and the ordinary equilibrium of saturation is reached by precipi­tation of solid from solution.

The quantity of substance, or solute, which a given quantity of liquid or solvent will dissolve in presence of excess of the solute measures the solubility of the solute in the given solvent in the conditions of temperature and pressure. The solubilities of solids may be expressed in terms of the mass of solute which will dissolve in 100 grammes of water.

The following may be taken as examples :—

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Solute. | Chemical Constitution of the Solid. | Solubility | | |
| at 0° C. | at 20° C. | at 100°C. |
| Sodium chloride . | NaCl | 35·7 | 36∙0 | 39·8 |
| Potassium nitrate . | KNO3 | 13·3 | 31∙2 | 247∙0 |
| Barium chloride . | BaCl2 | 30∙9 | 35·7 | 58·8 |
| Copper sulphate . | CuSO4 | 15·5 | 22∙0 | 73·5 |
| Calcium carbonate | CaCO3 | 0∙0018 | — | 0∙0018 |
| Silver nitrate . | AgNO3 | 121∙9 | 227∙3  (at 19°∙5 | 1111·0  (at 110°) |

When dealing with gases it is usually more convenient to express the solubility as the ratio of the volume of the gas absorbed to the volume of the absorbing liquid. For gases such as oxygen, and nitrogen dissolved in water the solubility as thus defined is inde­pendent of the pressure, or the mass of gas dissolved is propor­tional to the pressure. This relation does not hold for very soluble gases, such as ammonia, at low temperatures. As a general rule gases are less soluble at high than at low temperatures—unlike the majority of solids. Thus oxygen, 4∙89 volumes of which dissolve at atmospheric pressure in 1 volume of water at 0° C., only dissolves to the extent of 3·10 volumes at 20° and 1∙70 volumes at 100o.

*Cause of Solubility.—*At the outset of the subject we are met by a fundamental problem, to which no complete answer can be given: Why do certain substances dissolve in certain other substances and not in different substances? Why are some pairs of liquids miscible in each other in all proportions, while other pairs do not mix at all, or only to a limited extent? No satisfactory correlation of solubility with chemical or other properties has been made. It is possible to state the conditions of solubility in terms of the theory of available energy, but the result comes to little more than a re-statement of the problem in other terms. Nevertheless, such a re-statement is in itself sometimes an advance in knowledge. It is certain then that when dissolution occurs the available energy of the whole system is decreased by the process, while when equilibrium is reached and the solution is saturated the available energy is a minimum. When a variable quantity is at a minimum a slight change in the system does not affect its value, and therefore, when a solution is saturated, the increase in the available energy of the liquid phase produced by dissolving in it some of the solid must be equal to the decrease in the available energy of the solid phase, caused by the abstraction from the bulk of that part dissolved. The general theory of such equilibria will be studied later under the head of the phase rule.

It is possible that a correlation may be made between solubility and the energy of surface tension. If a solid is immersed in a liquid a certain part of the energy of the system depends on, and is proportional to, the area of contact between solid and liquid. Similarly with two liquids like oil and water, which do not mix, we have surface energy proportional to the area of contact. Equilibrium requires that the available energy and therefore the area of contact should be a minimum, as is demon­strated in Plateau’s beautiful experiment, where a large drop of oil is placed in a liquid of equal density and a perfect sphere is formed. If, however, the energy of surface tension between the two substances were negative the surface would tend to a maximum, and complete mixture would follow. From this point of view the natural solubility of two substances involves a negative energy of surface tension between them.

*Gibbs's Phase Rule.—*A saturated solution is a system in equili­brium, and exhibits the thermodynamic relations which hold for all such systems. Just as two electrified bodies are in equilibrium when their electric potentials are equal, so two parts of a chemical and physical system are in equilibrium when there is equality between the *chemical potentials* of each com­ponent present in the two parts. Thus water and steam are in equilibrium with each other when the chemical potential of water substance is the same in the liquid as in the vapour. The chemical potentials are clearly functions of the composition of the system, and of its temperature and pressure. It is usual to call each part of the system of uniform composition through­out a *phase;* in the example given, water substance, the only component is present in two phases—a liquid phase and a vapour phase, and when the potentials of the component are the same in each phase equilibrium exists.

If in unit mass of any phase we have *n* components instead of one we must know the amount of *n —* 1 components present in that unit mass before we know the exact composition of it. Thus if in one gramme of a mixture of water, alcohol and salt we are told the amount of water and salt, we can tell the amount of alcohol. If, instead of one phase, we have *r* phases, we must find out the values of r(n-1) quantities before we know the composition of the whole system. Thus, to investigate the composition of the system we must be able to calculate the value of *r(n-1)* unknown quantities. To these must be added the external variables of temperature and pressure, and then as the total number of variables, we have *r* (n+1) + 2.

To determine these variables we may form equations between the chemical potentials of the different components—quantities which are functions of the variables to be determined. If *μ∖* and μ2 denote the potentials of any one component in two phases in contact, when there is equilibrium, we know that μι=μ2. If a third phase is in equilibrium with the other two we have also μι = μ3. These two equations involve the third relation μ2=μ3, which therefore is not an independent equation. Hence with three phases we can form two independent equations for each component. With *r* phases we can form r —1 equations for each component, and with *n* components and *r* phases we obtain *n*(r—1) equations.

Now by elementary algebra we know that if the number of inde­pendent equations be equal to the number of unknown quantities all the unknown quantities can be determined, and can possess each one value only. Thus we shall be able to specify the system com­pletely when the number of variables, viz. *r* (n—1)+2, is equal to the number of equations, viz. n(r —1); that is when *r=n* -+-2. Thus, when a system possesses two more phases than the number of its components, all the phases will be in equilibrium with each other at one definite composition, one definite temperature and one definite pressure, and in no other conditions. To take the simplest case of a one component system water substance has its three phases of solid ice, liquid water and gaseous vapour in equilibrium with each other at the freezing point of water under the pressure of its own vapour. If we attempt to change either the temperature or the pressure ice will melt, water will evaporate or vapour con­dense until one or other of the phases has vanished. We then have in equilibrium two phases only, and the temperature and pressure may change. Thus, if we supply heat to the mixture of ice, water and steam ice will melt and eventually vanish. We then have water and vapour in equilibrium, and, as more heat enters, the tem­perature rises and the vapour-pressure rises with it. But, if we fix arbitrarily the temperature the pressure of equilibrium can have one value only. Thus by fixing one variable we fix the state of the whole system. This condition is represented in the alge­braic theory when we have one more unknown quantity than the number of equations; *i.e.* when r(n —1) + 2=n(r-1)+ 1 or r = n+1, and the number of phases is one more than the number of components. Similarly if we have F more unknowns than we have equations to determine them, we must fix arbitrarily F co­ordinates before we fix the state of the whole system. The number F is called the *number of degrees of freedom* of the system, and is measured by the excess of the number of unknowns over the number of variables. Thus F = *r(n —* 1) + 2 — *n(r* — 1) = n — r + 2, a result which was deduced by J. Willard Gibbs (1839-1903) and is known as Gibbs’s Phase-Rule (see Energetics).

The phenomena of equilibrium can be represented on diagrams. Thus, if we take our co-ordinates to represent pressure and tem­perature, the state of the systems with ice, water and vapour in equilibrium is represented by the point O where the pressure is that of the vapour of water at the freezing point and the tem­perature is the freezing point under that pressure. If all the ice be melted, we pass along the vapour\* pressure curve of water OA. If all the water be frozen, we have the vapour pressure curve of ice OB; while, if the pressure be raised, so that all the vapour vanishes., we get the curve OC of equilibrium between the pressure and the freezing point of water. The slope of these curves is determined by the so-called “ latent heat equation ”