be deduced that the molecule of hydrogen and of chlorine con­tains two atoms (see Atom) ; and similar considerations show that oxygen, nitrogen, fluorine, &c., are also diatomic. Physical methods may also be employed. For instance, in monatomic gases the ratio of the specific heat at constant pressure to the specific heat at constant volume is 1·66; in diatomic gases 1·42; with other values for more complex molecules (see Mole­cule). This ratio may be determined directly by finding the velocity of sound in the gas (Kundt) or by other methods, or indirectly by finding the specific heats separately and then taking the ratio. It is found that the gases just mentioned are diatomic, whereas argon, helium, neon and the related gases, and also mercury and some other metals when in the gaseous con­dition, are monatomic. A knowledge of the atomicity of a gas combined with its density (compared with oxygen and hydrogen) would therefore give its atomic weight if Avogadro’s law were rigorously true. But this is not so, except under extremely low pressures, and it is necessary to correct the observed densities. The correction involves a detailed study of the behaviour of the gas over a large range of pressure (presuming the densities are already corrected to 0°),and may be conveniently written in the form *a*=1/*pvd*(*pv*)/*dp*. Thus if D be the observed *pv dp*

relative densities of a gas to hydrogen at oo and under normal atmospheric pressure, *ax* and *a*H the coefficients of the gas and hydrogen, then the true density, or ratio of molecular weights, is D× (1+ax)/(1+*a*H).

Lord Rayleigh and D. Berthelot have corrected several mole­cular weights in this fashion. The importance is well shown in the modification of Morley's observed density of oxygen, viz. 15∙90, which, with Rayleigh’s values of *a*O *=* — 0∙00094 and *a*h = + 0∙00053, gives the corrected density as 15∙88. And this value is the atomic weight, for both hydrogen and oxygen molecules contain two atoms. Compound gases can also be experimented with. For example Gray (*Journ. Chem. Soc.,* 1905, 87, p. 1601) found that it was easier to prepare perfectly pure nitric oxide than to obtain pure nitrogen, and he therefore determined the density of this gas from which the atomic weight of 14∙012, or, corrected for deviations from Avogadro’s law, 14∙006, was deduced.

The principle indicated here is applicable to the determination •of the molecular weight of any vaporizable substance by the so-called method of vapour-density (see Density).

*Solutes.*—The theory of solution permits the investigation of the molecular weights of substances which dissolve in water or some other solvent. It is shown in Solution that a solute lowers the freezing point and raises the boiling point of the solvent in a regular manner as long as dilute solutions are dealt with. It has been shown that if one gram molecule of a solute be dissolved in 100 grams of solvent then the boiling point is raised by 0∙02 T2∕*w*. (say D) degrees, where T is the absolute boiling point and *w* the latent heat of vaporization of the solvent ; this constant is known as the molecular rise of the boiling point, and varies from solvent to solvent. If we dissolve say *m* grams of a substance of molecular weight M in 100 grams of the solvent and observe the elevation in the boiling point, then M is given by M = *m*D*/d.* Similar considerations apply to the freezing points of solutions. In this case D = 0∙02 T2∕*w*, where T is the absolute freezing point of the pure solvent and *w* the latent heat of solidification. To apply these principles it is only necessary therefore to determine the freezing (or boiling) point of the solvent (of which a known weight is taken), add a known weight of the solute, allow it to dissolve and then notice the fall (or rise) in the freezing (or boiling point), from which values, if the molecular depression (or elevation) be known, the molecular weight of the dissolved substance is readily calculated.

The following are the molecular depressions and elevations (with the freezing and boiling points in brackets) of the commoner solvents.

Molecular depressions: aniline (6°), 58·7; benzene (5∙4°), 50·0; acetic acid (17∙0°), 39·0; nitrobenzene (5∙3°), 70-0; phenol (40°), 72; water (0°), 18∙5.

Molecular elevations: acetic acid (118∙1°), 25·3; acetone (56°), 17·1; alcohol (78°), 11·7; ether (35°), 21·7; benzene (79°), 26∙7; chloroform (61°), 35∙9; pyridine (115°), 29∙5; water (100°), 5∙1.

The apparatus used in cryoscopic measurements is usually that devised by Beckmann *(Zeit. phys. Chem.* ii. 307). The working part consists of a tube 2-3 cms. in diameter, bearing a side tube near the top; the tube is fitted with a cork through which pass a differ­ential thermometer of a range of about 6° and graduated in 50ths or 100ths, and also a stout platinum wire to serve as a stirrer. The lower part of the tube is enclosed in a wider tube to serve as an air-jacket, and the whole is immersed in a large beaker. The ther­mometer is adjusted so that the freezing point of the pure solvent comes near the top of the scale. A weighed quantity of the solvent is placed in the inner tube, and the beaker is filled with a freezing mixture at a temperature a few degrees below the freezing point of the solvent. The thermometer is inserted and both solvent and freezing mixture are stirred. When the temperature is about 0∙3° below the correct freezing point the tube is removed from the beaker and the stirring continued. There ensues a further fall in the thermometer' reading until ice separates, whereupon the temperature rises to the correct freezing point. The ice is then melted and the operation repeated so as to obtain a mean value. A known weight of the substance is introduced through the side tube, and the freezing point determined as with the pure solvent. The difference of the readings gives the depression; and from this value, knowing the weight of the solute and solvent, and also the molecular depression, the molecular weight can be calculated from the formula given above.

In the boiling point apparatus of Beckmann the solvent is con­tained in a tube fitted with side tubes to which spiral condensers can be attached; the neck of the tube carries a stopper through which passes a delicate differential thermometer, whilst the bottom is perforated by a platinum wire and contains glass beads, garnets or platinum foil to ensure regular boiling. The tube is surrounded by a jacket mounted on an asbestos box, so that the heating is regular. In conducting a determination the thermometer is adjusted so that the boiling point of the pure solvent is near the bottom of the scale. A known weight of the solvent is placed in the tube, the thermometer is inserted (so that the liquid completely covers the bulb), and the condensers put into position. The liquid is now cautiously heated, and when the thermometer becomes stationary the boiling point is reached. The temperature having been read, the apparatus is allowed to cool slightly, and the observa­tion repeated. A known weight of the substance is now intro­duced, and the solution so obtained treated in the same fashion as the original solvent.

A different procedure wherein the boiling tube is heated, not directly, but by a stream of the vapour of the pure solvent, was proposed by Sakurai *(Journ. Chem. Soc.,* 1892, 61, p. 994). Sakurai’s apparatus has been considerably modified, and the form now princi­pally used is essentially due to Landsberger *(Ber.,* 1898, 31, p. 461). The boiling vessel is simply a flask fitted with a delivery tube, which is connected with the measuring tube. This consists of a graduated tube fitted with a stopper through which passes a ther­mometer and an inlet tube reaching nearly to the bottom. The measuring tube is surrounded by an outer tube which has an exit to a condenser at the side or bottom, communication being made between the measuring tube and jacket by. a small hole near the top of the former. In outline the operation consists in placing some solvent in the measuring tube and passing in vapour until the condensed liquid falls at the rate of one drop per second or two seconds. The temperature is then read off. A known weight of the substance is introduced and the boiling point determined as before but immediately the temperature is read the tube must be disconnected, so that no more vapour passes over and so alters the concentration of the solution. Two methods are in use for determining the quantity of the solvent. Landsberger weighed the tube; Walker and Lumsden *(Journ. Chem. Soc.,* 1898, 73, p. 502) graduated the tube and thus measured the volume of the solvent; in W. E. S. Turner’s apparatus *(Journ. Chem. Soc.,* 1910. 97, p. 1184) both the weight and volume can be determined. Whilst the calculations in both the Beckmann and Sakural-Landsberger methods are essentially the same the “ molecular elevations ” differ according as one deals with 100 grams or 100 ccs. of solvent. In all these methods it is necessary to carefully choose the solvent in order to avoid dissociation or association. For example, most salts are dis­sociated in aqueous solution; and acids are bi-molecular in benzene but normal in acetic acid.

Other methods are available for dissolved substances such as measurements of the. osmotic pressure, lowering of the vapour pressure and diminution of solubility, but these, are little used. Mention may also be made of Ramsay and Shield's method, of finding the molecular weights of liquids from surface tension measurements. (See Chemistry : § *Physical.)*