Appendix A: Fundamental Constants and Units

Speed light (in vacuum)	$C = 2.99792458 \times 10^{8}$ m s^{-1}
Planck's constant	$h = 6.6260755 \times 10^{-34}$ Js
Gas constant	$R = 0.0820584$ L atm mol^{-1} K^{-1}
	$R = 8.314510$ J mol^{-1} K^{-1}
Gravitational constant	$g = 9.8066$ m/s^{2}
Faraday constant	$F = 9.6485309 \times 10^{4}$ C mol^{-1}
Avogadro number	$N_A = 6.0221367 \times 10^{23}$ mol^{-1}
Electron charge	$e^{-} = -1.60217733 \times 10^{-19}$ C
Electron mass (rest)	$m_e = 9.1093897 \times 10^{-31}$ kg $= 0.00054858$ amu
Proton mass (rest)	$m_p = 1.67262 \times 10^{-27}$ kg $= 1.007276$ amu
Neutron mass (rest)	$m_n = 1.67493 \times 10^{-27}$ kg $= 1.008665$ amu
Solar constant (sea level)	1,370 W/m^{2}
Solar luminosity	3.85×10^{26} W

Nomenclature for powers of 10

Prefix	Symbol		Prefix	Symbol	
atto	(a)	10^{-18}	kilo	(k)	10^{3}
femto	(f)	10^{-15}	mega	(M)	10^{6}
pico	(p)	10^{-12}	giga	(G)	10^{9}
nano	(n)	10^{-9}	tera	(T)	10^{12}
micro	(μ)	10^{-6}	peta	(P)	10^{15}
milli	(m)	10^{-3}	exa	(E)	10^{18}

Length

$\mathring{A} = 10^{-10}$ m
inch = 2.54 cm
mile = 1.609 km
knot = 1 nautical mile/hr
= 1.1516 mile/hr
= 1.853 km/hr

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Area
acre = 43,560 ft^2
= 4,047 m^2
hectare = 10^4 m^2
square mile = 640 acres
= 259 hectares

Volume
1 ft^3 = 28.317 L
1 m^3 = 1,000 L
1 gal (US) = 3.785 L
= 4 quarts
= 128 fluid oz.
1 gal (Imp) = 4.546 L
= 4 quarts
= 160 fluid oz.
1 barrel (US) = 31.5 US gal
1 barrel (Imp) = 36 gal (Imp)
1 barrel (oil US) = 42 US gal
= 158.9873 L

Mass
1 lb. = 453.6 g
1 ton = 2,000 lb.
1 tonne = 1,000 kg
= 2204.6 lb.
1 kg = 2.2046 lb.
1 amu = 1.66054×10^{-24} g
= 931.4874 MeV

Pressure
1 atm = 1.01325 bars
= 760 torr
= 101,325 Pa

Energy
Joule (J) – 1 volt (V) × 1 amp
1 eV = 1.6021×10^{19} J
= 4.450×10^{-26} kWh
1 MeV = 9.65×10^{10} J/mol
Watt (W) = 1 J/sec
Curie (Ci) = 3.7×10^{10} disintegration/sec
Becquerel (Bq) = 1 disintegration/sec
1 calorie (cal) = 4.183 J
1 horsepower (HP) = 745.7 W
1 kWh = 3,412 Btu
1 Btu = 1055.06 J
$\approx$ 1 kJ = 2.931×10^{-4} kWh
1 Quad $\approx 10^{15}$ Btu
$\approx 10^{15}$ kJ
= 10^{12} ft^3 (CH_4)
= 2.93×10^{11} kWh

$\approx 40 \times 10^6$ tons coal
$= 170 \times 10^6$ bbl crude oil
$= 8.0 \times 10^9$ US gal gasoline
1 bbl oil = 42 gal (US)
$= 5.8 \times 10^6$ Btu
$= 1.65 \times 10^3$ kWh
= 159 L
= 136 kg
= 5.8 M Btu
1 ft^3 Natural gas (CH_4) = 1,035 Btu
= 0.310 kWh
1 lb. coal = 3.84 kWh
1 gal (US) gasoline = 36.7 kWh
1 ton oil equiv. (toe) $= 4.19 \times 10^{10}$ J
$= 10^7$ kcal
1 ton coal equiv. (toe) $= 2.93 \times 10^{10}$ J
$= 7 \times 10^6$ kcal
1 therm $= 10^5$ Btu 1 kg TNT $= 10^9$ J

On July 23, 1983 a new Boeing 767 (Air Canada Flight No. 143) refueled in Montreal. The fuel gauge was not working so it was decided to refuel by the manual use of a dipstick which correctly showed the fuel in the aircraft to be 7,682 L. The required fuel for the trip was 22,300 kg. The mechanics, using 1.77 as the density conversion factor, calculated the required fuel necessary,

$$7682 \times 1.77 = 13{,}597 \text{ kg on board}$$
$$22{,}300 - 13{,}597 = 8703 \text{ kg to be added}$$
$$8703 \div 1.77 = 4916 \text{ L of fuel to be added}$$

They believed 1.77 represented the conversion of liters to kilograms, in fact it was the conversion of liters to pounds, i.e., 1.77 Ib/L is the density of the jet fuel. The density of the jet fuel in proper units is 0.803 kg/L and the amount of fuel which ought to have been added was 20,163 L. Using 1.77 without any units led to a near disaster.

Further Readings

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3. The Gimli Glider http://www.acs.org/VC2/2my/my2—143.html
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Appendix B: Viscosity

Introduction

Viscosity is that property of a fluid that opposes the relative motion of adjacent portions of the fluid and can consequently be regarded as a type of internal friction. Viscosity can be defined as the force required to move a layer of fluid of unit area with a velocity 1 cm/s greater than the velocity of another layer 1 cm away (see Fig. B.1). Since force is proportional to the velocity difference between the layers and inversely proportional to the distance between the layers, then

$$F \propto \frac{VA}{x} \tag{B.1}$$

where F is force, V is velocity difference, x is distance between layers, and A is area of layer. Therefore,

$$F - \frac{\eta V A}{x} \tag{B.2}$$

where η, the proportional constant, is the viscosity.

The units of viscosity are dyne second per square centimeter or gram per second per centimeter (1 dyne second per square centimeter is simply called 1 poise, after Poiseuille). The reciprocal of viscosity is called the fluidity and is often represented by ϕ; it is a measure of the ease with which a liquid flows.

In a gas the viscosity increases as the temperature increases, whereas in a liquid the converse is true. The interpretation of viscosity in a gas utilizes the high kinetic energy of the molecules and involves the transfer of momentum for one layer of the gas to another, leading to a relationship of the form $\eta \propto v$, where v is the average speed of the gas molecules. In liquids, a completely different interpretation is required, since the molecules are closely packed except for the presence of holes. Over half a century ago it was found that the fluidity of a substance at its melting point is proportional to $V - b$, where V is the volume of liquid and b is the van der Waals constant. This is the effective space occupied by the molecules. $V - b$ is, therefore, the free volume of the liquid. Since most solids expand approximately equal at this temperature the free volumes of liquids are approximately the same; therefore, we could expect the viscosities of most liquids at their melting points to be approximately equal. This is correct within an order of magnitude. The theory of the significant structures of liquids has been able to relate the viscosity mechanism to fiuidized vacancies and to

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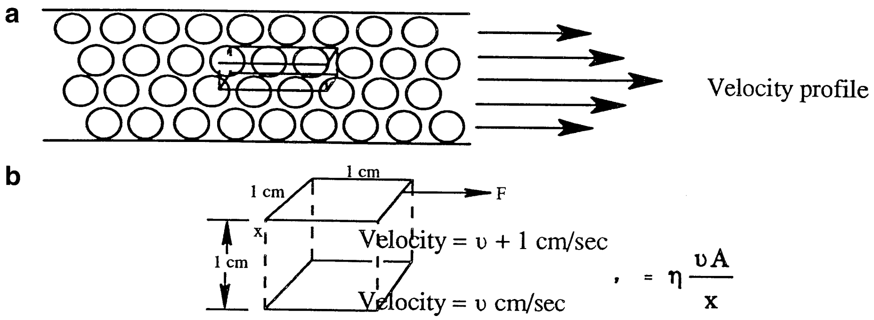

Fig. B.1 Schematic representation of the viscosity of a liquid. (**a**) Liquid near the walls of a tube moves slower than liquid near the center or furthest from the walls. Velocity profile depends on the viscosity of the liquid. (**b**) Viscosity is the force required to maintain a unit velocity gradient for 1 cm^2 plates 1 cm apart

show that the effect of temperature on viscosity is associated with the energy required to create a hole in the liquid. The influence of temperature on the viscosity of a liquid is often represented by the following equation:

$$\eta = Ae^{Evis/RT} \tag{B.3}$$

where E_{vis} is the energy of activation of viscosity, R is the gas constant, T is the absolute temperature, and A is a constant depending on the substance.

It is interesting that the average heat of vaporization of a liquid is approximately three times the activation energy of viscosity. This means that three times as much energy is required to remove a surface molecule as to move a bulk molecule past a neighbor. The ratio $n = E_{vap}/E_{vis}$ was shown byEyring to be equal to the ratio of the size of a molecule to the size of a hole needed for viscous flow. It has been found that, since a hole of molecular dimensions is not required if, for example, two molecules rotate about their point of contact, the value of n is about 3 for a spherically symmetric nonpolar molecule and increases to 5 as the deviation from spherical symmetry increases.

Measurement of Viscosity

The viscosity of a liquid can be measured by several methods. The most convenient for laboratory work are the Ostwaid viscometer and the falling ball methods.

Ostwald Viscometer

In 1846 the viscosity of a liquid was related by Poiseuille to the rate of flow of a liquid through a tube under a pressure differential. The Poiseuille equation is as follows:

$$Q = \frac{\pi P r^4}{8\eta l} \tag{B.4}$$

where Q is the volume of liquid flowing per unit time through a tube of radius r and length l, across which there is pressure drop P. If the pressure drop is due to gravity, then $P \sim hdg$ where h is the height of the liquid, d is the density, and g is the acceleration due to gravity. By substituting hdg and P in (B.4), we obtain

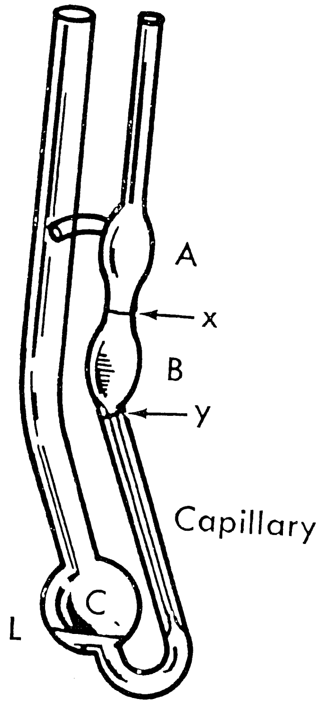

Fig. B.2 *Ostwald viscometer*. The quantity of liquid (volume *V)* required is such that when the liquid is drawn into bulb A, the level in reservoir C is not below level L. The time of flow *t*, from level *x* to y, is recorded and compared with other liquids of identical volume *V* and of known density *d*

$$\eta = \frac{\pi r^4 hdg}{8Ql} \tag{B.5}$$

The measurement of absolute viscosity by this method requires an exceptional amount of care and patience. For most purposes, it is sufficient if relative viscosities are known. Hence, if the time for a fixed volume of liquid to flow through a capillary is measured, then the comparison of its time of flow with that of another liquid enables us to calculate a relative viscosity. Since

$$Q = V/t \tag{B.6}$$

where V is the volume of liquid, and t is the time of flow, then

$$\eta = \frac{\pi r^4 hdgt}{8Vl} \tag{B.7}$$

For a fixed apparatus as shown in Fig. B.2, V, h, g, r, I are constant. Therefore, for one liquid,

$$\eta_1 \propto d_l t_l \tag{B.8}$$

Hence, for two liquids,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \tag{B.9}$$

The viscosities of several substances at different temperatures, which can conveniently be used as references, are given in Table B.1.

Table B.1 Viscosities of several substances at various temperatures, in units of centipoise

		Temperature (°C)						
Name	Formula	0	10	20	30	40	50	60
Water	H_2O	1.79	1.31	1.00[a]	0.801	0.656	0.549	0.469
Ethanol	C_2H_5OH	1.77	1.47	1.20	1.00	0.834	0.702	0.592
»-PropanoI	$n\text{-}C_3H_7OH$	3.88		2.25	1.72	1.41	1.13	
Isopropanol	$iso\text{-}C_3H_7OH$	4.56		2.37		1.33		
Benzene	C_6H_6		0.758	0.652	0.564	0.503	0.442	0.392
Toluene	$C_6H_5CH_3$	0.772		0.590	0.526	0.471		
Chlorobenzene	C_6H_5C1	1.03		0.799		0.631		
Ethyleneglycol	$C_2H_4(OH)_2$			19.9		9.13		4.95

[a] Viscosity of H_2O at 20.20°C is 1.0000 centipoise

Falling Bail Method

The viscosity of a liquid may be determined from Stokes' law. In 1850 Stokes showed that a sphere of radius r under a constant force F will move with constant

$$\frac{\eta}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

velocity v in a viscous liquid of viscosity η according to the following relation:

$$F = 6\pi r \eta v \tag{B.10}$$

If the sphere is acted on by gravity alone, then

$$F = 4/3\pi \mathrm{r}^3 (d - d')\mathrm{g} \tag{B.11}$$

where d is the density of sphere, d' is density of fluid, and g is acceleration due to gravity.

Therefore

$$\eta = \frac{2r^2 (d - d')g}{9\upsilon} \tag{B.12}$$

Since $v = I/t$ then

$$\eta = \frac{2r^2 g}{9l}(d - d')t \tag{B.13}$$

Since r, d, g, I are constant, then the relative viscosity can be easily determined from the following equation:

$$\frac{\eta_1}{\eta_2} = \frac{(d - d_1)t_1}{(d - d_2)t_2} \tag{B.14}$$

For very viscous liquids the falling ball viscometer is generally more suitable than the Ostwald viscometer.

The viscosity and the activation energy of viscosity of a pure liquid substance can tell us very little about the substance. However, the viscosity of a solution is much more informative. Thus, if acetone and chloroform are mixed and the viscosities of the various solutions are measured, it can be determined whether or not "compound" formation can exist. These two substances form a hydrogen bond about 11.3 kJ/mol, and the appearance of a maximum about 1:1 molecular ratio supports this view. Many such compounds, first detected by viscosity anomalies, are now being characterized by more elegant methods. It is interesting to note that substances that show this viscosity effect generally show a volume change when mixed. This suggests a change in the free volume of the solution compared with the free volume available for each of the individual substances.

It must be pointed out that a viscosity effect in the mixture of two or more substances does not necessarily prove the formation of a compound, since other effects, such as steric hindrance[1] and the association of one of the components may give rise to a viscosity anomaly.

Applications of Viscosity

Molecular Weight of Polymers

From the measurements of viscosity of solutions of polymeric substances, it is possible to determine the average molecular weight of the solute. The empirical relation is as follows:

$$[\eta] = KM^a \tag{B.15}$$

where K and a are constants that depend on the solute, solvent, and temperature, M the average molecular weight, and [q] the intrinsic viscosity and fractional change in the viscosity of a solution per unit concentration of solute at infinite dilution. This is represented as

$$[\eta] = \underset{C \to 0}{\text{limit}} \left[\frac{1}{C} \left(\frac{\eta - \eta_0}{\eta_0} \right) \right] \tag{B.17}$$

where η_0 and η are the viscosity of the solvent and the solution, respectively, and C is the concentration of the polymer, usually in wt.%. Although other methods for determination of molecular weight of polymers are more accurate and more reliable, the intrinsic viscosity can give relative molecular weights with reasonable accuracy and facility. It is often the first determination made for the molecular weight of a polymer.

Drag Reducers

As the flow of a fluid in a tube increases as a result of increasing applied pressures, the Reynolds number (Re) increases to the onset of turbulence where

$$\text{Re} = \text{u}d/v \tag{B.17}$$

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[1] Steric hindrance is the spatial interference experienced in molecules because of the specific location of bulky chemical groups.

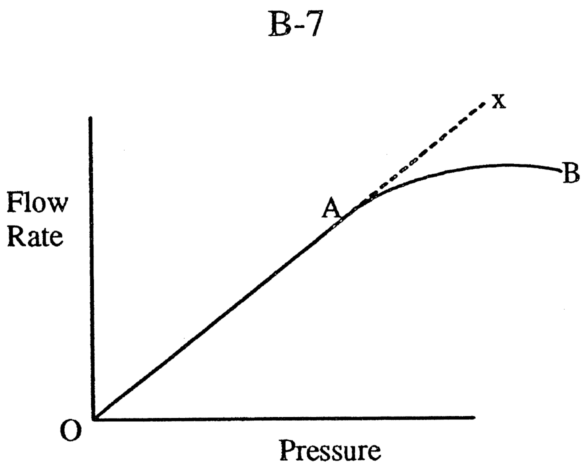

Fig. B.3 Reduction of turbulence by the addition of a drag reducer (DR) to a fluid OAB, fluid only; OX, with DR

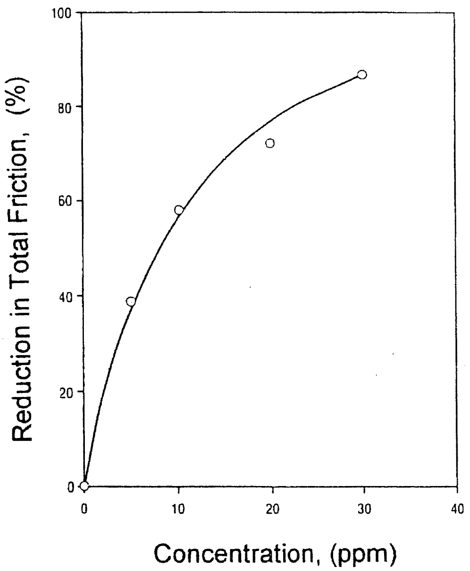

Fig. B.4 Effect of polyethylene oxide on the flow rates of water through 1,000 ft of a 1.5 in. hose at various pressures

u is the velocity of flow, d is the diameter of the tube, and v is the kinematic viscosity[2] and equal to η/ρ, where ρ is the density of the fluid.

This is shown in Fig. B.3 where at point A, turbulence occurs, i.e., Re > 2,000. When a low concentration of a long chain soluble polymer is dissolved in the fluid it prevents the onset of turbulence and the flow rate-pressure line is extended from O to X along the straight line plot. This effect is called *drag reduction* and has been applied to the pumping of oil in pipelines, blood in arteries, and free flow of fluids. Figure B.4 shows the reduction in friction (viscosity) as the concentration of polyethylene oxide (PEO, mol. wt. = 5 MD) in water is increased. Figure B.5 shows the increased flow of water through a 1.5 in. hose as a function of pressure when PEO is added to the water. This is illustrated in Fig. B.6 where a 1.5 in. fire hose can deliver water at a rate equal to that of a 2.5 in. hose if polyethylene oxide has been added to the water.

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[2] $v = 0.0100\ \text{cm}^2/\text{s}$ (Stokes) at 20°C for water; $v = 6.8\ \text{cm}^2/\text{s}$ (Stokes) at 20°C for glycerol.

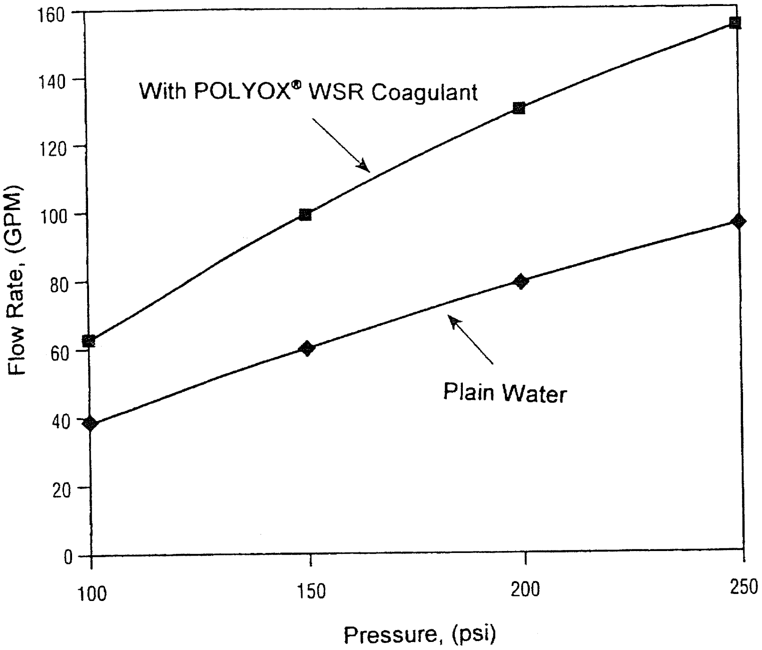

Fig. B.5 Effect of low concentrations of polyethylene oxide on friction (viscosity) reduction

Fig. B.6 Effect of high molecular weight polyethylene oxide) in increasing water flow through fire hoses. Hoses had been adjusted to throw water the same distance and then 30 ppm of polyethylene oxide) were injected into the hose on the left

Electrorheological Fluids

Some liquids with a suspension of solids or colloids can, under the influence of an applied potential, show an increase in viscosity by a factor as high as 10^5, i.e., the liquid is converted to what is essentially a solid. This is called the *Winshw effect* and the liquid is an electrorheologica! (ER) fluid.

Winslow (1949) reported that silica gel in a low-viscosity oil showed this effect under an electric field of 3 kV/mm. The fluid can be sheared with a force proportional to the square of the electrical field. For example, a 25% by volume of hydrophobic colloidal silica spheres of 0.75 pm diameter in 4-methylcyclohexanol showed ER responses at 40–4,000 Hz, although dc fields are also viable. Dispersants are often added to the suspension in order to prevent the settling of the solids.

The ER fluids can have applications as clutches, speed controllers, and valves. Other applications can be expected as work on the subject continues.

Exercise

1. From the data shown in Table B.1 convert the value of the viscosity of ethylene glycol at 20°C to SI units, i.e., mNsec/m^{-2}.
2. The viscosity of hexadecane is 3.6 mNsec/m^{-2} at 22°C. The flow of water (20 mL) in an Ostwald viscometer took 47 s at 22°C. Calculate the time it would take 20 mL of hexadecane (density = 0.7751 g/mL) to flow through the same viscometer at the same temperature.
3. Discuss the differences in viscosity expected for H_2O, H_2O_2, and D_2O.
4. Of the two propanols which one would you expect to have the higher viscosity? Give reasons for your answer.
5. (a) Calculate E_{vis} for trinitroglycerol (TNG) which has the value of $\eta = 360$ mNsec/m^{-2} at 20°C and $\eta = 13.6$mNsec/m^{-2} at 40°C, (b) calculate η for TNG at 60°C.
6. The fluidity of a liquid explosive doubles between 10° and 20°C. Determine (a) E_{vis} and (b) η_{60}/η_{10}.

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Appendix C: Surface Chemistry

C1.1.1 Surface Tension

A surface is the boundary between two phases. The chemistry of this interface is of great importance to a variety of subjects such as adhesion, corrosion, surface coatings, and many others. The differential attraction of surface molecules in a liquid results in a surface energy that is also called *surface tension,* and accounts for the tendency of a free or suspended liquid to assume a spherical shape in droplets or to expose as small a surface area as possible. Thus the surface of a liquid in contact with air or another liquid phase in which it is immiscible may be considered similar to a rubber elastic membrane or balloon that assumes a spherical shape. To distort this to any other shape would require the expenditure of energy, since the surface area would increase; i.e., the rubber membrane would stretch. A surface energy can therefore be associated with a liquid–gas interface and can be defined as the energy or work required to increase the surface area of a liquid by 1 cm^2 by bringing bulk molecules to the surface; i.e., work per square centimeter. Since the surface is under a tension, a force called the surface tension y can be defined as the force applied to increase the surface area of a liquid when acting on 1 cm of surface; i.e., force per centimeter. The units of surface energy are

$$\frac{ml^2t^2}{l^2}$$

and those of surface tension as force are

$$\frac{mlt^{-2}}{l}$$

The surface energy and surface tension both have units of mt^{-2} and are equivalent (see Fig. C.1).

When a drop of liquid is placed on a solid, a definite angle of contact exists at the point where the liquid meets the solid. This is shown in Fig. C.2 where the angle θ is called the *contact angle.*

The contact angle has one of two values, advancing or receding, depending on whether the liquid–solid interface area is increasing or decreasing. This is commonly called a *hysteresis* effect. Until recently, it was believed that the ratio of these two angles depended only on the roughness of the surface. It is now reasonably well established that the hysteresis is due to the penetration of the liquid molecules into surface discontinuities and, therefore, depends on the size of the molecules relative to the intermolecular pores of the solid surface. The contact angle thus depends on the type of solid surface, liquid, and to a lesser degree, temperature. Table C.1 lists the values of the contact angles for various substances as well as some surface tension values.

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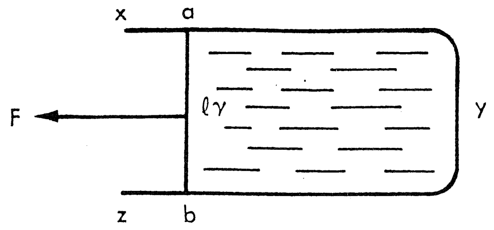

Fig. C.1 Thin film of liquid *{ayb)* is stretched on an inert wire frame *{xyz).* A wire barrier *(ab)* of length/is pulled toward *xz* with force *F*. Since the liquid increases in area on both sides of the frame, then at balance, $F = 2ly$, where *y* is the surface tension of the liquid

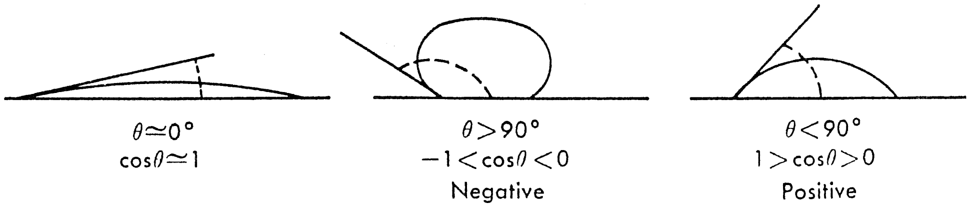

Fig. C.2 A drop liquid is placed on a solid surface. The angle formed at the interface is called the contact angle. If the volume of the drop is increased, the advancing angle is measured. If the volume of the drop is decreased, the receding angle is measured

Table C.1 Contact angles and surface tensions for various substances

Contact angle θ[a]

Water on siliconized glass:				Water on:	
T(°C)	γ(dyne cm^{-1})	θ_A	θ_R	Glass	0°
4	75	104°	75°	Paraffin	108°
22	72	106°	76°	Polyethylene	94°
75	63	104.5°	76.5°	Teflon	110°
				Graphite	86°
				Kel F	90°

Standard surface tension in dynes per centimeter, versus air at 20°C

Water	72.8
Acetone	23.7
Benzene	28.9
Toluene	28.4
Choloroform	27.1
Carbon tetrachloride	26.8
n-Hexane	18.4
n-Octane	21.8
n-Octanol	27.5

[a] θ_A is advancing angle and θ_R is receding angle. When one value of θ is given, it is usually the arithmetic average of θ_A and θ_R

The contact angle depends on the relative bonding between liquid and solid molecules (B_{ls}), compared with the bonding between liquid molecules (B_u). Thus, if B_{us} is greater than B_u, *6* is usually less than 90° and the solid is considered to be wetted by the liquid. However, if B_{ls} is less than B_u, then θ is usually greater than 90° and the solid is not wetted by the liquid. It must be pointed out that the angle of 90° chosen for the demarcation between wetting and nonwetting is quite arbitrary.

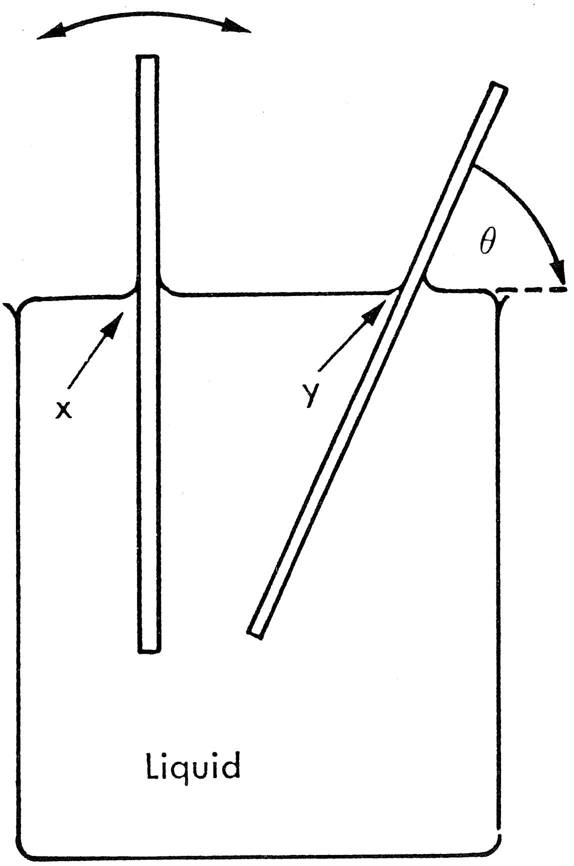

Fig. C.3 Measurement of contact angle. A solid slide of the material is immersed in the liquid and the meniscus x at the air interface is noted. The slide is then rotated about the point of contact with the liquid surface until the meniscus flattens *(y)*. The advancing and receding angles are associated with decreasing and increasing contact angles, respectively

The contact angle can be measured by direct observation with the use of magnification of the liquid drop on a flat surface of the solid material, or by inclination of a slide of the solid in the liquid until the meniscus flattens out. The latter method is shown in Fig. C.3.

The wetting of a solid by a liquid is exceedingly important for several applications, including soldering, welding, adhesion and gluing, painting, and dyeing. The presence of fluxes to remove oxide layers in soldering, and the need of special wetting agents in epoxy glues, adhesives, and paints are related to the contact angle and surface tension.

Measurement of Surface Tension

The surface tension of a liquid can be measured in a variety of ways, including capillary tube rise, du Noüy ring method, bubble pressure, and drop weight. These methods vary greatly in their applications.

Capillary Tube Rise Methods

The simplest and most common method of determining the surface tension of a liquid is the *capillary tube rise method.* If a glass capillary tube is immersed in a liquid such as water, the liquid in the capillary tube will rise above the outside level of the liquid. This is due to the greater liquid–solid force than the liquid-liquid intermolecular forces, and the liquid tends to wet as much of the solid

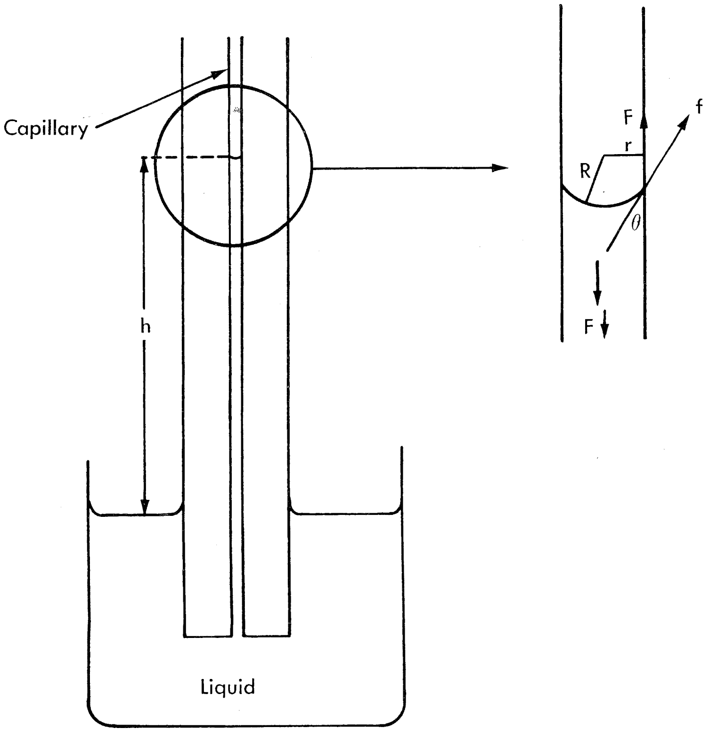

Fig. C.4 Measurement of surface tension by capillary rise. The liquid rises in the capillary until equilibrium is reached where the gravitational force is balanced by the upward surface tension force. The radius of the meniscus *R* is assumed to be approximately equal to the radius of the capillary, *r*

as possible until the gravitational pull of the column of liquid is equal to the surface tension force (see Fig. C.4).

If the radius of the capillary tube is *r* and the density of the liquid is *d*, then the force down, $F\downarrow$, which is due to the column of liquid, is defined as follows:

$$F \downarrow = \pi r^2 hdg \tag{C.1}$$

The force *f* along the contact angle θ is equal to the surface tension x the length of the liquid–solid contact, *f*; i.e., $f = \gamma l$. Since *f* is equal to $2\pi r$, then *f* is defined as follows:

$$f = 2\pi ry \tag{C.2}$$

However, the vertical force $F\uparrow$ is defined as follows:

$$F \uparrow = f cos\theta \tag{C.3}$$

Therefore,

$$\mathrm{F} \uparrow = 2\pi ry \cos\theta \tag{C.4}$$

When the column of liquid has reached the same equilibrium position from either a lower or a higher height. (The effect of contact angle hysteresis may make these two heights slightly different.)

$$\mathrm{F}\downarrow -\mathrm{F}\uparrow \tag{C.5}$$

$$\pi r^2 hdg = 2\pi r\gamma \cos\theta \tag{C.6}$$

or

$$\gamma = \frac{rhdg}{2\cos\theta} \tag{C.7}$$

If $9 = 0$, then cos $9 = 1$ and

$$\gamma = \frac{rhdg}{2} \tag{C.8}$$

If $\theta = 90°$, cos θ is negative, and h becomes a negative value; i.e., instead of a rise in the capillary tube, there is a depression. This is observed for the mercury-in-glass system.

Ring or du Noüy Method

Just as it is possible to float objects heavier than water on the surface of water, it is possible to pull the surface upward (increase the surface area) by the application of a suitable force, and thereby calculate the surface tension. The *du Noiiy* method makes use of a clean platinum ring of radius r that is placed on the liquid surface. The liquid, which wets platinum, tends to adhere to the ring, which is slowly raised by the application of a force, which is previously calibrated, until the net force pulling the ring upward exceeds the surface tension and the ring breaks from the surface. At that point the surface tension force, F, is $2l\gamma$, where 1 is the circumference of the ring, and since $\mathrm{F} = mg$,

$$2l\gamma = mg \tag{C.9}$$

where m is the weight calibration for the system and g is the acceleration due to gravity. Since $1 = 2\pi r$, then

$$\gamma = \frac{mg}{4\pi r} \tag{C.10}$$

The factor 2 appears in (C.9) because two liquid surfaces (one on the inside and one on the outside of the ring) are formed as the ring is raised.

In practice, the absolute value is in error because of the diameter of the wire, the density of the liquid, as well as other terms, and it is often calibrated by a variety of substances to minimize such errors. The most important application of this method is the determination of interfacial tension between two liquids, where other methods do not apply very readily. The ring method is shown in Fig. C.5.

Bubble Pressure Method

If a tube is immersed in a liquid, and the gas pressure in the tube is increased slowly, the liquid level in the tube will drop until the end of the tube is reached, then a further increase in pressure will create bubbles. If P is the maximum pressure measured and P_h the hydrostatic pressure hdg, then

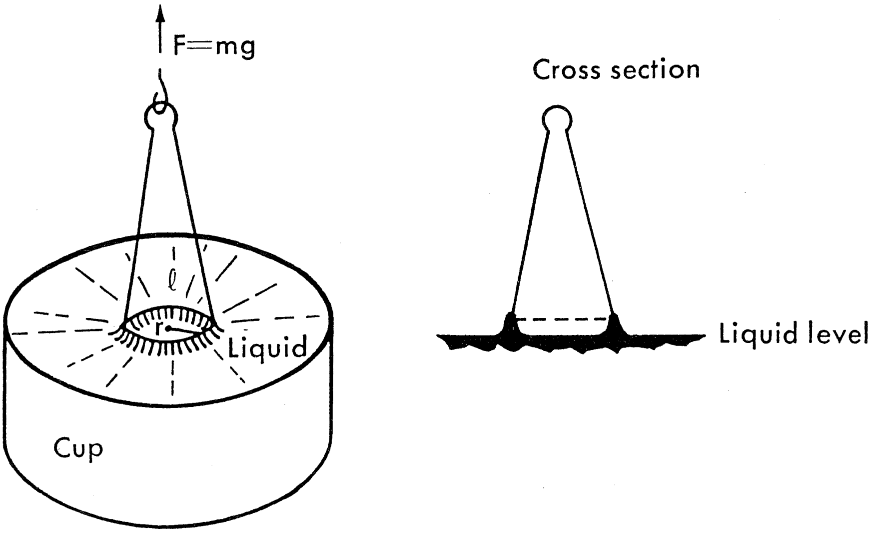

Fig. C.5 Measurement of surface tension by du Noüy method. The platinum ring of radius *r* is allowed to touch and be wetted by the liquid surface. It is then raised by a force *F* (effected by a torsion type of balance) until the ring breaks away from the liquid

$$P - P_h = P_s \tag{C.11}$$

$P_S \Delta V$ *is* the work done to increase the volume of the bubbles. However, if the volume increases, the area of the bubble increases, and the energy required to increase the surface area of the bubble is $y\Delta A$ (ΔA is the area increase) (see Fig. C.6). Therefore, at equilibrium,

$$\gamma \Delta A = P_s \Delta V \quad \text{or} \quad \gamma dA = P_s dV \tag{C.12}$$

If r is the radius of curvature of the bubble, then

$$A = 4\pi r^2, V = 4\pi r^3/3, \ dA = 8\pi r dr, dV = 4\pi r^2 dr$$

By substituting these values in (C.12), we obtain

$$\gamma 8\pi r dr = P_s 4\pi r^2 dr \quad P_s = 2\gamma/r \tag{C.13}$$

The value of r is equal to the radius of the tube when the bubble just breaks away from the tube; i.e., when the radius of the bubble is at a minimum, and the pressure is at a maximum. Since P_h — hdg, then if h, d, r, and p are measured, it is possible to calculate γ. It should be noted that γ, so evaluated, is independent of contact angle.

Drop Weight Method

When a liquid is allowed to flow slowly from a vertical capillary tube, it forms drops that grow and finally become detached from the end of the capillary tube. The size of the drops will depend on the outside radius of the capillary tube and the surface tension of the liquid. At the moment when a drop falls, the gravitational pull mg, or Vdg, is equal to the surface tension $2\pi r\gamma$, where m is the mass of the

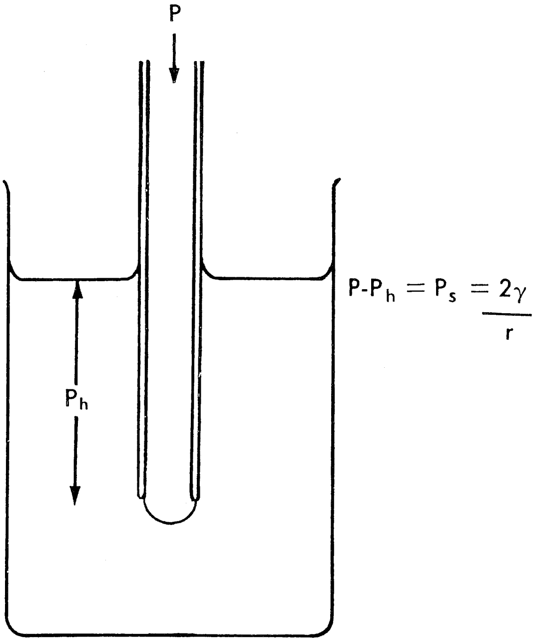

Fig. C.6 Measurement of surface tension by the bubble pressure method. The maximum pressure is the pressure above which the bubble breaks away from the tube. This value is corrected for the hydrostatic pressure P_h and gives P — $P_h = F_s = 2\gamma/r$

drop, V is the volume of liquid, d is the density of the liquid, r is the radius of the drop, and y is the surface tension. Thus, if we weigh and count the drops of a liquid, we can determine the surface tension from the following equation if the density is known.

$$2\pi r\gamma - mg \tag{C.14}$$

In general, a correction is required, since not all the liquid forming the drop leaves the tip of the capillary tube and the surface tension does not act exactly vertical. Thus

$$\gamma = \frac{mg}{2\pi r\phi} \tag{C.15}$$

where Ø depends on the ratio $r/V^{1/3}$ and has the value of about 1.7 when $r/V^{1/3}$ is between 0.75 and 0.95.

For a given tip, it is possible, with reasonable accuracy, to determine the relative surface tension from the following relation:

$$\frac{\gamma 1}{\gamma 2} = \frac{m1}{m2} \tag{C.16}$$

The *drop weight method* is independent of contact angle and is suitable for the determination of interfacial tension if the tip is immersed into a second liquid immiscible with the heavier dropping fluid. Thus, if the dropping liquid can be collected free from the second liquid and weighed, the liquid-liquid interfacial tension can be determined.

Surfactants reduce the interfacial tension of water either between the two liquids or between liquid and solid. The important properties include:

1. The solubility of the surfactant in at least one of the phases.
2. The surfactant is composed of both hydrophilic and hydrophobic groups on the molecule.

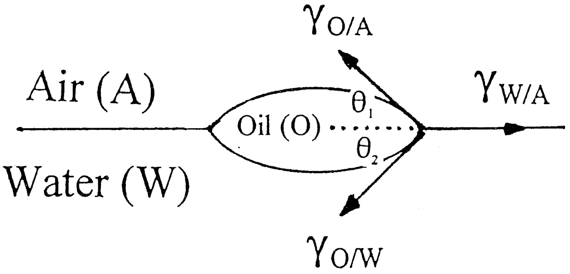

Fig. C.7 Cross section of a drop of an organic liquid such as oil (O) on the surface of water (W) at equilibrium

3. The surfactant molecules tend to orientate on the surface of the liquid.
4. The surfactant tends to concentrate at the interface.
5. The surfactant usually lowers the surface tension of the liquid.

The study of surface tension is really a branch of surface chemistry, and its development has been exceedingly rapid in the last decade. Thus, adhesion can be considered to be partially an exercise in wetting and spreading of liquids on solid surfaces. The flotation of ores is accomplished by gravity differences as well as by the adhesion of the solid particle to an air bubble, and it involves solid–liquid-gas interfaces. It is possible to reduce the vaporization of water from bodies of water with large surfaces such as reservoirs and lakes, by adding a monolayer of a substance such as hexadecanol or other surface-active agents. The action of soaps produces a decrease in surface tension on water. Many other applications in our modern environment can be readily identified.

The Spreading Coefficient

Consider a drop of an organic liquid (O) on a water surface (W) as shown in Fig. C.7. At equilibrium the forces exerted at the three interfaces (O-W, O-A, and W-A), where A represents the air phase will be given by

$$\gamma \mathrm{w/A} = \gamma \mathrm{o/A}\cos\theta_2 \tag{C.17}$$

when spreading occurs θ_l and θ_2 must approach zero ($\cos\theta = 1$) and

$$\gamma \mathrm{w/A} \geq \gamma \mathrm{o/A} + \gamma \mathrm{o/w} \tag{C.18}$$

A spreading coefficient is defined as

$$S = \gamma \mathrm{w}/A \text{——} (\gamma \mathrm{o/A} + \gamma \mathrm{o/W}) \tag{C.19}$$

and when $S \geq 0$ spreading occurs. When $S < 0$ a lens will form on the water surface.

The Solid-Gas Interface

There are two types of gas-solid interaction: (a) physical adsorption, which is due to van der Waals bonds and is reversible, (b) the chemisorption, where the gas forms chemical bonds with the solid surface and results in irreversible adsorption.

If the gas A forms a monomolecular adsorption layer on the solid surface it can be treated as a dynamic process

$$A(g)\underset{k_2}{\overset{k_1}{\rightleftharpoons}}A \quad \text{(adsorbed layer)} \tag{C.20}$$

If P = pressure of gas (A) above the surface and ∂ = fraction of surface covered by A, then at equilibrium, the rate at which the molecules leave the surface R_I is equal to the rate at which they condense onto the surface R_2, i.e.,

$$\begin{gathered} R_1 = R_2 \\ R_1 \propto \theta \quad \text{or} \quad R = k_1\theta \\ R_2 \propto P(1-\theta) \quad \text{or} \quad R_2 = k_2P(1-\theta) \\ k_1\theta = k_2P(1-\theta) \end{gathered} \tag{C.21}$$

Hence,

$$\theta = \frac{k_2P}{k_1} + k_2P = \frac{P}{a+P} \qquad \text{where} \quad a = \frac{k_1}{k_2} \tag{C.22}$$

If y = amount of adsorbed gas, ym = a monolayer of adsorbed gas (the maximum amount adsorbed), then $y/ym = \theta$. From (C.23) when P is small, $y \propto P$ and when P is large, y = constant. A plot of y versus P is shown in

$$y = \frac{ymP}{a+P} \tag{C.23}$$

and

$$P/y = a/ym + P/ym \tag{C.24}$$

Thus a plot of P/y versus P is a straight line with slope $= 1/ym$ and intercept $= a/ym$. This is called the *Langmuir adsorption isotherm*. For multilayer adsorption, the more complicated treatment developed by Brunauer, Emmet, and Teller (BET) allows for the determination of surface areas (Fig. C.8).

If the solid is composed of narrow capillaries then, at high pressures, the gas will condense in the capillaries. This results in adsorption-desorption hysteresis.

Dubinin and his co-workers advance arguments favouring the view of the adsorption space may be expressed as a Gaussian function of the corresponding adsorption potential. For the standard vapour we have

$$\mathrm{W} = \mathrm{W_o}\exp(-\mathrm{k}(\varepsilon_0/\ \beta)^2) \tag{C.25}$$

where $\mathrm{W_o}$ is the total volume of all the micropores; ε_0 – the Polanyi potential; k is a constant characterizing the pore size distribution; β is a constant related to sorption free energy.

Dubinin has plotted the results for adsorption isotherms of nitrogen, saturated hydrocarbons, benzene, and cycloxehane and has found equation for calculation of the micropore volume $\mathrm{W_o}$:

$$\log \mathrm{x} = \log(\mathrm{W_o}\ \rho) - \mathrm{D}\ (\log\{\mathrm{p_{sat}}/\mathrm{p}\})^2 \tag{C.26}$$

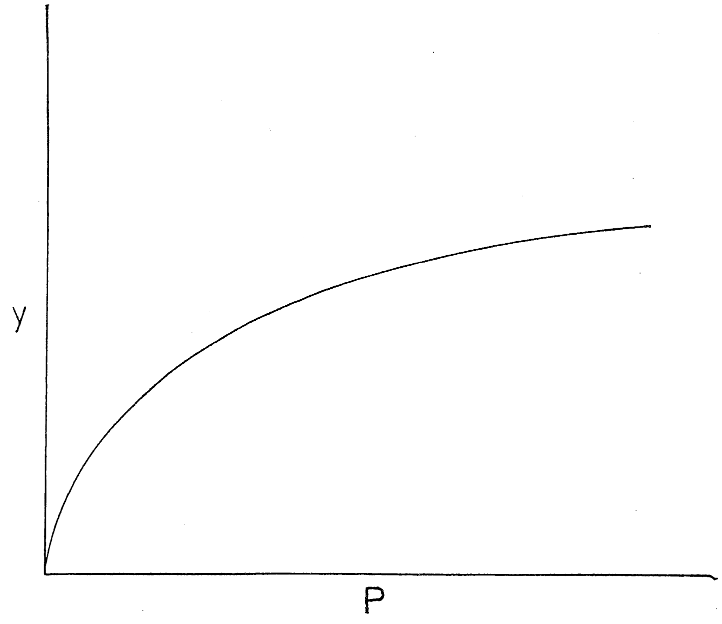

Fig. C.8 A Langmuir plot of *y*, the amount of gas adsorbed (per unit mass of solid) on a solid as a function of equilibrium pressure, *p* of the gas at constant temperature

where W_o is the total volume of all the micropores; $E = \beta \times E_o$ is the adsorption energy of another chemical; p_{sat} and p are vapor pressure at saturation and vapor pressure at equilibrium; R is universal gas constant; T – temperature, K; ε – the Polanyi potential; ρ is constant; D is a slope.

The slope D is equal:

$$D = 2.303(k/\ \beta^2)(RT)^2 \tag{C.27}$$

Thus a plot of log x against [log $(p_{sat}/p)^2$] should give a straight line, of slope D and with intercept log (W_o ρ).

The Dubinin's method makes it possible to calculate the micropore volume from the low pressure part of isotherm, the region where the adsorption is still much below the plateau value. It also offers the possibility of using different adsorbates as molecular probes.

The Solid–Liquid Interface

It is possible to treat the adsorption of a liquid onto a solid surface in a manner analogous to that given for the solid-gas system. However, in the liquid state it is usually a solute which is removed by adsorption onto the solid surface. The Langmuir equation is applicable in most cases. In other cases where the surface is heterogeneous the Freundlich adsorption isotherm

$$\frac{x}{m} = kCn \tag{C.28}$$

will usually fit the data better than the Langmuir equation, where *x* is the mass of material adsorbed on the solid, *m* is the mass of solid, *C* is the concentration (at equilibrium) of the solute being adsorbed, *n* is a constant with a value usually between 0.1 and 0.5, and *k* is a constant which depends on the system.

The empirical constants *n* and *k* can be determined from a plot of *logx*/*m* versus log *C*, where the resulting straight line has a slope equal to *n* and an intercept equal to log *k*.

Adsorption of impurities from solution is used to purify water, decolorize sugar in solution, and many other systems.

Exercises

1. It has been suggested by Bikerman that a solid can have no surface energy and that all phenomena attributed to the surface energy of a solid is due to impurities which are adsorbed on such large surfaces. Comment on Bikerman's viewpoint.
2. The traction of an automobile tire in snow can be increased by changing the wetting properties of the surface of the tire. Explain!
3. The contact angle of mercury on glass is about 120° ($\cos\theta = -0.5$). What is the significance of the -0.5 for the cos *9* in terms of the capillary method of determining surface tension.
4. The motion of a ship, boat, or torpedo through water is significantly influenced by the surface coating. Would friction be affected by changing a hydrophobic surface to hydrophilic and give reasons for your opinion.
5. The solubility of benzene in water changes the surface tension of water, $y_{W}/_{A}$ from 72.8 to 62.2 dynes/cm for a saturated solution. The solubility of water in benzene has only a small effect on the $\gamma o_{/A}$ (28.8 dynes/cm when $\gamma o/w = 35.0$ dynes/cm). If the value of $S = 9.0$ dynes/cm for benzene on water as an initial value—what will eventually occur as the water becomes saturated with the benzene?
6. The dissipation of oil slicks on water was initially effected by adding detergents. What does this do and why has this method ceased to be employed?
7. Methane can be encapsulated in molecular sieves 3A (zeolite) under high pressure and high temperature. The experimental data is given in Table C.A and can be shown to follow the Langmuir adsorption isotherm [(C.24)]. Plot the data in Table C.A and determine the maximum storage capacity by a plot according to (C.25).
8. Determine the parameters of the Freundlich adsorption isotherm [(C.28)] for the adsorption of acetic acid by active charcoal. The charcoal is used to absorb the acid from aqueous solutions of different concentrations. When equilibrium is reached the amount of acetic acid was determined by titration with standardized NaOH (0.1189 M). The data is given in Table C.B.

Table C.A Methane uptake in a 3A molecular sieve as a function of pressure

Pressure (Pa) × 10^{-8}	%CH_4 (w/w)[a,b]
0.12	1.5
0.69	3.7
0.69	3.8
1.38	4.7
2.07	5.7
2.76	5.8
3.79	6.6
4.14	6.4
4.14	6.9

[a] Based on weight of zeolite after activation under vacuum at 350 °C
[b] 2 hr encapsulation period at 350 °C

Table C.B Results for the adsorption of acetic acid by active charcoal

A[a]	B[b]	C[c]
50.0	10.0	42.23
25.0	10.0	20.3
10.0	25.0	17.8
5.00	50.0	14.3
2.50	50.0	4.70
1.00	50.0	0.22

[a] The volume of acetic acid (1.06 M) diluted to 100 mL for adsorption by 1.00 g of active charcoal

[b] The volume of solution at equilibrium taken for titration with standardized NaOH (0.1189 M) to determine the residual acetic not adsorbed by the active charcoal

[c] The volume of base used to neutralize the acetic not adsorbed by the carbon

Plot the mass of acetic acid adsorbed per gram of carbon (x/m) versus the equilibrium concentration of acetic acid.

Determine the Freundlich parameters from a plot of log x/m versus log C.

Further Readings

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Appendix D: Patents[1]

Introduction

It is easy to obtain a patent of your invention. It is more difficult to license, sell and profit from its implementation and use. Anyone can file a patent application in any country provided it is completed in the required language. Lawyers or patent agents may be useful but they are also costly and they could be engaged at a later stage when the application is ready to be filed or appealed.

With the availability of the provisional patent (in U.S.A., Australia, New Zealand, U.K.) it is possible to have a full year of protection before a formal patent has to be filed. During the 1 year period it would be possible for the inventor to discuss the invention (preferably under a non-disclosure agreement which ensures confidentiality and does not constitute a public disclosure and therefore, does not invalidate the filing of patents in foreign countries) with potential buyers without fear of losing rights or control of the invention unless, or course, the patent is not filed. Any public disclosure or sale of the product or operation of the invention for profit could invalidate the filing of patents in some foreign countries. A typical confidential non-disclosure agreement is shown in Fig. D.1.

If a patent is not filed in a specific country then it is possible for the invention to be made and sold there without fear of infringement. The product or process cannot be marketed in a country where it is covered by a patent except by the patent holder or a licensee.

Filing Fees

The cost of obtaining a patent (see Table D.1) varies from one country to another and the judicious choice of countries in which to file depends on the returns to be expected relative to the filing fees and subsequent maintenance fees.

Foreign patents can be filed under the Patent Cooperation Treaty (PCT). The cost depends on the number of pages (30 pages @ \$455 + \$10 for each additional page) plus a designation fee (about \$1,000) and some additional fees including transmittal fee, \$240, and search fee, \$1,002, making a total of over \$2,700 US excluding the Patent Agent's fee (about \$500). More fees (\$2,500) are required within 19 months for the examination of the PCT filing. Costs continue to mount as the countries are selected for specific attention, especially if translations are required.

Patent rules and regulations change and it is important to verify costs and time limitations as well as other items given in this description of patents.

O.V. Roussak and H.D. Gesser, *Applied Chemistry: A Textbook for Engineers and Technologists*,
DOI 10.1007/978-1-4614-4262-2, © Springer Science+Business Media New York 2013

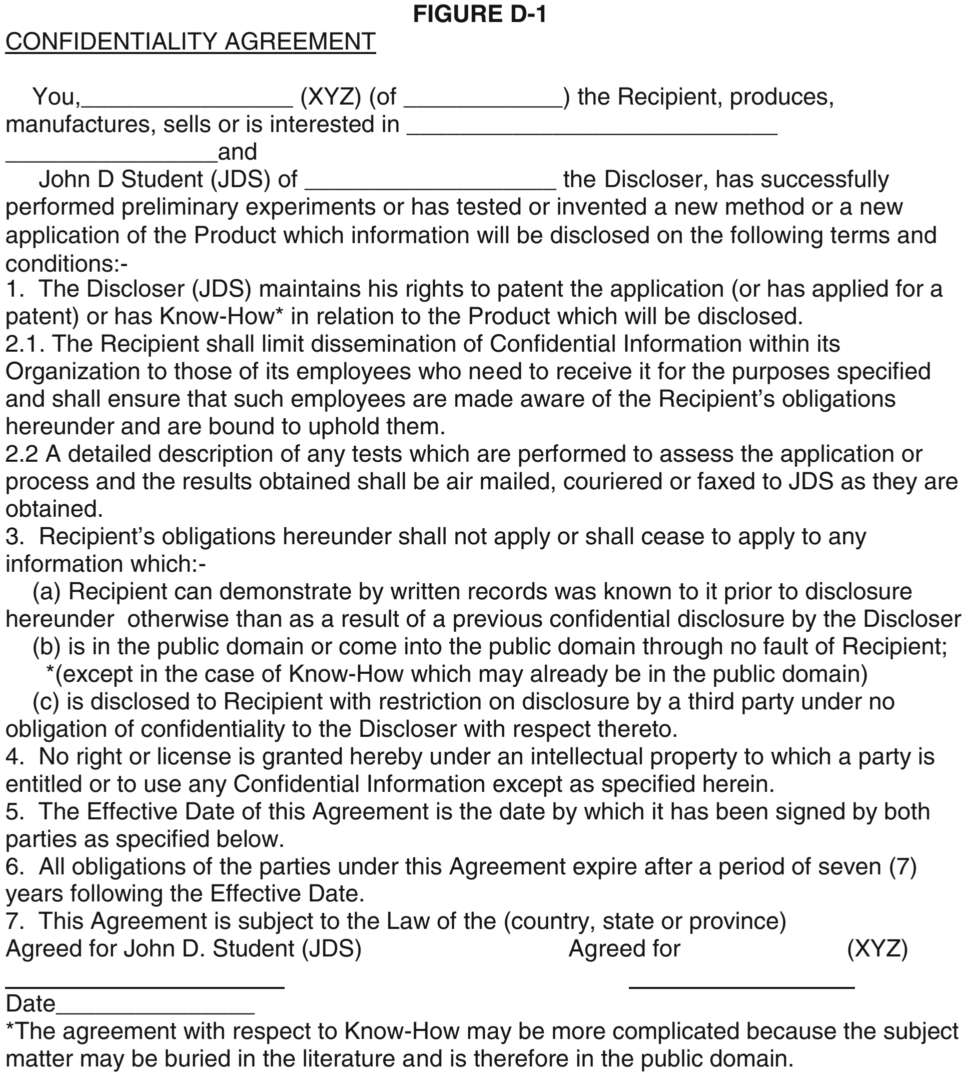

FIGURE D-1

CONFIDENTIALITY AGREEMENT

You,________________ (XYZ) (of ____________) the Recipient, produces, manufactures, sells or is interested in _____________________________ ________________and

John D Student (JDS) of ___________________ the Discloser, has successfully performed preliminary experiments or has tested or invented a new method or a new application of the Product which information will be disclosed on the following terms and conditions:-

1. The Discloser (JDS) maintains his rights to patent the application (or has applied for a patent) or has Know-How* in relation to the Product which will be disclosed.

2.1. The Recipient shall limit dissemination of Confidential Information within its Organization to those of its employees who need to receive it for the purposes specified and shall ensure that such employees are made aware of the Recipient's obligations hereunder and are bound to uphold them.

2.2 A detailed description of any tests which are performed to assess the application or process and the results obtained shall be air mailed, couriered or faxed to JDS as they are obtained.

3. Recipient's obligations hereunder shall not apply or shall cease to apply to any information which:-

(a) Recipient can demonstrate by written records was known to it prior to disclosure hereunder otherwise than as a result of a previous confidential disclosure by the Discloser

(b) is in the public domain or come into the public domain through no fault of Recipient;

*(except in the case of Know-How which may already be in the public domain)

(c) is disclosed to Recipient with restriction on disclosure by a third party under no obligation of confidentiality to the Discloser with respect thereto.

4. No right or license is granted hereby under an intellectual property to which a party is entitled or to use any Confidential Information except as specified herein.

5. The Effective Date of this Agreement is the date by which it has been signed by both parties as specified below.

6. All obligations of the parties under this Agreement expire after a period of seven (7) years following the Effective Date.

7. This Agreement is subject to the Law of the (country, state or province)

Agreed for John D. Student (JDS) Agreed for (XYZ)

Date_______________

*The agreement with respect to Know-How may be more complicated because the subject matter may be buried in the literature and is therefore in the public domain.

Fig. D.1 Confidentiality agreement

The invention usually starts with an idea that the inventor wishes to protect and which he or she often would like to discuss on a confidential basis with colleagues, friends and even potential buyers without fear of being robbed of the idea.

A search of the literature and patents would be necessary to determine if the idea is new and not already patented or published in the open literature. This can be done by a review of patent abstracts or by a computer search of appropriate data banks. Patent Agents can do this at a cost of from $100 to $500.

Having established the feasibility of the idea the inventor must now decide if a patent will be filed and where. For $125 (small entity) a provisional patent (PP) can be filed in the U.S.A. though other countries may be preferred if the formal patent will be filed there. This provisional patent can be in the form of a publication to be submitted, Za report or a preliminary draft of the patent. There is no requirement to include claims, though it is important to present the supporting data and results as well as the object of the invention and its novelty. The improvement of the invention over previous versions should be stressed. The life of a PP is 1 year.

After filing the provisional patent the inventor should be trying to license, sell or otherwise exploit the invention on a confidential non-disclosure agreement with the view that an interested company would within the 1 year period of grace, file the necessary patents in various countries on behalf of the inventor and, or course, pay all the application fees and maintenance fees. If this does not transpire, then it is up to the inventor to pay the application fees which would be classed as a small entity status and is therefore usually half of the regular filing fee.

A license is a means by which an owner (the licensor) grants to the user (the licensee) a license (which can be exclusive, non-exclusive or limited by time or district) under the patent to use the product or technology in exchange for annual (or semiannual or quarterly) royalties plus or including a minimum fee. Minimum royalty fees guarantee the inventor a return on the license and some diligence on the part of the licensee to market the invention. The royalty is usually based on a percentage of gross sales (e.g., 5%) or profits. Profits, however, can be manipulated and reduced by paying high consulting fees to sister companies thereby lowering or eliminating royalties. Other topics covered by the license include the duration, notice of cancellation, improvements, infringement suits and settlement of disputes by arbitration, etc.

Components of a Patent

A patent consists of the following main sections:

1. Title of Invention with the Names of the Inventors
2. Background of the Invention
   (a) Field of the Invention
   (b) Description of Prior (or Related) Art
3. Summary of the Invention
4. Brief Description of the Drawings
5. Description of the Preferred Embodiment
6. Claims.
7. Abstract

Though this topic will be discussed in sequence they usually appear in another order.

Title of Invention with the Names of the Inventors

A snappy title is worth some thought and can tell the reader exactly what the invention is all about. The home address(es) of the inventor(s) must be supplied.

Background of the Invention

The contents appear under two headings.

(a) *Field of the Invention*

The field may be broad as well as narrow and may differ from what the patent office may select. Other patents of the subject can be of great help and are essential for this, and the general jargon to be used.

Table D.1 Small entity fee schedule[a] for U.S.A. and Canada. (2011)

	U.S.A.	Canada
Basic filing fee	\$380/190	\$400/200
Independent claims in excess of 3, each	\$250/125	
Claims in excess of 20, each	\$60/30	
Utility examination fee	\$250/125	\$800/400
Patent post-allowance fees	\$1,740/870	\$200
Provisional application filing fee[a]	\$250/125	
Electronic filing[a]	\$105	

[a] Complete fee schedules are available from the respective Patent Offices and from the Web
http://www.uspto.gov/web/offices/ac/qs/ope/fee092611.htm#comp (U.S.A.)
http://www.cipo.ic.gc.ca/eic/site/cipointernet-internetopic.nsf/eng/wr01103.html (Canada)

(b) *Description of Prior (or Related) Art.*

This outlines the need for the invention and the problems to be solved. This means that it is important to describe the technology as it is at present and how the invention can change and improve the world. This is analogous to the review of the literature with references and examples wherever possible.

Summary of the Invention

This section now describes how the invention solves the problems mentioned in and how the invention improves on previously available units. It explains how the state of the art will be advanced and how it will be of benefit to mankind. The Summary is not a rewording of the Abstract but an anticipation of the Claims of the patent. This section is often referred to as Summary of Disclosure.

Brief Description of the Drawings

This section lists the captions or legends to the figures used to illustrate the various aspects of the invention. The components of the drawings are usually clearly numbered and referred to by number in the preferred embodiment, the next section.

If the drawings are inadequate then the examiner might ask for additional figures or clearer versions for some of the drawings. The patent office will supply detailed requirements and specifications for the drawings for a fee, if asked.

Description of the Preferred Embodiment

This is the heart of the patent where the inventor must now give all the details and basis of the invention. In principle, the details should be sufficient for anyone “skilled in the art” to duplicate the invention. This is not always adhered to and occasionally an important and essential step is omitted or a further improvement is kept secret to be included in another patent. This description makes use of the drawings and figures with examples, which represent tests and experiments, with tables of results where possible.

The section is usually ended with a general statement which is meant to indicate that, to one skilled in the art, other obvious applications and uses need not be described, e.g. “Since various modifications can be made in my invention as herein above described, and many apparently widely different embodiments of same made within the spirit and scope, it is intended that all matter contained in the accompanying specifications shall be interpreted as illustrative only and not in a limiting sense."

Claims

This section starts with: "What I claim as my invention is:"

1. The claims, which are numbered, are the main goal of the patent and the only parts which can be changed once the patent has been filed. The claims are classified as independent claims (limit of 3 – more cost extra) which stand alone, and dependent claims which refer to a previous claim. Extra claims (over 20 in all) add to the cost of the filing fee. Each country has different requirements concerning dependent and independent claims. If one or more of your claims are allowed by the examiner then the patent will be granted.

The first claim should cover the complete invention being broad and encompassing. Two or three independent claims are usually sufficient if supplemented by several dependent claims. These allow for variation in one or more of the parameters or components of the invention to be claimed.

Abstract

This is best written after the application is completed. It is a short paragraph which describes the invention, its purpose, operation and use. This abstract appears on the front page of the patent and in most collections and lists of patents and abstracts describing new issuances. It is this abstract which attracts potential buyers searching for new products and ideas to market and sell. Hence considerable care ought to be taken in its preparation.

The Provisional Patent

The best approach to writing a patent on your own is to obtain some previously issued patents on the subject and to acquire the jargon and style of the subject. Such patents can be ordered by number from the patent offices or can be downloaded from the WEB.

The response from the Patent Examiner is usually to deny the validity of all the claims based on previous patents which are included with his reply. The inventor would reply by changing the nature of the claims or point out to the Examiner that he/she is mistaken. A telephone call can do much to clarify the changes required to make the claims acceptable.

When there is no possibility of obtaining at least one claim, the patent will be finally denied. At this point it may be possible for the inventor to file a continuation-in-part in which new evidence and results are presented in the revised Embodiment to justify the new and altered claims. A patent agent at this time would be a great help in getting the patent approved.

Further Readings

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Appendix E: Experiments

Experiment No. 1. The Vapor Pressure of a Substance

Introduction

The vapor pressure of a substance at a given temperature is a unique property of that substance and is a measure of its volatility. The standard boiling point of a substance is the temperature at which its vapor pressure is 760 mm of Hg at one atmosphere pressure. A substance would boil at a lower temperature when measured at a mountain top compared to measurements at the earth's surface or in underground mines where it would "boil" at a higher temperature. The object of this experiment is to measure the vapor pressure of a substance at several temperatures and to obtain its Standard Heat of Vaporization

One method used to determine the vapor pressure of a substance (a liquid in this case) is to measure the volume of its vapor. In a closed system, at different temperatures as the temperature of the substance is heated. The small sample of the substance is placed at the closed bottom of a tube. A short plug of mercury about 3–5 mm long is added to the tube (approximately 5 cm above the surface of the liquid sample) using an eye-dropper that is made by pulling apart two parts of a glass tube that has been soften in the flame of a Bunsen burner This is done by inclining the tube at 20–35° before inserting the eye-dropper with the mercury. The sample tube, a thermometer and a centimeter scale are attached as shown in Fig. exp. 1.1 and clamped to insert into a beaker of water that is slowly heated and stirred. As the water is heated the air in the sample tube expands and the liquid vaporized to a increasing extent pushing the mercury plug towards the open end. It can be shown that the measured movement of the mercury plug from a low temperature (where the vapor pressure of the sample liquid is negligible) to an elevated temperature can be related to the vapor pressure of the liquid.

Care with Mercury

Mercury vapor is toxic and it is important to avoid breathing it vapors. [J. Chem. Edu. Vol 12, page A529 (1965)] The equilibrium vapor pressure of mercury is 0.000185 mm, at 0°C, 0.00120 mm pressure of Hg at 20°C and 0.0127 mm at 50°C The vapors of mercury should therefore not be inhaled. Mercury amalgamates with gold and silver and finger rings should be removed during the laboratory period. Mercury is also absorbed through the skin and it should, therefore, not be handled unnecessarily. Used mercury must be recovered and a receptacle is provided for it.

O.V. Roussak and H.D. Gesser, *Applied Chemistry: A Textbook for Engineers and Technologists*,
DOI 10.1007/978-1-4614-4262-2,

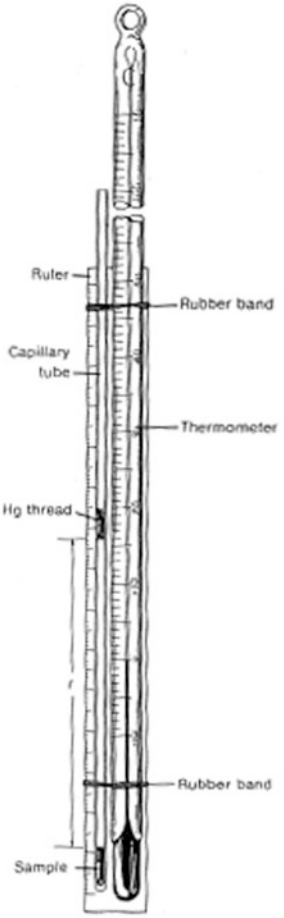


Fig. exp. 1.1 Mounted sample tube

DO NOT HANDLE MERCURY
DO NOT THROW MERCURY DOWN THE SINK
DO NOT STIR WATER BATH WITH THERMOMETER
DO NOT HEAT BEAKER DIRECTLY WITH BURNER FLAME
DO NOT HEAT PLASTIC RULER ABOVE 56°c
DO NOT USE COMPRESED AIR FOR DRYING
REMOVE RINGS COMPOSED OF GOLD OR SILVER BECAUSE THESE METALS READILY AMALGAMATE WITH MERCURY

A porous plug is added to the top of the sample tube to prevent excessive return of mercury vapor into the laboratory.

A. Theory

The change in vapor pressure P of a liquid or solid as a function of temperature Tis derived from thermodynamics and is given by the differential equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\left(V_g - V_o\right)}$$

where V_g is the volume of 1 mole of vapor, V_o is the volume of 1 mole of either liquid or solid, and ΔH is the heat of vaporization or sublimation per mole of substance. If the volume of liquid is small in relation to the gaseous volume; if the vapor behaves as an ideal gas and if ΔH can be treated as a constant (independent of temperature) then $\frac{dP}{dT} = \frac{\Delta H}{TV_g} = \frac{\Delta HP}{nRT^2}$ but since n = 1 for one mole

$$\frac{dP}{P} = \frac{\Delta H\, dT}{R\,T^2}$$

$$\text{Ln } P_2/P_1 = -\Delta\frac{H}{R}\ (1/T_2 - 1/T_1) = \Delta H(1/T_1 - 1/T_2)/R$$

$$\text{Log } P_2/P_1 = \Delta H(1/T_1 - 1/T_2)/(2.303\ R)$$

Hence if Log P is plotted as the ordinate against 1/T as the abscissa, then a straight line of negative slope – ΔH/2.303R will result. The Heat of Vaporization, ΔH, is given by ΔH = −2.303 R × Slope of line.

Experiment

The measurement of vapor pressure generally consists of an apparatus in which all air and foreign gases is evacuated from the sample. The compound is then kept at a constant temperature while equilibrium is obtained; the pressure in the apparatus is then measured. The simpler method to be used in this experiment assumes:

That the vapor and air behave as ideal gases.
The glass tubing has a uniform bore.
The thermal expansion coefficient of the glass and the plastic ruler are small and equal.

If a substance is placed in the bottom of a capillary it will exert its equilibrium vapor pressure when immersed in a constant temperature bath. When a droplet of mercury is then placed in the capillary tube, it isolates the substance, its vapor and some air. Hence as the temperature is increased, the air expands and the partial pressure of the vapor increases but the total pressure remains constant since the mercury plug moves to accommodate any pressure change.

Let P = the barometric pressure exerted on the system
E = the pressure exerted by the mercury plug
P_T = the total pressure exerted on the confined vapors

$$P_T = P + E \tag{E1.1}$$

If P_a = the partial pressure of air in volume V
and P_v = the vapor pressure of the liquid sample

$$\text{then}\quad P_a + P_v = P_T \tag{E1.2}$$

$$\text{at}\quad T_1, P_{a1} + P_{v1} = P_T \text{ or } P_T - P_{v1} = P_{a1} \tag{E1.3}$$

$$\text{at}\quad T_2, P_{a2} + P_{v2} = P_T \text{ or } P_T - P_{v2} = P_{a2} \tag{E1.4}$$

V is the volume of vapor and is equal to π r^2 L where r is the radius of the tube and L is the length between the sample and plug

$$\text{Then } P_{a1} = nRT_1/V_1 = nRT_1/V_1 = nRT_1/\pi r^2 L_1 \tag{E1.5}$$

$$\text{Similarly } P_{a2} = nRT_2/V_2 = nRT_2/V_2 = nRT_2/\pi r^2 L_2 \tag{E1.6}$$

Dividing (E1.4) by (E1.3) and combining (E1.5) and (E1.6)

$$(P_T - P_{V2})/(P_T - P_{V1}) = P_{a2}/P_{a1} = (nRT_2)/(\pi r^2 L_2)(nRT_1)/(\pi r^2 L_1) = (T_2/L_1)/(T_1 L_2) = \alpha \tag{E1.7}$$

$$(P_T - P_{V2}) = \alpha(P_T - P_{v1}) \text{ or } P_{v2} = P_T - \alpha(P_T - P_{v1}) \tag{E1.8}$$

If T_1 is sufficiently low then P_{v1} can be small and may be neglected, and

$$P_T - P_1 = P_T \tag{E1.9}$$

Hence

$$P_{v2} = P_T(1 - \alpha) \tag{E1.10}$$

Thus the vapor pressure can be calculated from a knowledge of the atmospheric pressure and the liquid-mercury distances at various temperatures. The approximation made in (E1.9) will be invalid when $P_{v1} \geq 50$ mm. However at higher temperatures the error introduced becomes less significant and it is possible by successive approximations to obtain very good results. See Question No. E6.

Apparatus

1. Three capillary tubes 2–3 mm I.D. 15 cm long
2. Plastic 6 in. ruler
3. Beaker (1,000) mL.
4. Bunsen burner, stand, wire gauze
5. Thermometer – 10° 110°C
6. Stirring rod
7. 2 Eyedroppers
8. Wall Barometer
9. Cork, rubber band, stopper, clamp and stand

NOTE. Do not heat the plastic ruler above 55°C; it will melt or deform.
Do not use compressed air for drying since it generally contains some oil.

Part A

1. The sample tubing is of soft glass: seal one end and allow it to cool.

2. The ruler should be cut down the middle to separate the centimeter scale from the inch scale. The centimeter scale can then be conveniently tied to the thermometer and capillary tube by rubber bands, as shown in Fig. exp. 1.1.
3. Prepare two long thin capillary eyedroppers that can enter the above sample tubes. They can be prepared from a 6″ length of 6 mm OD soft glass tubing in the following manner. (a) Firepolish both ends and allow them to cool. (b) Place the center of the glass tube in the Bunsen flame while holding the ends of the tube with your finger tips and rotating it. (c) When the tube has softened in the center and becomes difficult to hold and rotate, remove it from the flame and gently pull it apart and cut in two. If the eyedropper can enter the sample tube, insert the fire polished ends into the rubber bulbs and store the finished eyedropper safely.
4. Put a cork or rubber stopper around the top end of the thermometer to facilitate clamping it in the apparatus.
5. Make a stirring rod from a soft glass rod.

Part B

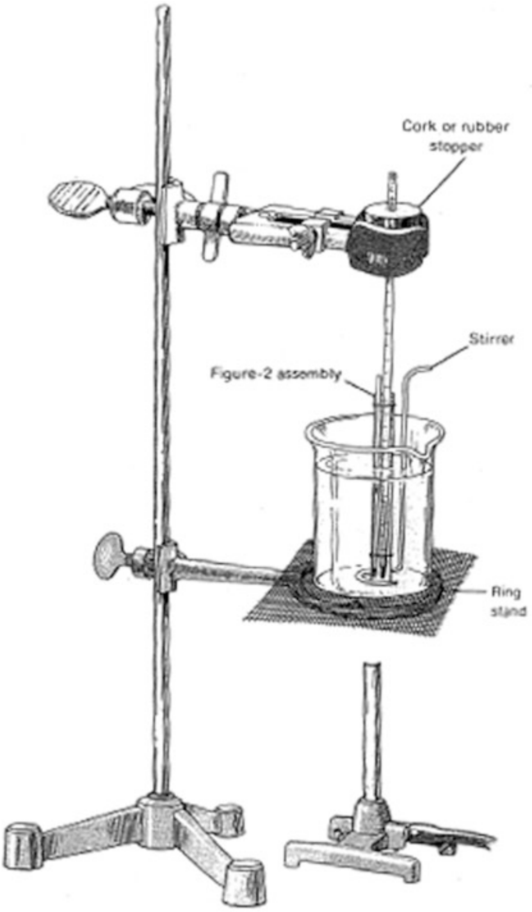
1. By means of the eyedropper, deposit a 0.5–1 cm length of the liquid sample at the bottom of the sample tube. Do not wet the inside capillary wall above the liquid level: a wet wall will cause the mercury (introduced in the next step) to drop into the liquid.
2. With the second eyedropper, plug the sample tube with a thread of liquid mercury about 5 mm long, leaving a gap of about 3–4 cm between the upper level of the liquid sample and the mercury plug. It will be necessary to do this with the sample tube tilted 10–30° from the horizontal.
3. Bind the sample tube and thermometer to the centimeter scale and thermometer and set up the apparatus as shown in Fig. exp. 1.2. Be sure that the mercury is at least one inch below the level of the top of the water bath.
   NOTE: If the mercury thread should break or fall into the liquid sample, it will mean starting over again with a new capillary tube (Part B. Step 1). If continued difficulties are encountered, consult your instructor about having the sample tubes treated with Drifilm to prevent the glass from wetting. (Drifilm is sold in supermarkets to waterproof shoes and boots). Place all used tubing in the receptacle provided since most can be cleaned and reused.
4. Measure the length of the mercury thread, E, and take the barometer reading, recording the data.
5. Record both the temperature of the water and the distance from the top of the liquid sample to the bottom of the mercury plug at about 10 intervals from 0°C (T_1) to about 50°C (not beyond 55°C, because he plastic ruler may melt).
   NOTE: The value of L and T for the lowest temperature. T_1 should be obtained with care since these are used as L_1 and T_1 in each of the successive calculations of vapor pressure.
6. The temperature readings can be estimated to 0.1°C and the distance can be read to about 0.02 cm. Allow equilibrium to be established before noting the readings at each temperature.

Results

Tabulate the results and calculate the vapor pressure for the propylalcohol provided. Plot the results (log Vp vs. 1/T) and compare the value of the heat of vaporization with the literature values given at the end of this experiment. Extrapolating from the straight line, obtain a value for the boiling point of the liquid.

Note: The plot can be done on semi-log graph paper that consists of a logarithm ordinate scale and a linear abscissa scale to represent the reciprocal of the absolute temperature. Plotting vapor pressure directly on the ordinate scale result in the logarithm of the vapor pressure being represented.

Fig. exp. 1.2 Apparatus for the pressure – temperature determination have been scanned together on one sheet



Discuss the results obtained with respect to the literature values listed in Table exp. 1.1 and comment on the sources of error. Then complete the assigned Exercises at the end of the section.

Questions

1. The vapor pressure of mercury at 20°C is 0.0012 mm of Hg. Calculate the equilibrium concentration of mercury in air in units of g/m^2.
   Note that the threshold toxic limit of mercury is 0.1 mg.m^3.
2. Show how the vapor pressure of a solution can be determined at a given temperature using the capillary-tube method.
3. It is possible to determine the vapor pressure of a liquid at temperatures above its boiling point. This can be done conveniently by sealing the top-end of the capillary tube and measuring the distance between the mercury thread and the sample and between the mercury thread and the top seal. If $\boldsymbol{l}$ is the distance between the sample and the mercury and λ is the distance between the mercury thread and the top seal, Δ is the change from $\boldsymbol{l}_1$ to $\boldsymbol{l}_2$ and λ_1 to λ_2 for the temperature interval T_1 to T_2, that is, $\boldsymbol{l}_2 = \boldsymbol{l}_1 + \Delta$, and $\lambda_2 = \lambda_1 - \Delta$. P_a is the partial pressure of air in the

Table exp. 1.1 Vapor pressure

TemperatureC								
Pressure	1 mm	10 mm	40 mm	100 mm	400 mm	760 mm	MP°C	H_{vap} kJ/mol
Substance								
Water	17.3	11.3	34.1	51.6	83.0	100	0	40.66
Methanol	−44.0	−16.2	5.0	21.2	49.9	64.7	−97.8	35.2
Ethanol	−31.3	−2.3	19.0	34.9	63.5	78.4	−112	35.2
n-propyl alcohol	−15.0	14.7	36.4	52.8	82.0	97.8	−127	41.4
Isopropyl alcohol	−26.1	2.4	23.8	39.5	67.8	82.5	−85.8	39.9
Acetone	−59.4	−31.1	− 9.4	7.7	39.5	56.5	−94.6	29.1

sample segment of the capillary tube, and P_v is the vapor pressure of the sample at temperature T. P_l is the initial pressure in the sealed upper part of the capillary tube at T_l where it is assumed that

$P_{v1} = 0$. Show that

$$P_{v2} = 7(P_l T_2)/T_1?7(\lambda_1/\lambda_2) - (l_1/l_2)?\square =; P_l T_2/T_1?\square 7\ \lambda_1/(\lambda_1 - \Delta)? - 7l_1/(l_1 + \Delta)?\square$$

Hint: $P_l + E = P_a + P_v$ and assume that $E = 0$, and $P_{v1} = 0$ when $T_1 = 0°C$

4. The vapor pressure of Hg has been neglected in these calculations. Discuss the significance of this assumption in the open-tube method and in the sealed-tube method at higher temperatures.
5. If the vapor pressure of a substance in the solid state and the liquid state is known at various temperatures, it is possible to calculate the heat of fusion.
(A) explain this statement and (B) calculate the heat of fusion of benzene from the data given in Table exp. 1.1.
6. The vapor pressure of acetone was determined in an open tube and the data in the following table were obtained. Atmospheric pressure was 749.1 mm mercury, the length of the mercury thread was 6.2 mm. Determine the Heat of Vaporization of Acetone.

T (°C)	0.5	10.6	20.0	30.1	40.0	38.5	49.0	30.0
l (mm)	22.0	24.5	28.9	36.5	48.1	49.0	85.0	35.0

It must be realized that the assumption $P_{v1} = 0$ when $T_1 = 0°C$ is not valid. To obtain a more exact value of P_{v1} plot the logarithm of the vapor pressure against the reciprocale of the temperature (°K) and extrapolate the straight part of the line (at the higher temperatures) to 0°C (273 K). Using the extrapolated value for P_{v1} replot the data and calculate a heat of vaporization for acetone. A second extrapolation of the plot will improve the accuracy of the results.

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Experiment No. 2. The Speed of a Boat in Water

Object: To determine how the surface properties of a boat affects its speed in water.

Introduction

Water is the "best" hydrophilic substance and it has often been asked whether an object moving in water should be hydrophilic or hydrophobic for reduced friction. Both types of coatings are available on the market but based on the hydrophilic nature of fish scales, it is most likely that a boat with a hydrophilic surface may move faster or consume less fuel than a boat with a hydrophobic surface, This can be tested by dropping a "torpedo" (with successive characteristics) in a water column and timing the fall between two points along the column.

The Experiment

A diagram of an apparatus is shown in Fig. exp. 2.1 for the measurement of the effect of a coating on a "torpedo" in a water column and timing its fall between two points. The effect of speed on the difference between the two types of surfaces properties of the "torpedo" helps us understand the difference The hollow "torpedo" can be loaded with lead shot to increase its speed as it falls through the column of water.

Procedure

1. Set up the apparatus as shown in Fig. exp. 2.1 and prepare two clean glass test-tube type "torpedoes" with different weights by adding different amounts of BB shot to the "torpedoes".

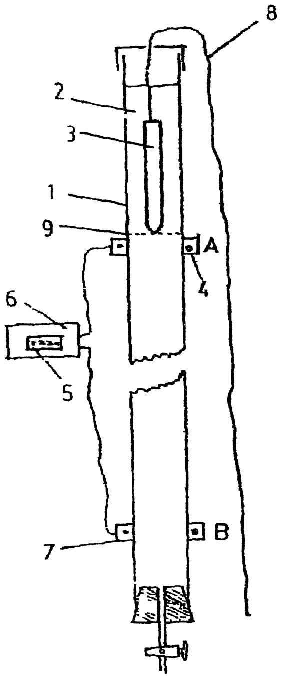


Fig. exp. 2.1 The glass tube (1), filled with water (2), with bob (3), sets off photo switch (4), that start the 4 digit timer (5), in electronic box (6). The photo switch (7) stops the timer. The polyester thread (8) is used to retrieve the bob bringing it to the start point (9) for the next test while the timer is reset. A and B represent the housing for the photo switches (4 and 7)

(The timed readings for the duration of the fall through the water column should be between about 5 and 15 s. and have four significant figures. The contact angle of a clean glass slide should not be more than 10 degrees).

2. Attach an appropriate length of fish twine to retrieve the "torpedo" from the bottom of the flow tube. Reset the timing unit after each run when the "torpedo" has been raised above the start line of the water column.
3. Repeat the drop between 5 and 10 times to obtain an average drop time and determine the mean deviation for the "torpedo" with the hydrophilic wetting (W) surface.
4. Repeat the drop-speed times as in step #3 and again calculate the average of the 5 or 10 drop times and mean deviation for the wetting "torpedo".
5. Repeat the drop-speed times as in step #3 and again calculate the average of the 10 or 5 drop times and mean deviation for the wetting "torpedo".
6. Report the results obtained in a Table listing the type of surface treatment and time of fall through the water and suggest further applications and experiments to verify your conclusions.
7. Set up a table for the results and calculate the significance of the wetting process on the speed of the "torpedos" through water and potential usefulness of hydrophilizing boats to save fuel and/or time in marine traffic.
8. If time permits repeat the above with another "torpedo" having a different mass to give a different fall speed.

Provide answers to the questions below.

Questions

1. Suggest how you can improve upon the results obtained, e.g. decrease the errors involved.
2. Suggest some other application and advantages of a hydrophilic surface.
3. Barnacles and other marine life interfere with a submerged surface in the sea. Suggest systems or methods that can be used on boats to keep surfaces clean and hydrophilic.
4. The human body has several hydrophilic surfaces. What are these surfaces and show how a water insoluble hydrophilic coating can be of benefit to us.
5. Examine the literature (from the WEB and US Patents) to determine what the speed enhancement systems have been reported for a boat moving in water.

Experiment No. 3. The Permeation of Lquids Through Solid Natural Beds

Introduction

The permeation of liquids through sand, gravel or soil is governed by the pressure head and wetting of the solid by the liquid (surface tension). It is the object of this experiment to show this effect and how it might be possible to circumvent the effect.

Procedure

The ground glass or glass beads (d = 0.5–5 mm) are cleaned by boiling in acid and rinsing in distilled water before being placed in a glass column fitted with a stopcock. A drawing of the apparatus is shown in Fig. exp. 3.1. To avoid air spaces in the glass column it is best to add the glass beads to the

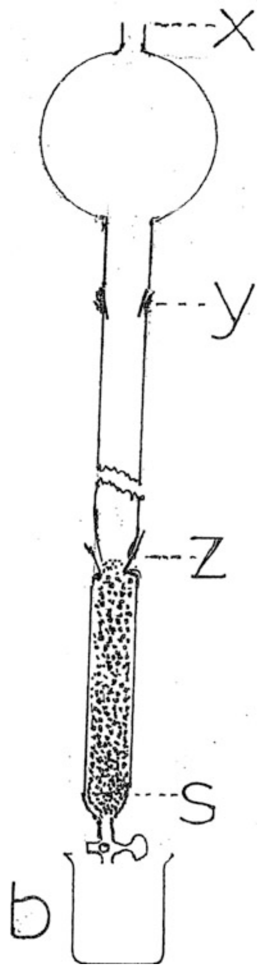


Fig. exp. 3.1 Diagram of the apparatus used to measure the rate of flow of water (or other fluids) from a full reservoir (XY), through a column of packed solids (ZS), (glass beads) used to determine the effect of the solid surface properties (contact angle on the rage of flow. YZ is a variable length that is used to change the flow rate of water through the packed bed

column filled with water. The glass taper joint on the top of the glass beads are used to add a straight column that provides the pressure head that pushes the water through the column of beads. Columns of different lengths can be used to provide different speeds through the column and will show the effect of speed on the influence of the surface. A stopwatch is used to time the flow of water through the column to the top of the glass bead taper joint. The results of 10 experiments are averaged and the mean deviation is determined. The glass beads are then dried and treated with silanes to make them non-wetting (hydrophobic). The beads when dry, are then placed into the flow column and the flow experiments are repeated and the results are compared with the flow of water through the beads with a hydrophilic surface. Using statistical formulae determine the significance of the differences between the two averages and the surface effect on the speed of water through the packed beds of different surface wetting caractor.

It is also feasible to perform the experiment with oil as the liquid and to start with the oil and change the surface of the glass beads between the hydrophilic and hydrophobic states. The oil will show improved flow with hydrophobic beads.

NOTE: To avoid air being trapped in the packing it may be desirabale to fill the solid bed from the bottom up by attaching a rubber tube to the exit spout of the column and slowly raising the reservoir. Alternitly it is also best to add the beads slowly to the water filled column to avoid air pockets.

Questions

1. Why would you expect vapor holes to appear in the glass bead bed?
2. Under what conditions would the surface conditions become irrelevant?
3. What factors would you use to select a wall material for a flow system through which all types of liquids flow?
4. Explain why the wall effect disappears when the diameter of the flow tube is 5 cm or greater.
5. What wall material would you use to improve the flow of oil?

Experiment No. 4. The Molecular Weight of a Polymer by Viscosity Measurements

The viscosity of a gas is well understood. However the viscosity in the liquid state is more complex and readily influenced by many factors. Some of these factors will be examined in other laboratory experiments. At this time we restrict ourselves to simple well understood systems. The viscosity of a polymeric solution as discussed in Chap. 11.

The viscosity of a polymer solution is much higher than that of a simple solute and it increases as the molecular weights (M_n and M_w) a polymer increases. Figure 11.1 shows the relative position of these two quantities in terms of the changing average molecular weights of a typical polymer and its Degree of Polymerization (DP) Fig. 11.2. The average molecular weight of a polymer, M_v, as determined by viscosity measurements is given by

$$[\acute{\eta}]=KM_v\ P-1$$

where $[\acute{\eta}]$ is the intrinsic viscosity; K and α are empirical constants.
$[\acute{\eta}]$ is determined by the limit $[\acute{\eta}] = \text{Limit } n_{sp}/c$

$$c \rightarrow 0$$

Procedure

(1) Prepare a solution of the polymer in the solvent. 500 mg in 100 mL (0.5%) and store in a glass bottle with a well fitting ground glass stopper. If necessary filter the solution through a course grade sintered glass filter. Prepare the water bath for the viscometer which must be supported in the bath and which must be visually observable in order to time the flow of the solution through the capillary part of the viscometer. Figure B.2 of Appendix B shows up how to set up an Ostwald viscometer.

Complete the following table by dilution of the prepared solution:

One method is to divide the 100 mL into 80 and 20 mL and dilute these each to 100 mL giving solutions **B** and **E** with 0.4 and 0.1 mg/100 mL respectively. The 0.3 mg/100 mL solution (**C**) can be made by taking 75 mL from the 80 mg/100 mL solution (**B**) and diluting it to 100 mL. Similarly, a volume of 66.7 mL of solution (**C**) diluted to 100 mL would give solution **D**. Viscosity measurements should be performed in a minimum of triplicates and averaged with mean deviations determined and plotted to indicate the possible error of each value.

Polymer Soln.	Flow time	Relative viscosity	Specific viscosity	Reduced viscosity
mg/100 mL	sec.	$\acute{\eta}_r = \acute{\eta}_s/\acute{\eta}_o = t_s/t_o$	$\acute{\eta}_{sp} = \acute{\eta}_r - 1$	$\acute{\eta}_{red} = \acute{\eta}_{sp}/C$
Pure solvent	$t_o =$			
: **A** 0.5	$t_5 =$			

(continued)

Table X Intrinsic viscosity–Molecular weight constants (K and a for equation P-1)

Polymer	Solvent	T (°C)	$K \times 10^4$	a
Polystyrene	Benzene	25	1.02	0.74
	Toluene	25	1.10	0.72
Polyvinylacetate	Acetone	25	1.88	0.69
PolymethylMethacrylate	Acetone	25	0.75	0.7
	Toluene	25	0.75	0.71
		30	0.7	0.72

Polymer Soln.		Flow time	Relative viscosity	Specific viscosity	Reduced viscosity
B	0.4	$t_4 =$			
C	0.3	$t_3 =$			
D	0.2	$t_2 =$			
E	0.1	$t_1 =$			

Plot the results of η_{red} against C (g/100 mL) and extrapolate the line to zero value of C. The ordinate value at $C = 0$ gives the value of Limiting Viscosity Number or Intrinsic Viscosity $(\eta) = KM^a$ where estimated values of K and $\underline{a}$ for hydroxyethylmethacrylate are 0.75×10^{-4} and 0.71 respectively. Calculate the molecular weight of the polymer. Answer the assigned questions that follow:

Questions

1. Why is viscosity of a polymer a direct function of its molecular weight?
2. What can you do to reduce the viscosity of a polymer?
3. Under what conditions is the intrinsic viscosity, $[\acute{\eta}]$, independent of the molecular weight of the solute?
4. A 1.232 g of Carboxy terminated polybutadiene (CTPB) is dissolved in a toluene-ethanol mixture and reacted with 2.9 ml of 0.0965 N KOH to the neutralization to a phenolphthalein end – point. Calculate the molecular weight of the sample polymer.
5. What is meant by the term “Degree of Polymerization”?
6. Why does a polymer have different “Molecular Weights”?
7. Comment on the variability of the intrinsic viscosity parameters in the Table X.

Experiment No. 5. Surface Chemistry

Introduction

The surface of a solid can be a very active and reactive substance. We are familiar with the Gas Mask which was initially used to remove poison chemicals from the air. The gas mask consists of a solid with a large active surface area that can trap poisonous vapors. Similarly the removal of unhealthy substances in water can be effected by passing the water through an active solid which has a large surface area that can trap the unwonted chemicals.

This experiment will illustrate the removal of an acid–oxalic acid (HOOCCOOH) from water using an activated form of carbon that has a large active surface area.

Background

Carbon prepared by various methods can be converted into an activated form that has a large surface. Such active carbons can have surface areas that range from about 50 m^2/g to over 1,000 m^2/g Molecules that encounter such surfaces tend to stick to the surface due to the attractive forces of the residual atom or molecules that constitute the material. The study of this adsorption process is called surface chemistry which was developed over 100 years ago and was initiated by the Freundlich equation

$$x/m = kc^{1/n} \tag{5.1}$$

where x = mass of substance adsorbed, m = the mass of the absorbent (charcoal), c is the equilibrium concentration of the unabsorbed substance, k and n are constants. The logarithmic equation is

$$\log x/m = \log k + (1/n) \log c \tag{5.2}$$

A plot of log x/m versus log c should be a straight line with a slope of 1/n.The Langmuir equation was developed about 1920 and is based on a kinetic principle concerned with the equilibrium between the adsorption and desorption occurring continuously.

$$F = kc/(1 + kc) \tag{5.3}$$

where F = the fraction (x/m) of solid surface covered by the adsorbed molecules, k is a constant at constant temperature and c is the concentration of the substance being adsorbed. The saturated surface is represented as F = S. Thus (B.13) becomes

$$c/F = c/S + 1/kS \tag{5.4}$$

A plot of c/F versus c will be a straight line with slope equal to 1/S.

Materials

Oxalic acid solution, 0.5 N (1.0 M); 1 l, Active charcoal 25 g; $KMnO_4$ 0.2 N (1.0 M); 5–250 mL Erlenmeyer flasks with stoppers.

Weigh out 2 g of the active charcoal to each of 5 flasks suitably labeled and add 100 mL of oxalic acid solution each diluted to give solutions of 0.4, 0.3, 0.2, 0.1 N and the undiluted solution 0.5 N

The equation:

$$5C_2O_4{}^{2-} + 2\,MnO_4{}^{-} + 16H^{+} = 10\,CO_2 + 2\,Mn^{2+} + 8H_2O \tag{5.5}$$

The oxalic acid solution is used to standardize the permanganate solution (10 mL). 2.0 g of active charcoal is added to each of the five flasks. 100 mL solutions of different strengths oxalic acid is added to the flasks. The solutions are:

1. 0.5 N stock solution-100 mL;
2. 80 mL of stock solution + 20 mL of water = 0.4 N;
3. 60 mL stock solution + 40 mL of water = 0.3 N;
4. 40 mL of stock solution + 60 mL of water = 0.2 N,
5. 20 mL of stock solution + 80 mL of water = 0.1 N.

Thus the five flasks are prepared to contain each 2.0 g of active carbon, 100 mL of oxalic acid with concentrations of 0.1–0.5 N and stoppered and shaken to achieve equilibrium in the ½–1 h. Equilibrium is established when two successive titration of the oxalic acid with the permanganate solutions are close together indicating that equilibrium has been established.. This is done by removing 10 mL of the oxalic acid solution and by titrating it with the permanganate solution. Two successive equivalent titration values would indicate that equilibrium has been established. It is important to titrate the solutions of oxalic acid separated from the carbon which had adsorbed the oxalic acid from the solution. This can be done by filtering the solutions keeping them separate for titration of 25 mL portions with the standard permanganate solution.

Calculate the weight of oxalic acid used in each of the flasks and the weight adsorbed in the sample. Calculate the weight of oxalic acid adsorbed in each sample and determine the values of x/m, from the slope of the line. If the adsorption sites are independent of temperature then from the Langmuir equation the slope of c/F versus c is a straight line with slope = 1/S which would be independent of temperature though the intercepts would vary. Calculate the surface areas per unit weight of sample and comment on the differences determined by the two equations.

Questions

1. Two other methods have been reported more recently, The BET method that accounts for multilayers of adsorbed species and the Dubinin method. Comment on these two approaches in relation to the two described in this older approach.
2. Based on the size of molecules and assuming close-packing calculate the maximum area of a surface that a single layer of a mole of gas could cover.
3. A desorption curve of an adsorbent on a surface usually does not follow the adsorption curve. How this is usually explained?
4. Describe some of the interesting aspects of Surface Chemistry.
5. The different adsorption characteristics of substances are used in Gas Chromatography to separate and identify minute quantities of volatile substances. Explain how this is accomplished.

Experiment No. 6. Colorimetric Analysis–Filter Photometry

It is possible to determine the concentration of a liquid dissolved substance by optical methods. Prior calibration is essential. To enhance the visible perception of color as an indication of the concentration of the dissolved substance it is necessary to filter out the irrelevant components that interfere with the optical detection. Visual light consists of a continuum range of wavelengths from about 450 to 800 nm. Since most substances absorb light over a relatively narrow wavelength range it is helpful filter out the light that is not involved with the detection of the desired substance. Thus the substance with a red color will transmit at the high end of the wavelength spectrum between 600 and 800 nm and the stray or non-effective light that can be removed is from 600 nm down to the UV which is in the blue and green part of the spectrum which is shown in Table exp. 6.1.

Table exp. 6.1 Light and filters

Wavelength range	Color of light	Compliment color	Wavelengths
780–620	Red	Blue-Green	600–450 nm
580–520	Yellow	Purple-Violet	450–520, 580–780
530–500	Green	Red-Purple	450–530, 500–780
500–400	Green-Violet	Red-Yellow	500–780

The eye or a camera light detector can be used to detect differences in transmitted light intensity. Thus by removing the non-relevant light that passes through the unknown sample it is possible to use the eye as a detector for the degree of adsorption by the solution.

The optical adsorption usually follows the Beer's Law which states that the absorbed light at a specified frequency (or wavelength) is proportional to the concentration of the absorbing species. This can be expressed as $I_o - I \propto C$ where I_o is the incident light intensity and I is the intensity of light transmitted after passing through the material in question and C is the concentration of the absorbing substance. I_o is the same for the two solutions, (the known and the unknown) that have different concentrations of a light absorbing substance. I_t is the transmitted light that is adjusted in length l for one of the samples to make the transmitted light I_t equal for the two solutions.

$$\text{Since } \mathrm{Log}(I_{t1}/I_o) = a l_1 C_1 \text{ and } \mathrm{Log}(I_{t2}/I_o) = a l_2 C_2$$

Then $l_1 C_1 = l_2 C_2$ and since the lengths of the light path through the solution are known and the concentration of one of the solutions is known it is possible to determine the concentration of the remaining unknown solution.

The optical filters are selected to remove the light that is NOT absorbed by the solution.

Procedure

1. Test the equivalence of the two optical paths by examining the light passed through two identical solutions samples of the same path length and satisfy that $I_{t1} = I_{t2}$ when $l_1 = l_2$
   Make the necessary adjustments of light and solution length and location until this is achieved.
2. Replace one of the known sample tube with the unknown solution and adjust the heights of the solution until the transmitted light is of the same intensity. Measure the length of the two light-paths and calculate the concentration of the unknown solution. If it is not possible to match the colors of the two solutions, it may mean that the concentrations are too high. Try to dilute the samples by a factor of 2, 5, or 10 to achieve good visible contrast. See your instructor or demonstrator if the problem persists. NOTE: Some people are color-blind or have difficulty in determining the difference for a particular color.
3. Report the results.

Questions

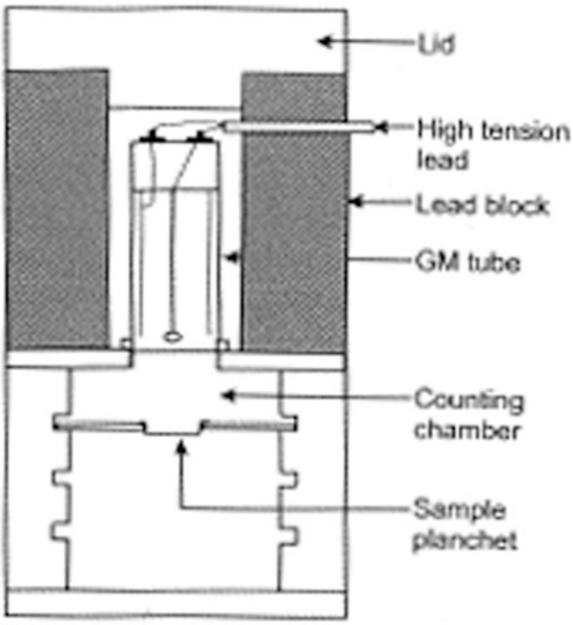
1. Explain why long tubes are used. Would an meter long tube be better? Why?
2. What is the limit on the length of tubes that can be used?
3. Explain why the filters can improve the accuracy of the analysis
4. Why would black glass tubes be better than the clear glass tubes that are used?
5. The Duboscq Colorimeter is an instrument used to analyze samples by differences in color intensity. Explain how an accuracy of 2% is achieved.

Experiment No. 7. Characteristics of Geiger – Muller counters

A. Introduction

The Geiger-Miller (G.M.) counter is a simple device for detecting radiation. G.M. counters are of different sizes and design depending upon their usage. It consists of a chamber the inner surface of which is coated with an electrical conductor that acts as the cathode of the tube (Fig. exp. 7.1). The anode is a tungsten wire of about 0.1 mm diameter at the central axis of the chamber, which is insulated

Fig. exp. 7.1 Outline diagram of the G.M. detector



from the cathode and is, made the anode. The cylindrical cathode is made vacuum tight at both ends. The chamber is filled with a monoatomic gas, usually argon or helium, at a pressure of 5–10 cm of Hg. Usually a quenching gas e.g., Butane or ethyl alcohol is filled at a pressure of 1–2 cm of Hg. Quenching is the termination of ionization current pulse in a G.M. tube. For accurate quantitative work, G.M tubes are contained on a lead block or “castle”, which also surrounds the sample chamber. The lead serves to shield the tube and chamber from outside radiation (see Fig. exp. 7.1). The G.M. tube is connected to a high voltage power supply and a scaler that counts the pulses of emitted electrons.

Working

If a beta emitter is brought near the window of the tube, some of the beta particles penetrates the window and pass into the gas inside the tube. This results in the formation of positive ions and electrons. When a high potential difference is applied across the electrodes the ions move toward the electrode of opposite charge. The accelerated ions also react with the gaseous atoms in the tubes to produce more ions and this chain reaction continues resulting in great mass of ions an amplification of 10^6–10^8. On reaching the electrodes the mass of ions is neutralized to producing a flow of electrons in the external circuit and provide potential of 1–10 V (Figs exp. 7.2 and 7.3).

The above reaction is terminated by quenching the accelerated ions with organic or halogen gas. If this is not done, the chain reaction would continue for some time and during which the tube would not detect another beta particle. The circuit is designed to indicate the total number of counts which are dependent the disintegration rate of the radioactive sample and the potential applied across the electrodes. At low voltage count rate/voltage curve is exponential. A slight change in the voltage causes considerable change in count rate. At higher voltage the curves becomes almost linear and horizontal. This is termed as plateau region of the G.M. tube which now operates at its maximum efficiency.

The efficiency of the tube = (counts per second from the sample/disintegrations per second from the radioisotope) × 100%.

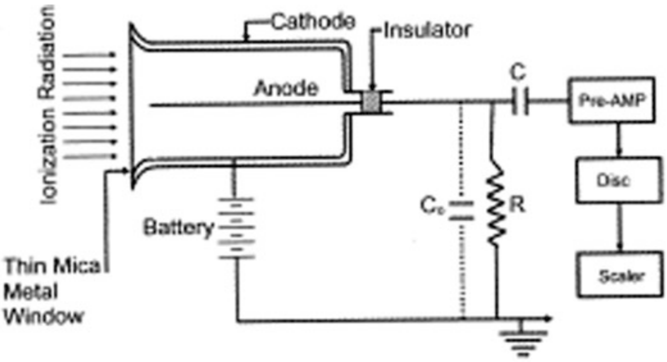


Fig. exp. 7.2 Electronic counting set up of the G.M. counter

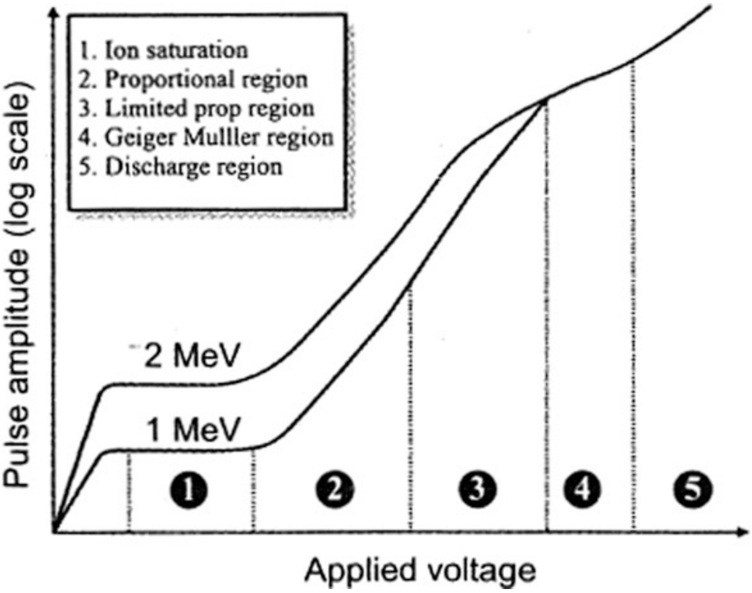


Fig. exp. 7.3 Variation of the charge induced at the anode with the applied voltage in an ionization counter

Determination of the Geiger – Muller Plateau

Geiger – Muller tube must be operated at an acceptable voltage which has to be determined for each tube.

Source Preparation

1. Prepare a slurry from uranium oxide, acetone and a small amount of adhesive in a plastic beaker.
2. Transfer small amounts of the slurry by a pipette or a glass rod to a planchet.
3. Spread evenly and dry under lamp ensuring that the acetone does not boil.
4. Cover the planchet by an aluminum foil of thickness equivalent to 54 mg/cm^2 (0.0008$^{\text{II}}$).
5. Count the planchet and if a count rate of 15,000–20,000 counts per 100 s is not achieved remove the foil and build up additional layer of U_3O_8 by adding small amount of slurry.
6. Seal the foil with an adhesive and label it.

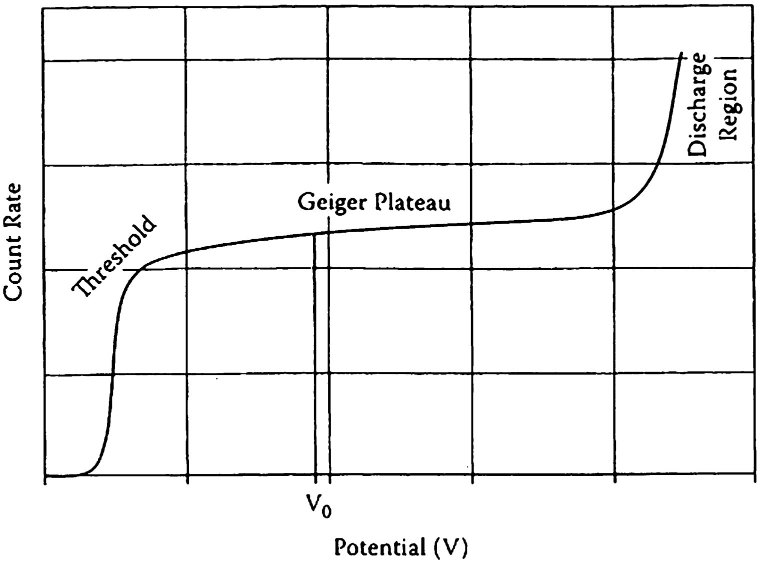


Fig. exp. 7.4 Characteristic voltage response of the G.M counter

Procedure

1. Insert the radioactive standard under the counter tube. Use shelf number two of a source holder for U_3O_8 and shelf number one for other weaker sources.
2. Set the operating voltage at 0 V. Increase the voltage until counts are registered. This will give fairly accurate indication of the starting voltage.
3. Starting from the threshold (starting) voltage perform 100 s counts at 25 V increments. Counts should be noted in each case.
4. Immediately beyond the threshold voltage a rapid rise in counting rate will occur until the plateau is reached. The termination of the plateau region will be noted by a second rapid increase in the counting rate as the voltage is further increased.
5. As soon as this second increase in the counting rate is noted decrease the voltage, as the G.M tube will be damaged if it is allowed to operate in this region.
6. Plot the counting rate (counts per minute) versus voltage as shown in Fig. exp. 7.4.

The plateau threshold voltage V_0 is the voltage at which the linear portion of the graph (the plateau) begins. The plateau slope can be calculated from the following equation:

$$(C_2 - C_1)/C_M \times 100/(V_2 - V_1)$$

Where, C_2 and C_1 = Two count values on the linear portion of the plateau (C_2 being greater than C_1). V_2 and V_1 = Respective voltages of C_2 and C_1.

As the G.M. tube ages, the slope increases and shortens. Therefore, the G.M. counter is usually at a voltage near the middle of the plateau or about 100 V above the threshold.

Determination of Counter Efficiency

Since all radioactivity detecting devices are not able to detect all the activities in a given sample, the efficiency of the counter must be determined so that the actual number of atomic disintegrations may be calculated.

Overall counter efficiency is determined by preparing standard sample sources and unknowns.

For measuring beta radioactivity of unknown composition, use a standard solution of Cs-137 or Sr-90 in equilibrium with its daughter. For alpha calibration use standard solution of natural uranium salt, Pu-239 or Am-241.

Determine the number of counts per minute in the standard sample by making three 1 min counts and three 10 min counts. Determine counting efficiency by comparing actual counts obtained with the known number of disintegration occurring per minute in the standard.

Counter efficiency = (counts per minute from the sample/disintegration per minute from radioisotope) × 100%.

Compare statistically 1 and 10 min counts by applying analysis of variance.

To Determine the Effect of Distance on Counting

The radiation emitted by a radioactive substance is scattered in all directions at random. Therefore, as the distance between the radioactive source and the G.M. tube becomes greater, less radioactivity is detected.

Procedure

Distance between the planchet and the tube is varied. Take three counts at each of the planchet positions for a period of 1 min. Tabulate the data.

Experimental data.

Voltage count rate	Voltage count rate	Voltage count rate

Calibrated standard ——————— ——————— ——————

Observed Activity at V_0 ———— cpm ——————— cpm ————— cpm

Report

1. Using Microsoft Excel™ or similar, plot the count rate, R, against the voltage, V, and determine the operating voltage, V_0, of the G.M. detector.
2. Determine the efficiencies with which the calibrated reference sources were measured at V_0. Efficiencies.

Source	dpm	cpm	Efficiency
Source	dpm	cpm	Efficiency
Source	dpm	cpm	Efficiency
Source	dpm	cpm	Efficiency
Source	dpm	cpm	Efficiency

3. Explain any differences observed in the efficiencies.
4. Determine the effect of distance on counting.

Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute
Distance	Counting per minute

5. Explain the effect of distance on counting.

Questions

1. What is the standard for measuring radioactivity?
2. What activity in cpm is expected from a 0.035 μCi of P-32 when it is measured with 5.4% efficiency?
3. Would it be possible to determine the operating voltage if a source emitting a different type of radiation were used? For example, if a beta-emitting source were used in this experiment, would a gamma source give approximately the same result?
4. Why is it a good idea to periodically check the high voltage (HV) plateau for G.M. detector?
5. Make the following conversions:
   (a) From 1 pCi to **X** dpm;
   (b) From 1 nCi to **X** pCi;
   (c) From 1 mCi to **X** pCi.

Sources

1. Katz SA, Bryan JC (2011) Experiments in nuclear science. CRC Press/Taylor and Francis Group, Boca Raton, p 168
2. Aery NC (2010) Manual of environmental analysis. CRC Press/Taylor and Francis Group, Boca Raton/London/New York. Ane Books Pvt. Ltd. p 413

Experiment No. 8. Biofuel Ethanol

The century of inexpensive fuel automobiles and other vehicles is soon to end. Alternates are already in the market, but still very expensive. Some of these are worth examining: (1) alcohol from the juice of fruit plants, (2) glucose from corn or potatoes, and (3) hydrolyzed cellulose by (a) microwaves and (b) ultrasonics.

It must be pointed out that the paths (1) and (2) have been with us for several thousand years and do not need any explanation other than to consider such cost saving systems as continuous fermentation and production. The fuel (alcohol) from cellulose is still in the experimental stage or rather the economizing stage. However recent studies have shown that the exposure of complex cellulose to microwave heating or ultrasonics can liberate some of the bound glucose which can now be subject to fermentation and the formation of ethanol which has become a prominent candidate to replace gasoline.

The Fermentation Process

Most canned sweet fruit juices can be used directly to convert the glucose (sugar) to ethanol with little preparation. Select a bottle or can of fruit juice and pour 200 mL into a 250 mL Erlenmeyer and add 3 g of dry active yeast. Seal the opening with a one hole rubber stopper into which a glass tube is inserted and attached to a rubber hose that is immersed in a flask containing a solution of calcium hydroxide to exclude oxygen and to absorb the CO_2 emitted.

The fermentation is allowed to proceed for a week before being examined for the yield.

The Characterization of the Alcohol

1. Examine the solution and characterize the product by (a) density, (b) taste, (c) freezing point. When half of the solution is slowly frozen the liquid is separated and the above three tests repeated. (NOTE: freezing removes water preferentially leaving an enriched alcohol solution).
2. The Microwave/Ultrasonic Degradation of Cellulose.

Place two weighed samples of cellulose cotton (3 g) in separate beakers and add 50 mL of distilled water to each beaker. Soak and thoroughly wet the cotton and place the beakers in **M** a microwave oven and heat the sample for 5, 10 and 25 min and in **U** an ultrasonic bath and apply the ultrasonics to the sample for 5, 10 and 25 min. Ideally, it would be best to examine the water in the ultraviolet to determine if a part of the cotton had reacted to produce glucose or some other organic substance. Determine if a reaction had occurred and if so, what is the product.

Report the results and suggest other methods to convert cellulose into glucose and methods to test the process.

Questions

1. The present cost of producing ethanol from grain or farm sources is too expensive. Explain why this is the case and suggest changes that might reduce the costs.
2. The alcohol from the fermentation process can be enriched by freezing the solution or by separating the alcohol by distilling it. What differences can you expect in the quality of the wine from these two different processes?
3. It is claimed that making wine is more of an art than a science. Do you agree? Explain.
4. It is possible to convert cellulose into fermentable glucose. Comment on the consequence of an economical process being developed that can produce ethanol from cellulose based crops.
5. Comment on the difference between ethanol and methanol with regard to price and suitability as a “beverage” or “fuel”.

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