<sub>2</sub>
- (ii) CCl<sub>4</sub>
- (iv) CN<sup>-</sup>

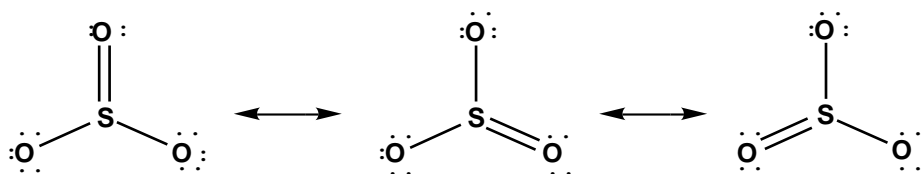
- (c) Third row elements in molecules sometimes exceed the octet rule as shown below:

Molecule	Total number of valence electrons	Lewis structure
PCl <sub>5</sub>	40	
SF <sub>6</sub>	48	
I <sub>3</sub> <sup>-</sup>	22	

Note that when it is necessary to exceed the octet rule the extra electrons are placed on the central atom.

Write Lewis structures for each of the following species:

- (i)  $\text{SF}_2$   
 (ii)  $\text{Br}_3^-$   
 (iii)  $\text{BrF}_3$   
 (iv)  $\text{SF}_4$
- (d) Sometimes more than one valid Lewis structure can be drawn for a molecule, these are known as **resonance** structures. For example, sulfur trioxide has three resonance structures:



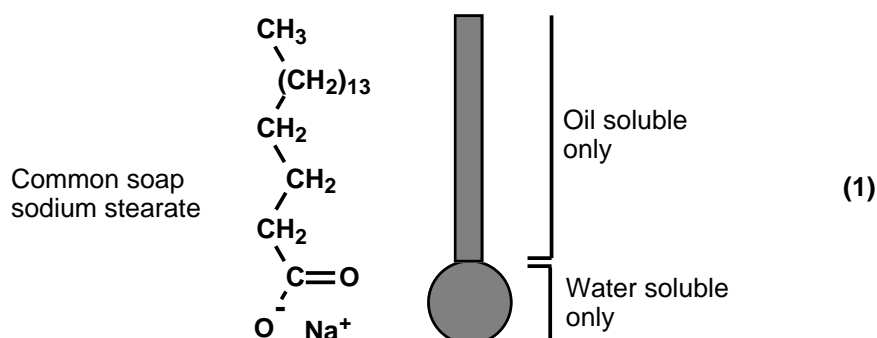
Write Lewis structures (including resonance structures) for each of the following species:

- (i)  $\text{SO}_2$   
 (ii)  $\text{NO}_3^-$   
 (iii)  $\text{O}_3$

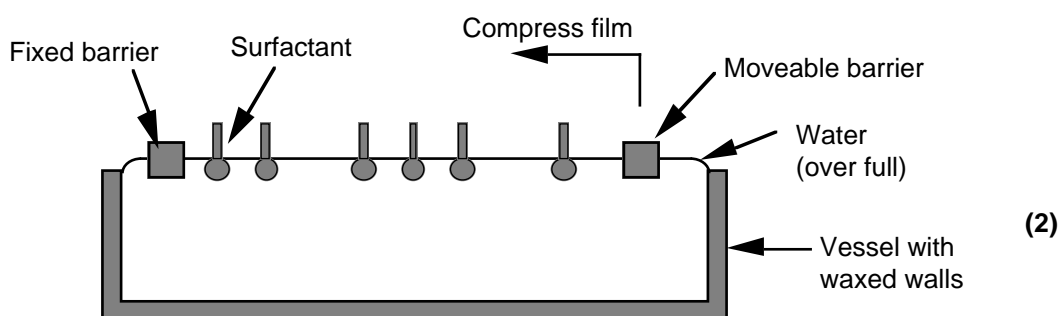
### Q19

The expansion of a balloon as it is heated is easy to visualise for we have first-hand experience of life in three dimensions. Changes in the three states of matter are explained to us in terms of how a particular state will fill a given volume. Consider now the loss of a dimension; a world where changes in state occur on a surface! This interesting notion celebrates an important centennial this year for in 1891 Fräulein Agnes Pockels demonstrated how such a world might be observed.

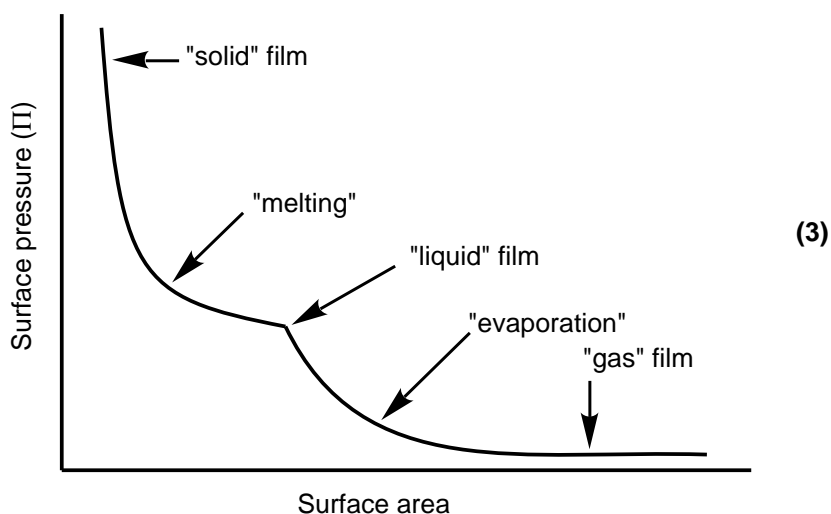
Many of the chemicals she studied were of a class that we now call surfactants (surface active agents). These molecules have two parts; one soluble in water only, the other part being soluble in oil only. The result is that the molecules are held right on the surface where oil and water meet. Soaps are the best known example of surfactants, see (1)



If a small amount of a surfactant is placed on the surface of water it will spread to occupy the available area. The water soluble part will face the water and the oil soluble 'tail' will point into the air. Fräulein Pockels found that a surfactant film could be compressed by reducing the available area with a moveable barrier, see side view (2).



Just think of the 3D case when a piston compresses a gas. It is now understood that by compressing the surface film one can consider the molecules, initially free to skate about the surface, as going from a “gaseous” film to a “liquid” film and finally, at high enough surface pressures, to a “solid” film. Just as you might plot pressure as a function of volume when talking about 3D gases, so you can plot surface pressure as a function of surface area. A surfactant film showing the “states” of matter in a two dimensional sense can be generalised, see (3).



- (a) (i) Considering the “gaseous” film only write down the analogous ideal gas equation for this two dimensional case. What are the units for surface pressure (usually denoted,  $\Pi$ )?
- (ii) Why would this equation **not** predict accurately the behaviour of a real “gaseous” film? What assumptions are made?
- (iii) Again for the “gaseous” film only sketch roughly how the surface pressure as a function of surface area would vary with temperature.
- (b) If the moveable barrier compressed the film beyond the “solid” state what might you expect the film to do? Support any conclusions with a simple sketch of how the surfactant molecules would arrange.
- (c) Benjamin Franklin too had observed thin films on water. Fascinated by the way “oil calms troubled waters [waves]” he reported a now famous experiment performed on a pond on Clapham Common in 1774. He wrote,

“... the oil, though not more than a teaspoonful [5 mL], produced an instant calm over a space several yards square, which spread amazingly, and extended itself gradually till it reached the lee [far] side, making all that quarter of the pond, perhaps half an acre [2020 m<sup>2</sup>], as smooth as a looking glass.”

- (i) Assuming the oil he used was olive oil (mainly oleic acid, *cis*-9-octadecenoic acid, density 0.891 g mL<sup>-1</sup>) and had formed a single layer what would be the average area occupied by each surfactant molecule?
- (ii) Given that it was a warm English day of 20°C what would be the surface pressure of Franklin’s film when it occupied the final “half acre”?
- (iii) If oleic acid “sublimes” (in a 2D sense) at a surface pressure of around 0.005 N m<sup>-1</sup> (at 20°C) what “state” would you consider Franklin’s film to be in ?