SOLUBILITY EXPLAINED

By A. G. SHARPE, M.A., PH.D., F.R.I.C.

Lecturer in Inorganic Chemistry, Cambridge University

A *solution* is a homogeneous mixture of two (or more) components. In this context, homogeneity denotes not merely uniformity under observation by the eye, but incapability of separation into constituents by any mechanical means: in a true solution the particles of both constituents are separate molecules or ions, though there is sometimes quite strong interaction between one molecule or ion and a small number of others in its immediate environment. It is common practice to discuss solubility in terms of a solvent and one (or more) solutes; the *solvent* is the component that dissolves the *solute, i.e.* retains its own physical state after addition of the solute. In some instances, however, it is not clear which component is the solvent and which the solute. Such a case exists for two liquids such as ethanol and water, which are miscible in all proportions; the distinction is of no real importance in these circumstances, but it is conventional to refer to the component present in greater amount as the solvent.

Solutions are often classified on the basis of their physical state (gaseous, liquid, or solid) and the physical state of the pure solute at the ordinary temperature. There are then nine types of solution, and these are listed, with an example of each, in the table.

TYPES OF SOLUTION

| Solution	Example
Gas in gas ..	Air
Liquid in gas ..	Water (vapour) in nitrogen
Solid in gas ..	Iodine (vapour) in nitrogen
Gas in liquid ..	Carbon dioxide in water (soda-water)
Liquid in liquid	Ethanol in water
Solid in liquid	Sodium chloride in water
Gas in solid ..	Hydrogen in palladium
Liquid in solid	Mercury in silver (amalgam)
Solid in solid ..	Copper in nickel (coinage alloy)

This article is concerned mainly with solutions of gases, liquids and different types of solid in liquids, since these are the solutions with which the chemist, especially in the early stages of his training, is most concerned. The general principles on which solubility is discussed apply, however, to all types of solution, and the aim of this account is to provide a brief introduction which, although reasonably self-contained, will serve as an introduction to a more advanced understanding of the whole field of solubility. No part of this, it is interesting to note, is more difficult to treat quantitatively than the solubility of salts in water, the subject with which the student usually makes his first acquaintance with solubility phenomena.

Most pairs of substances (other than pairs of gases) are only partially miscible. When sucrose (ordinary sugar) is stirred with water at 25°, for example, the concentration of the solution eventually reaches a constant value; the solution is then said to be *saturated*, and its concentration is the *solubility* of sucrose in water at this temperature. This solubility may be expressed in several ways. From a physicochemical viewpoint, the most fundamental of these is in terms of the ratio of the number of gram-molecules, or moles, of sucrose to the total number of gram-molecules (of sucrose and water) in the liquid phase— *the mole fraction* of sucrose. Also in common use are *molarity* (the number of moles per litre of solution), *molality* (number of moles per 1,000 g of solvent) and *weight per cent* (number of grams of solute per 100 g of solution) as units of solubility; the second of these is especially widely used in dealing with solutions of electrolytes, where the term 'gram-formula-weight' replaces 'gram-molecule.' For solutions of gases in liquids the absorption coefficient (the volume of gas, reduced to 0°C at 1 atm, dissolved by one volume of solvent at the temperature of the experiment under a partial pressure of the gas of 1 atm) is the unit most frequently employed.

The equilibrium which exists in a saturated solution is, like all other equilibria, a dynamic

one, as may be shown by isotopic tracer experiments: the rate of dissolution of the solute is equal to its rate of separation from the solution. The position of equilibrium is affected by heat and pressure in accordance with Le Chatelier's principle, and the solubility of a non-electrolyte is, in fact, an equilibrium constant. For substances which yield ions in solution, such as salts of formula MX, the equilibrium is of the form

$$MX \text{ (solid)} \rightleftharpoons M^+ \text{ (in soln)} + X^- \text{ (in soln)}$$
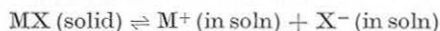
and the equilibrium constant is the product of the activities (approximately, of the concentrations) of M^+ and X^- in solution, the activities of solids being taken arbitrarily as unity; this equilibrium constant is known as the *solubility product* of MX at the temperature chosen. For a salt of formula MX_2, the solubility product is $[M^+][X^-]^2$, and so on. Since $[M^+]$ and $[X^-]$ are proportional to the amount of dissolved salt, we see that the relation between solubility and solubility product depends on the formula of the salt concerned.

One feature of discussions of solubility which calls for particular comment is the use of the term 'insoluble.' Most chemists tend to describe as 'insoluble' any substance which dissolves in a liquid to the extent of less than about 1 g in 1,000 g of solvent. Silver chloride and cupric sulphide, for example, are by this criterion insoluble in water. Their solubilities, 10^{-5} and 10^{-22} g-formula-weight per litre, and solubility products, 10^{-10} and 10^{-44} (g-ion/litre)^2, at 25°, however, are very different, and (as will be seen later) from the point of view of the energy change which would be involved in getting a g-formula-weight of solute into aqueous solution there is very much more difference between silver chloride and copper sulphide than between silver chloride and sodium chloride, the solubility of which is 0·62 g-formula-weight per litre at 25°.

We must now see why it is important to know something about such energy changes. It is well known that there are several forms of energy, such as mechanical, electrical, chemical and thermal energy. All forms of energy can be converted into heat, but the converse is not always true, and this has led to the division of the *total heat content* (H) at absolute temperature T of a system into two parts: that part which can be converted into other forms of energy without change of temperature is known as *free energy* (G), whilst the part which is not convertible ($H - G$) is defined as the product of the absolute temperature and a quantity called the *entropy* (S) of the system. Thus

$$H = G + TS$$

or, for a change taking place at constant temperature T,

$$\Delta H = \Delta G + T\Delta S$$

The quantity S may also be looked at in another way, as a measure of the degree of randomness of the system. This aspect may be illustrated by considering what happens if we mix equal quantities of hot and cold water: the resulting liquid all has the same temperature, and instead of there being molecules describable as belonging to one of two different categories, all are now mixed up—the randomness of the system has increased. At the same time, although no heat has been gained or lost, the possibility of using the system to obtain electrical energy by putting thermocouples in the water at different temperatures has disappeared. Gain in entropy is therefore accompanied by a corresponding loss in free energy if there is no change in the total heat content of the system. Just as every substance has a standard heat of formation, it has also a standard free energy of formation and a standard entropy, and from tables of such quantities (which may be determined independently by a variety of methods) it is possible to compute changes in them for different reactions.

The very existence of endothermic (heat-absorbing) processes which take place spontaneously (*e.g.* the dissolution of most substances in water) is a proof that it is not the change in heat content (ΔH) which determines how far a reaction goes, *i.e.* its equilibrium constant. This quantity is the free-energy change, which is therefore a quantity of the greatest importance throughout chemistry. It is not essential in obtaining some understanding of the significance of the

concept of free energy in chemistry to master the numerical form of all the relationships involved, but one such relationship is of outstanding importance: if a reaction is carried out on a very small scale (say, one-millionth gram-formula quantities) in the presence of all the reactants and products at unit activity, and the free-energy change is multiplied (in this case by a million) to give the so-called standard free-energy change, ΔG°, the latter is related to the equilibrium constant for the reaction by an equation of the form

$$-\Delta G^\circ = \boldsymbol{R} T \ln K$$

where K is the equilibrium constant expressed in suitable units, $\boldsymbol{R}$ is the gas constant, T the absolute temperature, and ln denotes logarithm to base e, or $2\cdot3 \log_{10}$. Substitution of the values of $\boldsymbol{R}$ and T leads (for $T = 25°C$) to the equation

$$-\Delta G^\circ \text{ (in kcal)} = 1\cdot36 \log_{10} K$$

The special feature of this relationship which must be noted is that it is an exponential one. Since it is the logarithm of the equilibrium constant that is related to $-\Delta G^\circ$, a small change in the latter quantity makes a very large difference to how far a process goes; a change of 4 kcal in ΔG, in fact, alters K by a factor of a thousand. In the case of an ionic solid dissolving in water, the energies of interaction of the ions with one another in the solid and with water molecules in solution are both very large, and it is the small difference between these two large quantities (neither of which may be accurately known) which determines the magnitude of the solubility product (the equilibrium constant) and hence of the solubility; this is why the calculation of solubilities of salts from thermal data presents such a formidable task.

This competitive picture of the dissolution of salts may now be generalized to include all processes of solution. There will always be an increase in the entropy of the system when two constituents mix to form a solution, because of the increase in randomness, and in cases where there is no heat of solution this increase in entropy provides the driving force for the dissolution: such a case is illustrated by many pairs of organic liquids, which are freely soluble in one another without absorp-

tion or liberation of heat (if $\Delta H = 0$, $\Delta G = -T\Delta S$). Usually, however, it will be necessary to consider heat terms as well as entropy terms, and to what extent a solute A will dissolve in a solvent B will then be determined largely by the difference between the energy of interaction of A with B and the energies of interaction of A with A, and B with B. Looking at the problem in this way, we see that whether A dissolves in B depends just as much on the properties of the solvent as on the properties of the solute: hydrocarbons, for example, dissolve only very slightly in water, not because of strong attraction between hydrocarbon molecules in pure hydrocarbons but because of the hydrogen bonding between molecules in liquid water; the C–H bond is much less polar than the O–H bond, and hence bonds of the latter type interact with one another preferentially.

We shall now discuss some different types of solution to illustrate the relative importance of heat and entropy terms in determining the position of equilibrium.

SOLUTIONS IN GASES

Since the molecules of an ideal gas exert no force of attraction on one another, a gas as a solvent offers no resistance to dilution with another substance; there is always a positive entropy of mixing, and the position of equilibrium is determined largely by the amount of energy needed to separate the units present in the structure of the solute. If this is another gas, a negligible amount of energy is needed, and hence all gases are completely miscible. If it is a liquid or a solid, the latent heat of vaporization or sublimation must be absorbed in order to transform it into the vapour phase; this then mixes freely with the gas, which is considered to be the solvent. The influence of temperature is thus confined to its effect on the vapour pressure of the solute, and solubilities of liquids and solids in gases always increase with rise in temperature.

Occasionally there is evidence for specific interaction between a gaseous solvent and a solid solute; some metal oxides (*e.g.* BeO) are significantly soluble in compressed steam at high temperatures owing to hydroxide formation.

SOLUTIONS OF GASES IN LIQUIDS

Solubilities of gases in liquids are usually cited as absorption coefficients, as has been mentioned earlier; since, however, by Avogadro's law the number of moles of a gas is proportional to its volume at standard temperature and pressure, the absorption coefficient is evidently proportional to the concentration in moles per litre. One of the difficulties which arises in the interpretation of absorption coefficients (and, indeed, of many other solubility data) is that the analytical methods employed in their determination do not reveal the chemical form in which the solute has dissolved. It may reasonably be supposed that nitrogen and oxygen dissolve unchanged, for they are sparingly soluble in all solvents; but hydrogen chloride in water is largely converted into hydrated H_3O^+ and Cl^- ions; the fact that 2M ammonia solution has quite a strong odour, whereas 2M hydrochloric acid is odourless, indicates that for ammonia the degree of interaction with the solvent is smaller. All very soluble gases do, in fact, undergo chemical change to an appreciable extent in the solvents in which they are very soluble.

The solubility of a gas at a given temperature is proportional to the pressure (Henry's Law). If n_1 and n_2 are the numbers of moles of solvent and gas in the saturated solution at pressure p_2 of the gas,

$$n_2/n_1 = kp_2$$

If the gas is not very soluble, n_2 is much smaller than n_1, and n_1 is then nearly equal to $n_1 + n_2$, so that $n_2/(n_1 + n_2) = x_2 = kp_2$, where x_2 is the mole-fraction of solute in the saturated solution. Now if we think of the solvent as non-volatile, p_2 becomes the vapour pressure of the volatile solute present in mole-fraction x_2 in the solution. If Henry's Law applies over the whole concentration range from pure solvent to pure liquefied solute, then when x_2 is unity p_2 becomes $p_2°$, the vapour pressure of the pure solute, so that $k = 1/p_2°$. Hence

$$x_2 = p_2/p_2° \quad \text{or} \quad p_2 = x_2 p_2°$$

This is, of course, Raoult's law for a liquid mixture. With its aid we can calculate the ideal solubility of any gas if the vapour pressure above its liquid is known at that temperature (i.e. if it is below its critical temperature). At 25°C, for example, the vapour pressure of pure liquid ethane is 42 atm; if $p_2 = 1$ atm, $x_2 = 1/42 = 0·024$ mole-fraction. For gases above their critical points the hypothetical vapour pressure of the liquid can be estimated (from the Clausius–Clapeyron equation) on the assumption that the heat of vaporization remains constant; in this way it can be shown that the ideal solubility of nitrogen should be about 10^{-3} mole-fraction.

These calculated values, it should be noted, apply to *any* solvent so long as the solutions show ideal behaviour; the actual values for ethane and nitrogen in solvents such as hydrocarbons and carbon tetrachloride are about 0·018 and 6×10^{-4} mole-fractions, respectively, showing that there is some departure from ideality. It is, however, very striking that so simple a treatment leads to a result which is in error by less than a factor of two. When water is the solvent this is not so, for the intermolecular attraction in liquid water complicates the picture by making all gases which dissolve in molecular form much less soluble than they are calculated to be; the gain in entropy of mixing is offset by the work which has to be done against this intermolecular attraction in forcing molecules of solvent apart. Water is the outstanding example of a polar solvent with strong intermolecular attraction, but nitrobenzene, aniline and ethanol also show this behaviour to some extent; another manifestation of this in the case of ethanol is the fact that its boiling point is 100° higher than that of dimethyl ether, which has the same molecular weight.

The inverse dependence of x_2 on $p_2°$ at a particular temperature also explains two other features of the solubility of gases. Since the pressure above the liquid is less for gases with relatively high boiling points, gases such as butane and carbon dioxide are much more soluble in all solvents than are hydrogen, oxygen, nitrogen and carbon monoxide. Furthermore, since for any gas $p_2°$ increases with increase in temperature, the solubilities of all gases decrease with rise in temperature.

The latter conclusion may also be reached by Le Chatelier's principle: dissolution of a gas in a liquid may be considered as involving first the condensation of the gas, followed by mixing of the two liquids; since the condensation stage is accompanied by liberation of heat, lowering the temperature will cause more gas to dissolve.

SOLUTIONS OF LIQUIDS IN LIQUIDS

Mixtures of two volatile liquids which are miscible in all proportions are in many ways like solutions of gases in liquids. If in the preceding solution $p_2°$ is less than 1 atm at $25°$ and the phase designated the solvent has an appreciable vapour pressure, we have a typical binary liquid system. Each liquid in such a mixture exerts a vapour pressure equal to its mole-fraction times its vapour pressure in a pure state at the same temperature (Raoult's Law); solutions for which this law holds are called ideal solutions, and typical examples are usually mixtures of very similar substances such as ethyl bromide and ethyl iodide, or benzene and toluene. It would be rather surprising if there were many pairs of liquids which obeyed Raoult's law exactly, since the existence of a substance in the liquid phase at all is a proof of the presence of quite strong intermolecular attractions which can be overcome only by supplying the heat of vaporization. When an ideal solution is formed from two liquids there is no change in heat content; the driving force towards mixing is provided by the increase in entropy.

There are, of course, many pairs of liquids which are miscible in all proportions to yield mixtures which show deviations from Raoult's law, e.g. diethyl ether and acetone, heptane and ethanol, ethanol and water, perchloric acid and water. These deviations arise from the differences in properties of the constituents of the pairs, and in some cases there are appreciable heats of mixing. The nature of these deviations from Raoult's law is, however, of minor interest in connection with solubility, and will not be discussed further here.

When two liquids are less similar than the members of the pairs cited above, partial miscibility usually occurs; if a little phenol, aniline or ether, for example, is added to water, it dissolves, but further additions soon result in the formation of two layers, one a saturated solution of the organic compound in water, and the other a saturated solution of water in the organic compound. Similar behaviour also results with aniline and n-hexane, or methanol and carbon disulphide. Greater difference in nature (e.g. water and carbon disulphide, ethanol and mercury) results in immiscibility. The miscibility of liquids is often discussed in terms of their *internal pressures*, which may be regarded as measures of the dependence of internal energy on volume, i.e. of the strength of the cohesive forces. These may be estimated roughly by several methods, typical values at ordinary temperature being: hexane, 2,000; carbon tetrachloride, 3,500; phenol, 5,000; water, 16,000 atm. Increasing difference in internal pressures leads to decreasing solubility; increasing temperature overcomes the cohesive forces, and many pairs of partially miscible liquids become completely miscible at higher temperatures.

The observant reader will have noticed that no question of absorption or liberation of a heat of fusion or vaporization arises in the dissolution of one liquid in another; the overall heat of solution is therefore nearly always small and arises from different degrees of non-ideality in the liquids concerned. Clearly, entropy considerations play an important part; but it cannot be said that at the present time there is any simple theory which deals satisfactorily with all of the great variety of behaviour found in liquid–liquid systems.

SOLUTIONS OF SOLIDS IN LIQUIDS

Three types of solid will be considered in the following discussion: those having molecular, macromolecular and essentially ionic structures.

In molecular solids the shortest distances between atoms in different molecules are about twice the interatomic distances within molecules; the intermolecular bonding is weak, as is shown by the low heats of sublimation. Among substances which crystallize with molecular structures at the ordinary

temperature are iodine, mercuric chloride and nearly all organic compounds.

Macromolecular structures, such as those of diamond, silica and red phosphorus, contain no discrete molecules; strong covalent bonds extend through the structure in two or more directions, and it is only with great difficulty that the lattice can be broken up.

Ionic solids contain symmetrical arrangements of charged ions held together by electrostatic bonding, the energy of the lattice relative to isolated ions at infinity being proportional to $1/(r_+ + r_-)$, where $(r_+ + r_-)$ is the sum of the ionic radii, *i.e.* the interionic distance. Although salts have very high heats of fusion and vaporization, the ions are strongly attracted by polar molecules (especially water) and solvation energies of ions are sometimes greater than lattice energies of salts containing them.

If a molecular solid is melted (thereby absorbing the latent heat of fusion), the resulting liquid may form an ideal solution with a solvent; when this is so, the heat of fusion is equal to the heat of solution, and it can be shown by a rather lengthy thermodynamic argument (which will not be reproduced here) that the ideal solubility under constant pressure is given by

$$\ln x = -\frac{L_f}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

where T is the temperature at which the mole-fraction of the solute in the solution is x, L_f is the molar heat of fusion of the solid, and T_0 is its melting point. This equation may, for example, be used to calculate the ideal solubility of naphthalene in any solvent as 0·31 mole-fraction at 25°C. The solubilities in benzene, toluene, chlorobenzene and chloroform (all of which are non-polar liquids having internal pressures similar to that of liquid naphthalene) are all close to this value; those in aniline and acetone agree less well; in water, naphthalene is very sparingly soluble, since the strong attraction of water molecules for one another (made manifest in the high boiling point, entropy of vaporization, and internal pressure of water) serves to exclude molecules of the non-polar solute. It is, in fact, the abnormal character of water which is responsible for the low

solubility of most organic compounds in it; the organic compounds which are soluble in water all contain groups such as hydroxyl, carboxyl or sulphonyl, which can interact with water molecules as strongly as the latter interact with one another. Typical compounds in these classes are low-molecular-weight alcohols and acids, polyhydric alcohols such as sugars, and soaps.

For a macromolecular solid which is imagined to form an ideal molecular solution, similar considerations should apply; in this case, however, the latent heat of fusion is extremely high and hence the solubility in all solvents is extremely low.

For ionic solids the position of equilibrium is determined mainly by the balance of lattice energies and solvation energies. In a more refined treatment the latter would be split into heat and $T \times$ (entropy of solvation) terms, but for present purposes a discussion based on lattice energy and hydration heats will suffice; as has been stated earlier, both are very large quantities, but it is the small difference between them which determines solubilities. In the case of sodium chloride, for example, it requires absorption of 184 kcal/g-formula-weight to separate the solid into ions at infinity; since the heat of solution of sodium chloride in water is nearly zero (hence the independence of solubility on temperature) the sum of the hydration heats of Na^+ and Cl^- must also be 184 kcal. Most other salts absorb a few kcal of heat on dissolution in water, and hence are more soluble in hot than in cold water; the increase in solubility is, however, usually relatively small. In principle the hydration energy of an ion of radius r and charge z in a solvent of dielectric constant ϵ is given by the expression

$$\frac{z^2 e^2}{2r}\left(1 - \frac{1}{\epsilon}\right)$$

but the radius of an isolated ion in solution is not necessarily the same as that of the same ion in a crystal, and ϵ need not be the same near an ion as it is in the pure solvent; in practice, therefore, empirical methods play a large part in obtaining values for solvation energies. The importance of the $(1 - 1/\epsilon)$ term, however, is very great, for it means that only in solvents of high dielectric constant will the

sum of two solvation energies approach the lattice energy of the solid. Hence salts, if they dissolve at all, will normally do so only in media of high ϵ, such as water, ammonia, nitromethane and dimethylformamide. The few salts that dissolve in organic solvents of low dielectric constant (e.g. ether) nearly always contain very large ions and have very low lattice energies; tetrabutylammonium picrate is an example of such a compound.

The fact that the lattice energy of an ionic solid depends inversely on $r_+ + r_-$ taken together, whilst the sum of the solvation energies is proportional to $1/r_+ + 1/r_-$ taken separately, has other instructive consequences. For a set of compounds having the same structure and $r_- \gg r_+$ the lattice energies change little with increasing r_+; $1/r_-$ is constant and very small, whilst $1/r_+$ decreases rapidly with increase in r_+. Hence solubilities decrease as r_+ increases; this is what happens among, for example, the alkali-metal chloroplatinates or cobaltinitrites or the alkaline-earth metal sulphates in water. Insolubility in water thus need not denote covalent character; there is, for example, not the slightest evidence to suggest that the bonding between the metal and the anion in calcium fluoride, barium sulphate or potassium chloroplatinate is not ionic.

Silver ion has almost the same radius as sodium ion, and silver fluoride is freely soluble in water. Silver chloride, however, is very sparingly soluble, and it is instructive to compare the pairs NaF and NaCl, and AgF and AgCl. The observed lattice energies of these four compounds (all of which have the NaCl structure) are 216, 184, 228 and 216 kcal/g-formula-weight respectively. Despite the difference in size between F^- and Cl^-, we notice that the difference in lattice energy is only 12 kcal for the silver salts; for the sodium salts it has the much larger value of 32 kcal. We therefore infer that there is about 20 kcal of non-electrostatic bonding stabilizing the solid in the case of silver chloride; this term has no counterpart in the hydration energies of Ag^+ and Cl^- in water, which are the same as in solutions of silver fluoride and sodium chloride, and it is therefore the main factor underlying the striking difference in solubility in water between silver fluoride and silver chloride.

The foregoing account of the solubility of salts has been based on an electrostatic model for the solvated ion in solution, the charge on the ion interacting with the uneven charge distribution in the water or other solvent molecule. There is sometimes, however, very strong evidence that the solvation process is not a simple electrostatic one. Thus when a paramagnetic Co^{3+} ion is hydrated, it becomes diamagnetic, showing that an electronic rearrangement has taken place. When $Cr(H_2O)_6^{3+}$ ions from chrome alum dissolve in ^{18}O-labelled water, it is found that no exchange with water from the alum takes place during several hours; evidently the water attached to the cation is not free to exchange, a fact which again suggests covalent bonding. Finally, the highly specific interaction between salts of a few metals and organic liquids, e.g. the solubility of silver fluoroborate (which has the same structure as potassium fluoroborate) in benzene and toluene, indicates covalent interaction of a rather special kind, in this case between the aromatic compound and the silver ion. In all these cases, however, it should be remembered that the position of equilibrium is determined by the difference between the lattice energy of the solid and the *magnitude* (not the *nature*) of the interaction between ions and solvent: it is the magnitude of the free-energy change which determines how far the process of dissolution goes.

SOLUTIONS IN SOLIDS

The characteristic feature of a solid is that it contains atoms, molecules or ions occupying particular positions in a rigid structure. When the solute can be accommodated in the solvent lattice without appreciable change, the formation of a solid solution takes place readily: examples are provided by p-dichlorobenzene and p-dibromobenzene, potassium chloroplatinate and potassium bromoplatinate, magnesium oxide, MgO, and lithium ferric oxide, $LiFeO_2$ (Mg^{2+}, Li^+ and Fe^{3+} are the same size, and the average charge on Li^+ and Fe^{3+} is the same as on Mg^{2+}), and silver and gold. In such cases, there is a negligible change in heat content when a solid solution

is formed. Gases and liquids, on the other hand, are seldom very soluble in solids: the fact that they *are* gases and liquids implies a simple molecular structure in their solid phases, and solubility is then to be expected only in elements or compounds crystallizing with similar simple molecular structures. For a gas or a liquid to dissolve in a solid requires work to be done in forcing apart the units in the solid structure and, since the interatomic, intermolecular or interionic forces in solids are relatively strong, this energy factor militates against solubility. Gases usually interact with solids only to the extent of forming a monolayer held by surface forces and a weakly held layer, only a few molecules thick, on top of this. Where the solubility is appreciable, as in the case of hydrogen in palladium and other metals, strong chemical bonding must be involved to compensate not only for the work done in expanding the metal lattice, but also for the energy needed to break the strong bonds (103 kcal/mole) in hydrogen, which is present in the solid phase as single atomic units.

CONCLUSION

The positions of all equilibria are determined by thermodynamic factors. When solute and solvent are in the same physical state, the increase in entropy on mixing ensures solubility so long as (i) in the case of liquids, they do not differ too widely in their properties and internal pressures; (ii) in the case of solids, they have the same structure and, if ionic, contain ions of similar sizes. For other cases, heats of vaporization or fusion are involved as well as entropies of mixing. In all cases, however, the key to the interpretation of solubility lies in the evaluation of the free-energy change which accompanies the process of dissolution.

CLEANING OF APPARATUS: THE ALCOHOL — NITRIC ACID REACTION

At one time it was customary to cleanse dirty apparatus—especially containing tarry matter—by means of nitric acid and alcohol. It seems that in the early days this procedure was not considered particularly dangerous, but in recent years its hazardous nature has been increasingly emphasized and serious accidents have in fact occurred.

The reaction is well-known to be auto-catalytic. When pure nitric acid and alcohol are mixed, no reaction occurs at first, but reaction starts almost explosively after a varying lapse of time and is accompanied by violent bumping and the formation of nitrogen oxides. It seems likely that the manufacturers of nitric acid have progressively supplied a purer and purer product and that, in the early days, a treacherous latent period was not a marked feature of the reaction.

The difficulty can be avoided by the deliberate addition of nitrous acid. If 5-10 per cent of sodium nitrite is stirred into ordinary nitric acid (density 1·42), a red-coloured acid, containing dinitrogen tetroxide, is immediately obtained. If to this alcohol is added, reaction starts at once.

This modification of the usual procedure has now been used for cleaning apparatus over a number of years, and so far no indication that it might prove dangerous has been noted. The 'bumping' that is so characteristic of the pure nitric acid reaction does not occur. The reaction starts smoothly at the surface of the liquid, and its onset is so rapid that there would seem to be little risk of adding enough alcohol, in one lot, to generate dangerous pressure in a flask. Taking elementary precautions (fume-cupboard, avoid narrow-necked vessels and so on) it is difficult to see in what way it might prove dangerous. All that is necessary is that the nitric acid, before use, should have a rich reddish-brown colour. If this single point is attended to, even the mistaken use of sodium nitrate for nitrite should at once give warning that alcohol must not be added. If desired the nitric acid mixture may be kept bottled ready for use.

R. E. D. CLARK
Cambridge College of Arts & Technology.