The Twist Method for Indication of Equilibrium Gas Pressures

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A variety of experimental methods have been described [1-4] for the determination of vapour pressures or, more generally speaking, equilibrium gas pressures of chemical reactions. Nevertheless, the measurement of equilibrium pressures of reactions occurring at the higher temperatures (say, above 1500°C) is usually associated with difficulties. It is the purpose of the present note to describe a method which appears to permit reliable determinations of equilibrium pressures for high-temperature reactions, in the pressure range from a few torr upwards. The method may be considered a cross-breed between the torque-effusion and the boiling-point methods.

Consider a container with a small hole towards one side. Inside is the reacting system giving rise to a gas pressure. When an applied inert-gas pressure outside the container is greater than the reaction pressure inside, gas transport through the orifice takes place only by means of diffusion, with only a negligible net force acting on the container. When the external pressure is reduced just slightly below the inside reaction pressure, a directed flow of gas is set up, with a force in the reverse direction acting on the container. In practice, a cell with two tangentially arranged holes are used, just as in the torque effusion method. The method proposed here, however, appears to have a number of advantages over that of torque effusion. The latter requires an accurate knowledge of the geometry of the orifices and the magnitude of the torque, while only a qualitative knowledge of these parameters is needed in the present method. Since it is thus not truly a torque method, the term "twist method" is suggested.

The equipment for this method (apart from a suitable furnace) may be quite simple. A thin wire of otherwise unknown torsional properties, an aluminium disc with a zero mark, and a couple of permanent magnets to introduce some damping, are all that is basically required. This was also the equipment first used to test the method (measuring the vapour pressure of water contained in a suitable brass cell). For actually working with the method, a somewhat more refined arrangement was deemed desirable. An electromagnetic device has been designed which records a millivolt signal proportional to the torque acting on the reaction cell in the furnace. The observations are carried out at constant temperature and slowly decreasing inert-gas pressure. A solenoid valve in the pump line is actuated from a set point on the recorder, so that when the signal starts deviating from zero by a certain small amount, the valve is shut, and the gas pressure can be read at leisure on an ordinary mercury manometer.

The results of preliminary measurements (vapour pressure of Cd, equilibrium pressure of SiO(g) above $Si + SiO_2$) show that the pressures can be indicated reproducibly to a fraction of 1 torr. For a gas pressure of the order of 100 torr, this means a fraction of 1 percent. Now, the temperature dependence of equilibrium pressures in the range 1000−2000°C is generally of the order of 1 percent per degree. Hence the twist method, in order to be used to its full advantage, requires rather accurate control and measurement of temperature. The equipment is presently being improved on this point.

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