Chapter 5

SURFACE CHEMISTRY

LEARNING OBJECTIVES

At the end of this chapter on surface chemistry, students should be able to:

- Compile and interpret data on the surface properties of materials based on chemical and physical adsorption at gas-solid, liquid-solid and gas-liquid interfaces.
- Interpret Langmuir, Freundlich and BET isotherms.
- Investigate experimentally suitable liquid-solid systems.
- Evaluate the role of surface phenomena in separation processes
- Use standard methods to prepare and investigate the properties of colloidal systems.
- Carry out graphical calculations based on the Langmuir and BET Isotherms
- List techniques or methods for the surface characterisation of materials

5.0. WHAT IS SURFACE CHEMISTRY?

Surface chemistry is the study of molecules in or at a surface. A surface is the boundary or interface of different phases which are in contact. Examples of interfaces and their uses include:

1. Solid/Gas- used in catalysis, gas masks

2. Solid/Liquid- find application in dyeing, wetting properties.
3. Liquid/Liquid – emulsions(could be water in oil or oil in water emulsions, etc) .
4. Liquid/Gas – condensation, vapourisation.

The properties of material at a surface generally differ properties from the properties in the bulk. These differences give rise to many useful properties such as surface tension and the greater reactivity of catalysts and other materials.

Solid surfaces can be divided into two types:

1. Homogeneous- the surface is uniform and macroscopically energetically equivalent.
2. Heterogeneous – surface is not uniform, different sites have different energies for example, the adsorption of Pd on charcoal.

Surface properties may be enhanced by finely dividing the material resulting in a larger surface area, where for example, adsorption can take place. This is one of the reason for the activity of catalyst materials. Generally, the rate of reaction increases with an increase in the surface area of the material or catalyst.

Adsorption – is the uptake of a species(the adsorbate) by a *surface* (the adsorbent) to give a *surface* film. Note that adsorption is not the same thing as absorption which means to absorb into the bulk. Thus adsorption is a surface process, whereas absorption is an internal process, although sometimes, it is difficult to distinguish between adsorption and absorption.

The are many types of reactions that take place on the surface of a solid. The following are examples:

5.1. SOLID/GAS ADSORPTION

The amount of gas a solid can adsorb depends on the position of the equilibrium between the solid and the gas. The position of the equilibrium depends on the temperature,T, gas pressure and the effective surface area of the solid. The best adsorbents are highly porous solids such as charcoal and silica gel (surface area approx. $1000 m^2 g^{-1}$) and finely divided powders.

Two types of adsorption are possible(you should be able to distinguish between them):

1. Physical adsorption (Physisorption)- interactions between adsorbate and adsorbent are non-specific, for example, van der Waals.
2. Chemical adsorption (chemisorption)- interactions are specific and involve the formation of chemical bonds.

These two types of adsorptions can be distinguished by the characteristics shown in the table 5.1.

Table 5.1. Physical and Chemical adsorption

Physical adsorption	Chemical adsorption
Heat of adsorption is small $\approx$ 8-20 kJmol^{-1} and is about the same order as molecular forces.	Heat of adsorption is $\approx$ 40 –800 kJ mol^{-1} and is the same order as bond energies
Temperature of adsorption is low and is less than the boiling point of the adsorbate.	Temperature of adsorption can be high it depends on the activation energy
The activation energy of adsorption is negligible (zero).	The activation energy of adsorption is usually small.
Multilayer adsorption may occur	Monolyer adsorption only occurs.

5.2. THERMODYNAMICS OF ADSORPTION

For adsorption to be spontaneous ΔG must be negative. Adsorption causes a decrease in the entropy of the system (gas molecules become attached to a surface – more ordered, and as a result, the change in entropy, ΔS is negative (-ve).

Therefore because $\Delta G = \Delta H - T\Delta S$, then ΔH must be negative as well

The enthalpy of adsorption (ΔH) is always negative, and the equilibrium constant (K) decreases with increasing temperature. (see chapters 2 and 3).

This can be illustrated by the adsorption of NH_3 on charcoal. A plot of the volume of gas adsorbed against pressure of gas at different temperatures yields a number of isotherms as illustrated in figure 4.1.

ΔH_{ads}^{p} = enthalpy change for physisorption.

ΔH_{ads}^{c} = enthalpy change for chemisorption.

E_a = activation energy for chemisorption. This is given by the intersection of the two curves.
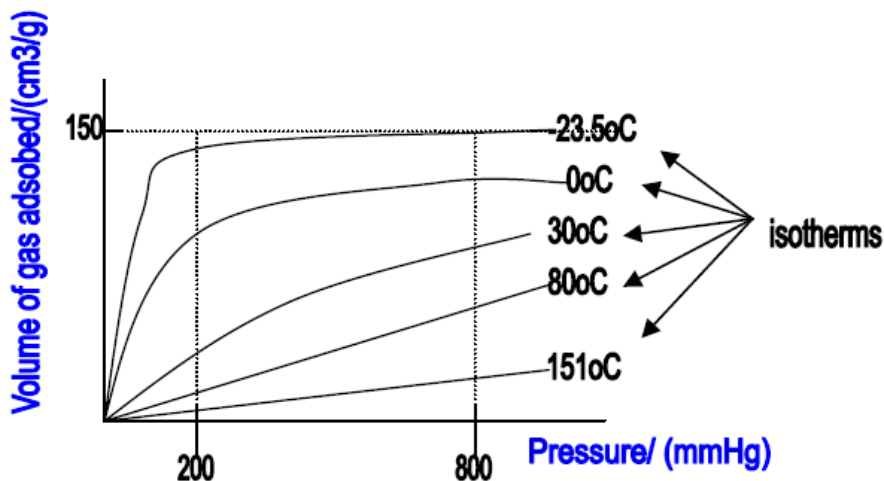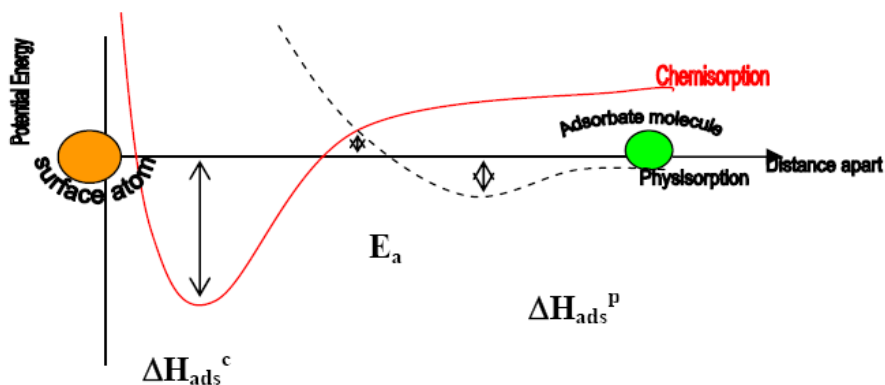
Figure 5.1. Adsorption Isotherms.

Figure 5.2. Potential Energy of Chemisorption and Physisorption.

Physical adsorption occurs readily and is reversible. On the other hand, chemisorption is a specific process requiring activation energy. A possible process that occurs during adsorption is that a molecule is rapidly physically adsorbed, then slowly chemically adsorbed. At low temperatures physisorption only may occur.

For example, consider the adsorption of H_2 on Ni as illustrated below

H-H

H   H
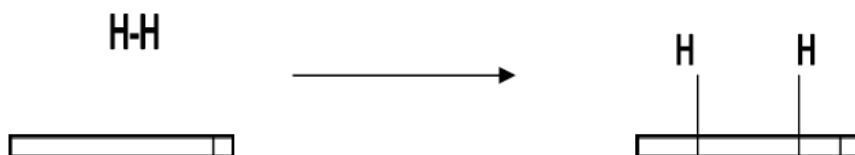
Before the hydrogen can be adsorbed it needs to dissociate. This requires a lot of energy. However if the hydrogen is physically adsorbed first then the energy required for dissociation is less and the hydrogen can be chemically adsorbed from this state.

H – – – – – – H   H-H bond broken as
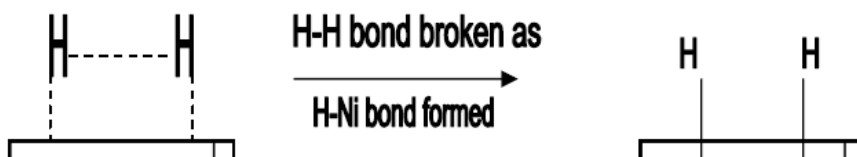   H-Ni bond formed   H   H

Figure 5.3. The adsorption of Hydrogen on Nickel.

This results in the activation energy observed and is how catalysts speed up reactions by reducing the activation energy.

5.3. ADSORPTION ISOTHERMS

As you have seen an adsorption isotherm is a plot of adsorbed amount as a function of the pressure at a constant temperature.

For physically adsorbed gases onto solids there are three phenomena

1. monolyer adsorption
2. multilayer adsorption
3. condensation into pores or capillaries.

These processes are represented in the shape of the isotherms.

There are 5 types of isotherms classified by Brunamer, Demming and Teller.

TYPE I - The plateau value is consistent with monolayer formation.

P_o is the saturated vapour pressure, above this the vapour condenses to a liquid.

V_m is the volume equivalent to one monolayer.

Rapid adsorption as the pressure increases to a limiting value which corresponds to monolayer coverage. We would expect chemisorption isotherms to have a type I shape.

TYPES II-V result from multilayer formation, with types II-III formed from non-porous solids and types IV-V formed from porous solids.

TYPE I

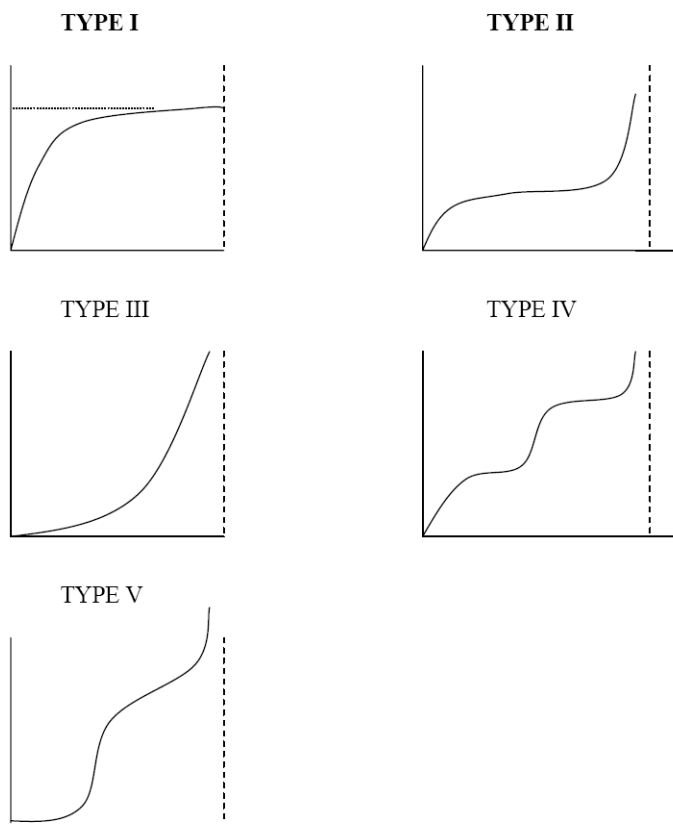**TYPE II**

TYPE III

TYPE IV

TYPE V

Figure 5.4. Adsorption Isotherms.

V_m is an important parameter as it can be used to determine the areas of solid surfaces. It is not easy to read V_m off these isotherms so numerous attempts have been made to fit equations to experimental data.

The equations most commonly used are :

(i) Langmuir

(ii) Freundlich
(iii) Temkin
(iv) Brunauer-Emmett-Teller (B.E.T)

We should now consider each of these Isotherms

5.2.1. The Langmuir Isotherm
Type I isotherm is based on the following assumptions

1. Homogeneous surface. That is all sites are equivalent
2. Monolayer coverage.-. intermolecular forces fall off rapidly with distance
3. No lateral interactions within the film. That is, the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites and ΔH_{ads} is constant regardless of the amount adsorbed at the surface.
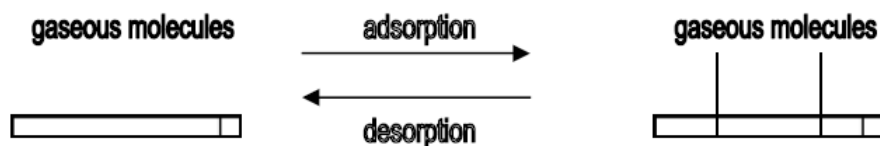

Figure 5.5. Processes involved in Type I Adsorption.

Consider a gas of pressure P in equilibrium with a solid surface. The fraction of sites occupied is θ

$$\text{i.e. } \theta = \frac{\text{number of sites occupied}}{\text{number of sites available}} = \frac{V}{V_m} \tag{5.1}$$

Because the system is at equilibrium, the rate of adsorption = rate of desorption.
The rate of adsorption is proportional to the gas pressure
And proportional to the fraction of surface *uncovered.* $= (1-\theta)$
The rate of desorption is proportional to fraction of surface *covered.* $= \theta$

Therefore, $R_{ads} = k_a(1-\theta)P.$ $\tag{5.2}$

$R_{desorp} = k_d\theta$ $\tag{5.3}$

At equilibrium, $k_a(1-\theta)P = k_d\theta$.   (5.4)

We can simplify equation [4.4] by saying that $b = k_a/k_d$. This gives (5.5)

$\theta = bP/(1+bP)$ Langmuir Isotherm equation   (5.5)

Since $\theta = V/V_m$ then $V/V_m = bP/(1+bP)$ (5.6)

This can be rearranged into a straight line form

$P/V = P/V_m + 1/bV_m$ (5.7)

The plot P/V_m vs P is a straight line of gradient $1/V_m$ and intercept of $1/bV_m$.

$b = k_a/k_d$ is constant at constant temperature and independent of θ. This means that the value obtained for V_m is dependent on the temperature at which the adsorption is carried out. For example, for the adsorption of CO_2 on charcoal, V_m = 231 cm^3g^{-1} at 196K and 113 cm^3g^{-1} at 303K. Thus this parameter is lower at higher temperatures in this case.

The limiting cases are :

Low P
$\theta = bP$
High P
$\theta = 1$ that is, $V=V_m$ and have achieved a monolayer
coverage. Usually, there is something intermediate between low P and high P.

5.2.2. Drawbacks of the Langmuir Isotherm

1. Assumes homogeneous surface- highly unlikely.
2. Monolayer coverage- this assumption is fine for chemisorption and physisorption at low pressures and high temperatures.
3. No lateral interactions within the film. ΔH_{ads} = constant is very unlikely.

i. The surface is unlikely to be uniform.
ii. Adsorbed molecules make the surface non-uniform.

These cases cause ΔH to decrease as coverage increases.

Adsorption will occur preferentially at certain sites. For example, see figure 4.6
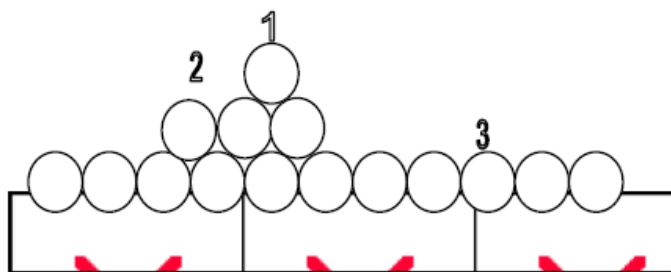
Figure 5.6. Adsorption Processes.

    1>2>3 (the activity of the various sites)

    Some adsorption sites may be more *active* than others and adsorption will occur preferentially at these sites. This will cause the adsorption to become less exothermic as θ increases. Another reason why ΔH is not constant is that there is likely to be interactions between adsorbed molecules. If this interaction is repulsive then this will cause ΔH to *decrease*. This effect will become more prominent at high θ.

    Despite these criticisms, a large number of experimental isotherms do fit the Langmuir isotherm well especially those relating to N_2, O_2, Ar on charcoal at $-183^{\circ}C$.

5.3. Freundlich Adsorption Isotherm

    Originally this was an empirical observation, but later it was shown that this was consistent with ΔH_{ads} decreasing exponentially with increasing coverage such that

$$V = kP^{1/n} \tag{5.8}$$

V = volume of gas adsorbed, P = pressure, k and n are constants.

The plot log V vs Log P is a straight line of gradient 1/n and intercept log k.

    This is consistent with ΔH_{ads} decreasing exponentially with increasing θ(surface coverage).

    Freundlich Adsorption Isotherm is obeyed by adsorption from solution at low concentrations.

5.4. Temkin Adsorption Isotherm

There is a linear variation of ΔH with surface coverage(θ)

$$\theta = k \ln cP \tag{5.9}$$

where k and c are constants.

Assumes linear variation of ΔH with surface coverage, θ.

5.5. B.E.T Adsorption Isotherm

The B.E.T isotherm deals with multilayer adsorption on non-porous solids and represents an extension of Langmuir isotherm. It was derived form balancing the rates of evaporation and condensation for various layers. The assumptions of the BET isotherm include:

1. Surface is homogeneous surface and all sites are equivalent
2. No lateral interactions within the film.
3. Each adsorption site that is filled forms a site for multilayer adsorption i.e no limit to adsorption therefore no plateau and no limiting value to adsorption.
4. All layers above the monolayer are all equivalent and like a bulk liquid.

This model is essentially a Langmuir adsorbed layer and multi-layers of liquid like adsorbate which are all energetically equivalent.
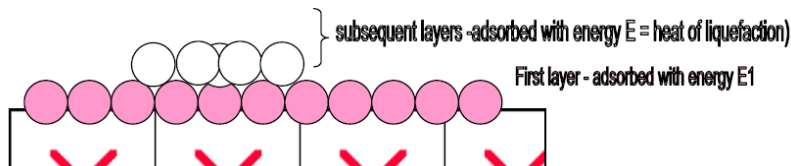

subsequent layers -adsorbed with energy E = heat of liquefaction)
First layer - adsorbed with energy E1

Figure 5.7.

$$V/V_m = cx/((1-x)(1-x+cx)) \quad \text{B.E.T Isotherm equation} \tag{5.10}$$

Where $x = P/P_o$ = relative pressure.

$$C = \exp((E_1 - E)/RT) \qquad (5.11)$$

The shape of the BET isotherm depends on the value of c. This describes the binding energy between the first and subsequent layers. This isotherm is used in calculating the area of solid surfaces.

Exercise 5.1.

Using the Langmuir Isotherm

The data given below are for the adsorption of C0 on charcoal at 273 K. Confirm that they fit the Langmuir isotherm, and find the constant K and the volume corresponding to complete coverage. In each case V has been corrected t0 1.00 atm.

P/Torr	100	200	300	400	500	600	700(x-axis)
V/cm^3	13.2	20.6	26.5	33.5	34.9	44.6	48.1
(p/Torr)/(Vcm^3)	7.58	9.71	11.32	11.94	14.33	13.45	14.55(y-axis)

From our discussion, we have shown that

$$Kp\theta + \theta = Kp$$

With $\theta = V/V\infty$, where $V\infty$ is the volume corresponding to complete coverage. This expression can be rearranged into equation [5.12] as

$$\frac{P}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty} \qquad (5.12)$$

Hence, a plot of p/V against p, figure 5.8, should give a straight line of slope $1/V\infty$ and intercept $1/KV_\infty$. The data to plot is highlighted in blue in the above table
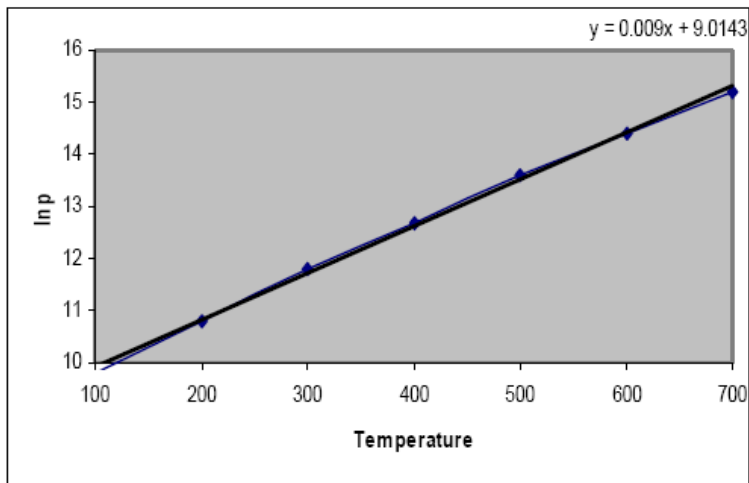
Figure 5.8.

Exercise 5.2.

Measuring the Isosteric Enthalpy of Adsorption

The data below show the pressures of C0 needed for the volume of adsorption (corrected to 1.00 atm and 273 K) to be 10.0 cm^3 Calculate the adsorption enthalpy at this surface coverage.

T/K	200	210		220	230	240	250
p/Torr	30.0	7.1		45.2	54.0	63.5	73.9
ln(p/Torr)	3.40	3.61		3.81	3.99	4.15	4.309(x-axis)
10^3/(T/K)	5.00	4.76		4.54	4.35	4.17	4.00(y-axis)

Solution

The Langmuir isotherm can be rearranged to

$$Kp = \frac{\theta}{1 - \theta}$$

(5.13)

Therefore, when θ is constant,

$$\ln K + \ln p = \text{constant}$$

It follows that

$$\left(\frac{\partial \ln p}{\partial T}\right)_\phi = -\left(\frac{\partial \ln K}{\partial T}\right)_\phi = -\frac{\Delta_{ad}H^\varnothing}{RT^2} \tag{5.14}$$

with $d(1/T)/dT = -1/T^2$, this expression rearranges to

$$\left(\frac{\partial \ln p}{\partial T\phi}\right) = -\frac{\Delta_{ad}H^\varnothing}{R} \tag{5.15}$$

Therefore, a plot of $\ln p$ against $1/T$, as in figure 5.9, should be a straight line of slope $\Delta_{ad}H^\varnothing/R$.

Solution Draw up the following table and plot $\ln p$ against $1/T$ and determine $\Delta_{ad}H^\varnothing$ from the slope.

T/K	200	210	220	230	240	250	
$10^3/(T/K)$	5.00	4.76	4.55	4.35	4.17	4.00(x-axis)	
$\ln(p/\text{Torr})$	3.40	3.61	3.81	3.99	4.15	4.30(y-axis)	
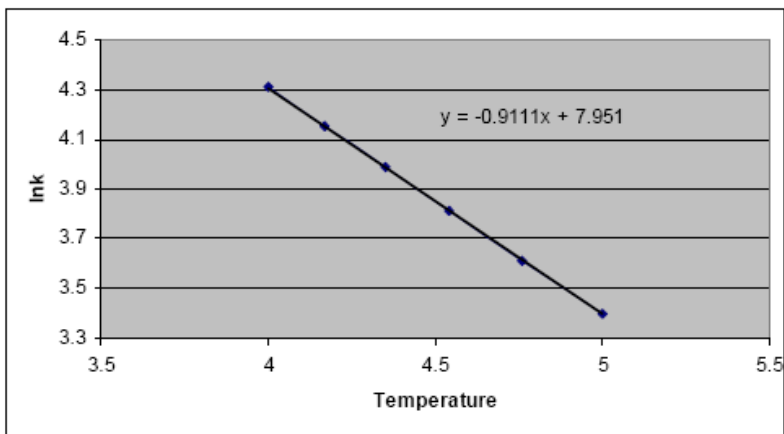
Figure 5.9.

Exercise 5.3.

Repeat the calculation using the following data:

T/K	200	210	220	230	240	250
P/Torr	32.4	41.9	53.0	66.0	80.0	96.0

[Ans = -9.0 kJ mol^{-1}]

Exercise 5.4.

Using the BET Isotherm

The data below relate to the adsorption of N_2 on rutile (TiO_2) at 75 K. Confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/torr	1.20	14.0	45.8	87.5	127.7	164.4	204.7
Vmm^3	601	720	822	935	1046	1146	1254

At 75 K, $p^* = 570$ Torr. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

The BET isotherm can be reorganised into

$$\frac{Z}{(1-z)\,V} = \frac{1}{cV_{mon}} + \frac{(c-1)\,z}{cV_{mon}} \qquad (5.16)$$

It follows that $(c-1)/cV_{mon}$ can be obtained from the slope of a plot of the expression on the left against z, figure 5.10 and cV_{mon} can be found from the intercept at z = 0. The results can then be combined to give c and V_{mon}.

Solution Draw up the following table:

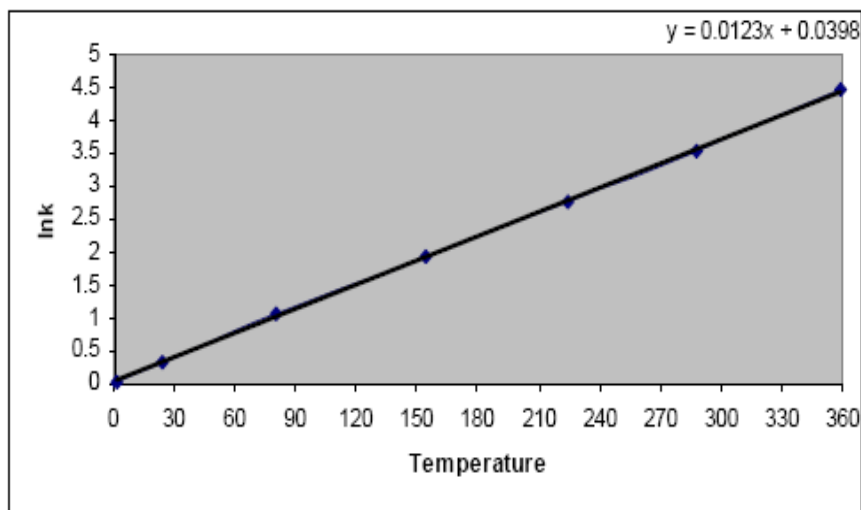| p/torr	1.20	14.0	45.8	87.5	127.7	164.4	204.7
$10^3 z$	2.11	24.6	80.4	154	224	288	359(x-axis)
$10^4 z/(1-z)$ (V/mm^3)	0.035	0.350	1.06	1.95	2.76	3.53	4.47(y-axis)

Figure 5.10.

The least squares best line has an intercept at 0.0406, so

$$\frac{1}{cV_{mon}} = 4.06 \times 10^{-6} \text{ mm}^{-3}$$

Thus $1 = cV_{mon} \times 4.06 \times 10^{-6} \text{ mm}^{-3}$

And hence $cV_{mon} = 246305.42 \text{mm}^3$

The slope of the line is 1.23×10^{-2}, so

$$\frac{c-1}{cV_{mon}} = (1.23 \times 10^{-2}) \times 10^3 \times 10^{-4} \text{ mm}^{-3} = 1.23 \times 10^{-3} \text{mm}^{-3}$$

The solutions of these equations are $c = 303$ and $V_{mon} = 814 \text{mm}^3$.

We should now discuss the practical uses of adsorption process. As you can imagine, these are many and varied.

5.6. Practical Uses of Adsorption Processes

There are many practical uses and applications of adsorption processes. Some of these are summarised as follows:
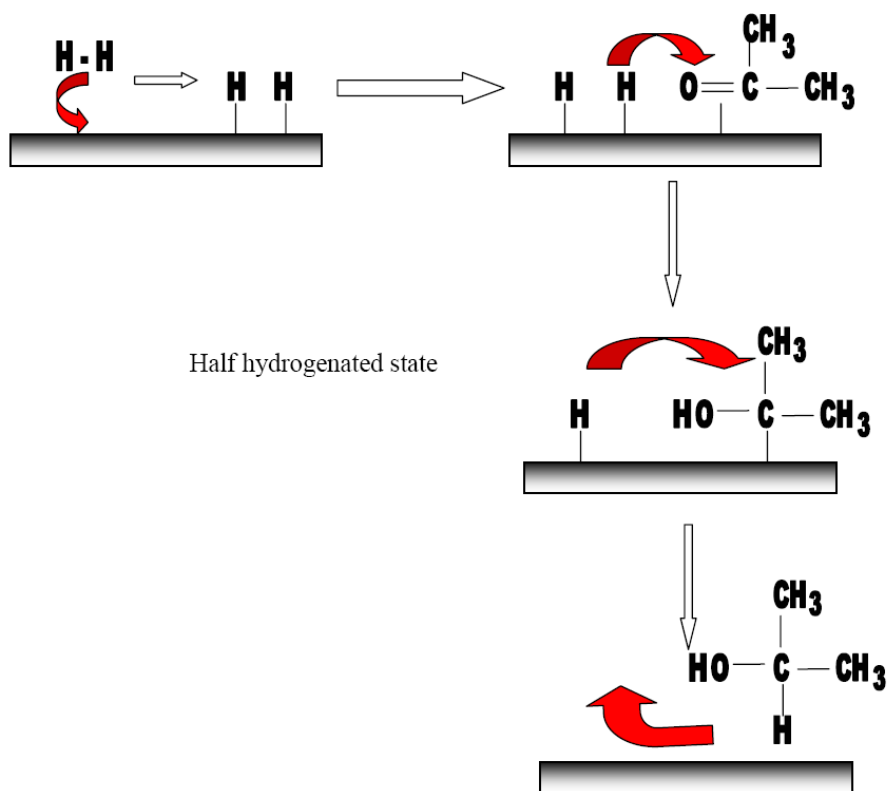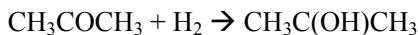
Figure 5.11.

1. Catalysis

Mechanisms vary widely and there are many types. Have seen that adsorption at solid surfaces allows reactions to proceed which either wouldn't occur or would occur slowly.

An example is the hydrogenation of unsaturated compounds.

$$CH_3COCH_3 + H_2 \rightarrow CH_3C(OH)CH_3$$

In the presence of a metal catalyst such as Ni or Pt, the hydrogen dissociates as shown below.

2. Determination of Solid Surface Areas

Examples include N_2 adsorption , BET

3. Adsorption of Impurities

Examples include sewage , gas masks, water, gas purification.

4. Surfactants

Example water loss from reservoirs in hot climates, washing powders, detergents (solubilisation and wetting).

5. Separation processes.

Example, Chromatographic techniques

SUMMARY OF CHAPTER FIVE

Surface chemistry deals with chemistry at surfaces – solid surfaces. We have discussed the isotherms that describe the reactions on these surfaces whether these be chemisorption or physisorption. We have also discussed the practical uses and applications of surface chemistry , such as in catalysis and surfactants. Finally, we have mentioned some of the techniques that are available for the characterisation of solid surfaces. Worked examples have been provided to aid the student in understanding the chapter and preparing for an examination in this subject or topic.

Revision Questions

Question 5.1.

(a) State two differences between the Langmuir and the BET isotherms
(b) List two practical applications of adsorption processes

The data below relate tot he adsorption of N_2 on titanium dioxide at 75 K. confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/torr	1.22	16.0	46.8	86.5	128.7	164.6	204.8
Vmm^3	600	740	820	940	1040	1140	1260

At 75 K, $p* = 570$ Torr. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

(c) List three techniques that may be used for the surface characterisation of materials

(d) State one industrial application of the BET isotherm

Solution

(a) Differences between the Langmuir and BET Isotherms

Langmuir isotherm applies to monolayer adsorption, of equivalent sites and uniform surface. On the other hand, the BET isotherm deals mainly with multilayer adsorption. It can be used to determine the surface area of solids in industry.

(b) Application of surface chemistry processes

Catalysis, hydrogenation, separation processes, surfactants, etc

The BET isotherm can be reorganised into

$$\frac{z}{(1-z)\,V} = \frac{1}{cV_{mon}} + \frac{(c-1)\,z}{cV_{mon}}$$

It follows that $(c-1)/cV_{mon}$ can be obtained from the slope of a plot of $z/(1-z)V$ against z, and cVm is obtained from the intercept at $z = 0$. The results can then be combined to give c and Vm. (see figure 5.10)

This is similar to the straight line equation, $y = mx + c$

The following table is drawn up:

p/torr	1.22	16.0	46.8	86.5	128.7	164.6	204.8
$10^3 z$	2.10	28.0	82.10	151.7	225.8	288.8	359.3
$10^4 z/(1-z)$ (V/mm^3)	0.026	0.346	1.01	1.87	2.79	3.57	4.44

The intercept of the plot is 0.002, so

$$\frac{1}{cV} = 2.0 \times 10^{-6}\ \text{mm}^{-3}$$

The slope of the line is 1.24 x 10^{-2}, so <u>c – 1</u> = (1.23 x 10^{-2}) x 10^3 x 10^{-4} mm^{-3} = 1.24 x 10^{-3}mm^{-3} cVm

The solutions to these equations are c = 621 and V_{mon} = 805.15mm^3.

(Note that Z = P/P*, where P* is 570 torr)

(c) Characterisation of the surface of Materials:

Any three of: Scanning tunnelling microscopy, Low energy electron diffraction, Electron loss spectroscopy, High vacuum techniques, Auger electron spectroscopy, Ionization techniques Atomic Force Microscopy, Molecular Beam Scattering

(d) Surface area determination

Question 5.2.

The pressures of CO needed for the volume of adsorption corrected to 1.00 atm and 273 K to be 10.0 cm^3 are given below. Determine the adsorption enthalpy at this surface coverage.

T/K	200	210	220	228	240	260
P/Torr	30	39.1	46.2	56.0	66.5	75.9

Solution to Question 5.2.

Enthalpy of Adsorption Determination

The Langmuir isotherm can be rearranged to

$$Kp = \frac{\theta}{1 - \theta}$$

Therefore, when θ is constant, $1n\ K + 1np$ = constant
It follows that

$$\frac{\left(\partial\,1np\right)}{\partial T} = \frac{-\left(\partial\ln K\right)}{\partial T} = -\frac{\Delta_{ad}H^{\varnothing}}{RT^2}$$

with d(1/T)/dT = -1/T^2, this expression rearranges to

$$\frac{\left(\partial \ln p\right)}{\partial T} = -\frac{\Delta_{ad}H^{\varnothing}}{R}$$

Therefore, a plot of $\ln p$ against $1/T$, figure 5.12, should be a straight line of slope $\Delta_{ad}H/R$.

The following table is drawn up:

T/K	200	210	220	230	240	260
$10^3/(T/K)$	5.00	4.76	4.54	4.34	4.16	3.84
$\ln(p/\text{Torr})$	3.40	3.65	3.83	4.02	4.19	4.32

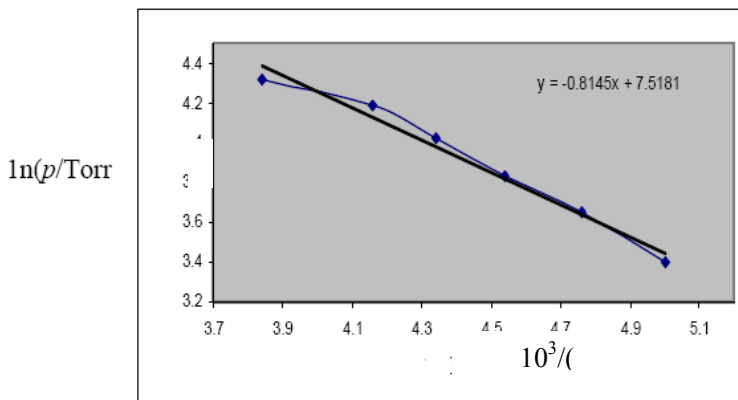
Figure 5.12.

The slope of the graph is -0.8145, so $\Delta_{ad}H^{\varnothing} = -(0.8145 \times 10^3 \text{ K}) \times R$
$= -6.77 \text{ kJmol}^{-1}$.

Question 5.3.

Using The Langmuir Isotherm

The data given below are for the adsorption of C0 on charcoal at 273 K. Confirm that they fit the Langmuir isotherm, and find the constant K and the volume corresponding to complete coverage. In each case V has been corrected t0 1.00 atm.

P/Torr	100	200	300	400	500	600	700
V/cm^3	10.2	18.6	25.5	31.5	36.9	41.6	46.1

Solution to Question 5.3

From $Kp\theta + \theta = Kp$ and with $\theta = V/V\infty$, where $V\infty$ is the volume corresponding to complete coverage, this expression can be rearranged into

$$\frac{P}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$$

Hence, a plot of p/V against p, figure 5.13, should give a straight line of slope $1/V_\infty$ and intercept $1/KV_\infty$.

The data for the plot are as follows:

p/Torr	100	200	300	400	500	600	700
(p/Torr) / (V/cm^3)	9.80	10.8	11.8	12.7	13.6	14.4	15.2

The (least squares) slope is 0.00904, so $V\infty = 111$ cm^3. The intercept at p = 0 is 8.99, so

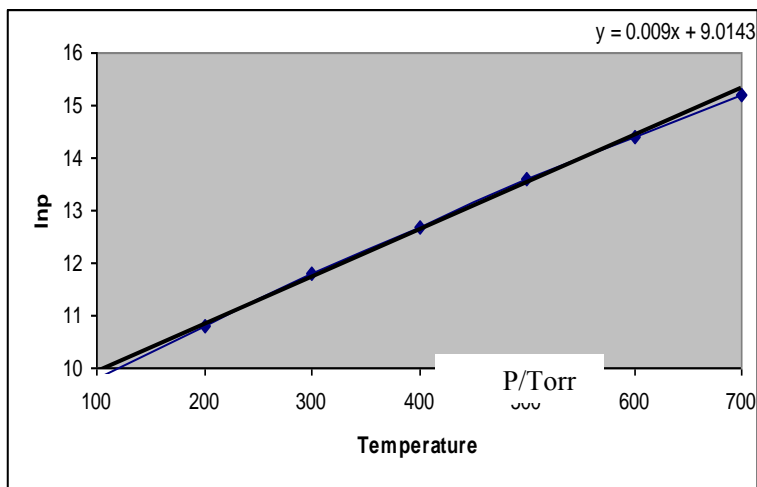$K = \dfrac{1}{(111\ \text{cm}^3) \times (8.99\ \text{torr cm}^{-3})} = 1.00 \times 10^{-3}$ Torr^{-1}

Figure 5.13.

Comment At high surface coverage, the data would deviate from a straight line. The dimensions of K are 1/pressure.

Question 5.4.

Measuring the Isoteric Enthalpy of Adsorption
The data below show the pressures of C0 needed for the volume of adsorption (corrected to 1.00 atm and 273 K) to be 10.0 cm^3. Calculate the adsorption enthalpy at this surface coverage.

T/K	200	210	220	230	240	250
p/Torr	30.0	37.1	45.2	54.0	63.5	73.9

Solution to Question 5.4.

The Langmuir isotherm can be rearranged to

$$Kp = \frac{\theta}{1 - \theta}$$

Therefore, when θ is constant,
$\ln K + \ln p = $ constant

It follows from equation 4.13 that

$$\left(\frac{\partial \ln p}{\partial T}\right)_\phi = -\left(\frac{\partial \ln K}{\partial T}\right)_\phi = -\frac{\Delta_{ad}H^\varnothing}{RT^2} \tag{5.14}$$

with $d(1/T)/dT = -1/T^2$, this expression rearranges to

$$\frac{(\partial \ln p)}{\partial T \quad \phi} = \frac{-\Delta_{ad}H^{\varnothing}}{R}$$

Therefore, a plot of $\ln p$ against $1/T$, figure 5.14, should be a straight line of slope $\Delta_{ad}H^{\varnothing}/R$.

Draw up the following table:

T/K	200		210	220	230	240	250
$10^3/(T$/K)	5.00		4.76	4.55	4.35	4.17	4.00(x-axis)
$\ln(p$/Torr)	3.40		3.61	3.81	3.99	4.15	4.30(y –axis)

The slope(of the least squares fitted line) is –0.904, so $\Delta_{ad}H^{\varnothing} = -(0.902 \times 10^3$ K) x R
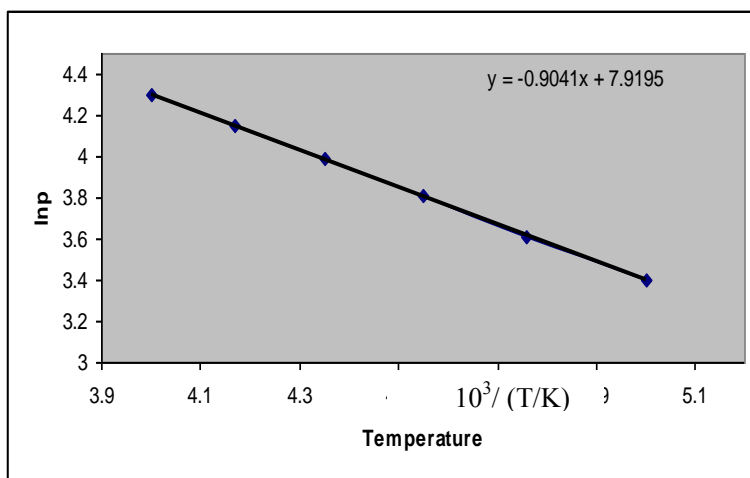
$= -7.50$ kJmol^{-1}.

Figure 5.14.

Comment the value of K can be used to obtain a value of $\Delta_{ad}G^{\varnothing}$, and then that value combined with $\Delta_{ad}H^{\varnothing}$ to obtain the standard entropy of adsorption.

Exercise 5.5.

Repeat the calculation using the following data:

T/K	200	210	220	230	240	250	
P/Torr		32.4	41.9	53.0	66.0	80.0	96.0

[Ans = -9.0 kJ mol^{-1}]

5.6. Using the BET Isotherm

The data below relate to the adsorption of N_2 on rutile (TiO$_2$) at 75 K. confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/torr	1.20	14.0	45.8	87.5	127.7	164.4	204.7
Vmm^3	601	720	822	935	1046	1146	1254

At 75 K, $p^* = 570$ Torr. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

Solution to Question 5.6
Equation 4.16 can be reorganised into

$$\frac{Z}{(1-z)\,V} = \frac{1}{cV_{mon}} + \frac{(c-1)\,z}{cV_{mon}}$$

It follows that $(c-1)/cV_{mon}$ can be obtained from the slope of a plot of the expression on the left against z, and cV_{mon} can be found from the intercept at z = 0. The results can then be combined to give c and V_{mon}, figure 5.15

We can draw up the following table:

p/torr	1.20	14.0	45.8	87.5	127.7	164.4	204.7
10^3z	2.11	24.6	80.4	154	224	288	359 (x-axis)
$10^4z/(1-z)$ (V/mm^3)	0.035	0.350	1.06	1.95	2.76	3.53	4.47 (y - axis)

The least squares best line has an intercept at 0.0406, so

$$\frac{1}{cV_{mon}} = 4.06 \times 10^{-6} \text{ mm}^{-3}$$

The slope of the line is 1.23×10^{-2}, so

$$\frac{c-1}{cV_{mon}} = (1.23 \times 10^{-2}) \times 10^3 \times 10^{-4} \text{ mm}^{-3} = 1.23 \times 10^{-3} \text{mm}^{-3}$$

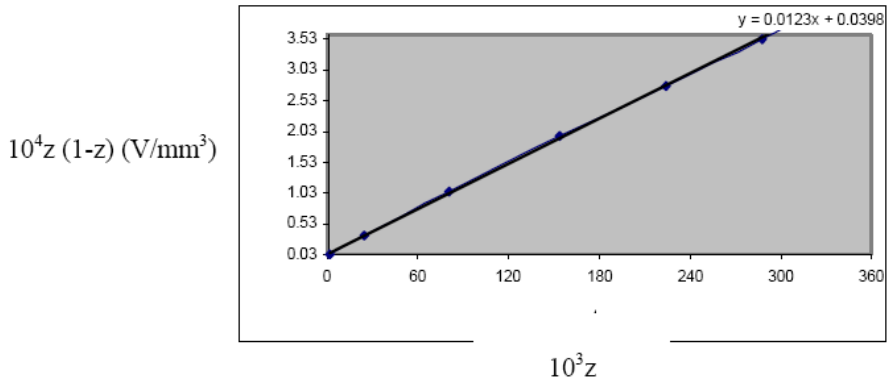The solutions of these equations are $c = 303$ and $V_{mon} = 814 \text{mm}^3$.

Figure 5.15.

Comment At 1.00 atm and 273 K, 810 mm^3 corresponds to 3.6×10^{-5} mol, or 2.2×10^{19} atoms. As each atom occupies an area of about 0.16 nm^2, the surface area of the sample is about 3.5 m^2.