CCCXII.—Two Heterogeneous Gas Reactions. By Cyril Norman Hinshelwood and Charles Ross Prichard.

THE number of gas reactions which proceed without disturbance by the walls of the containing vessel is so limited that a homogeneous change must be regarded as an exceptional case. At high temperatures the homogeneous reaction may predominate over the wall reaction owing to its greater temperature coefficient, and homogeneous reactions obviously come into play in the propagation of explosion waves through gases, but, under conditions when the change is slow enough to measure, it must be recognised that chemical reactions between gases, and especially gaseous decompositions in which only one molecule is involved, take place more readily on most surfaces than in the gas phase. Since this must now be recognised as a general rule, the influence of the solid surface should not be dismissed as a "disturbing factor," but some general explanation of it should be sought. The interest of the exceptional homogeneous reactions is, however, only increased.

It was proposed, therefore, to investigate various gas reactions

* The results will be published separately.

which might a priori have been expected to be unimolecular, with the object of ascertaining whether they would be markedly catalysed by the walls of the glass containing vessel and thus conform to the general rule, or whether they would be homogeneous reactions, in which case their dynamics would be of special interest. The reactions studied were the thermal decomposition of hydrogen peroxide, and of sulphuryl chloride in the gaseous state, and the thermal decomposition of chlorine monoxide. Diazoacetic ester was also examined, but found to be unsuitable for quantitative measurements, as tarry deposits were formed.

The decomposition of chlorine monoxide proved to be homogeneous, and the results are described in the following paper (p. 2730), whilst the hydrogen peroxide reaction and the sulphuryl chloride reaction were found to be typical heterogeneous reactions the details of which are described below.

The Thermal Decomposition of Hydrogen Peroxide.

Hydrogen peroxide readily decomposes into water and oxygen and the reaction is irreversible, but its course in the gaseous state does not seem to have been followed. The range of investigation is limited by the fact that at above 80° the reaction is extremely rapid, whilst at low temperatures the saturation pressure of hydrogen peroxide is small. The method was to place in a glass bulb of about 200 c.c. capacity a capillary containing a known weight of a 30 per cent. solution of hydrogen peroxide (Merck's perhydrol); the bulb was then evacuated and sealed off. The quantity of perhydrol was chosen so as to exert a pressure less than the saturation pressure of hydrogen peroxide at the temperature of the experiment. The bulb was then heated in a vapour-bath. The hydrogen peroxide boils off almost instantaneously, so that practically no decomposition can occur while it is in the vapour state. After a given time, the bulb was taken out, the tip broken under distilled water, and the undecomposed hydrogen peroxide estimated by titration with N/50-potassium permanganate.

Preliminary experiments showed that carbon tetrachloride, b. p. 76°, was a suitable liquid for the vapour-bath.

The approximate unimolecularity of the reaction is shown by the following results made by successive fillings of the same bulb. When the decomposition was allowed to proceed in a bulb containing glass wool previously treated with nitric acid to remove free alkali, the experiments failed to detect any trace of undecomposed hydrogen peroxide even after exceedingly short heating. Thus it may be concluded that the reaction is so strongly catalysed by glass that it must be a typical wall reaction.

The Thermal Decomposition of Sulphuryl Chloride.

The equilibrium $SO_2Cl_2 \implies SO_2 + Cl_2$ has been investigated by Trantz (Z. Elektrochem., 1908, 14, 534), who used a catalyst in



order that equilibrium might be attained. It is evident from his results that the equilibrium lies on the side of almost complete decomposition above about 200°. It was therefore considered worth while to investigate whether the homogeneous reaction might set in at some temperature above 200°, where the rate of reaction might still be measurable.

The pressure doubles during decomposition, so that the reaction was measured manometrically, the capillary leading from the reaction bulb to the mercury manometer being electrically heated to prevent condensation of the sulphuryl chloride, and filled with a

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buffer of air to prevent the chlorine formed from attacking the mercury. This device proved quite satisfactory.

The course of the reaction is shown by the curves in the figure.

Curves II and III refer to experiments in which the initial pressure of sulphuryl chloride was 180 mm. and 790 mm., respectively, and which were carried out in the same bulb, and show that the rate of reaction is independent of pressure. This is also shown by the following experimental data in which unimolecular velocity coefficients are calculated.

Temperature 283.5°.

t (minutes).	p (mm. of mercury).	$\frac{1}{t}\log \frac{p_{\infty}}{p_{\infty}-p}.$	t (minutes).	p (mm. of mercury).	$\frac{1}{t}\log_{e} \frac{p_{\infty}}{p_{\infty}-p}$
2.0	35	0.108	10.0	122	0.113
4.0	66	0.114	15	150	0.118
6.0	89	0.114	8	180	

The effect of the walls of the reaction vessel may be seen by comparing curves II and III with curve I, which refers to a different bulb. Addition of fine glass rods to the bulb increased the reaction velocity in approximate proportion to the increased surface. This is illustrated by comparison of curve I with curve V and of curves II and III with curve IV.

The addition of glass wool had the effect of diminishing the time required for the completion of half the reaction at 211° from 172 minutes to 6.6 minutes.

The influence of temperature is shown below. The experiments were carried out successively in the same vessel.

Temperature.	" Half-life " in minutes.	Ratio for 10°.	Heat of activation.
211.0° 237 283	$\left. egin{array}{c} 172 \\ 26\cdot 5 \\ 1\cdot 6 \end{array} ight\}$	$2.06 \\ 1.85$	35,000 cals. 34,000 ,,

In a vessel containing glass wool two successive experiments gave the results : at 211.5° , half-life 6.6 minutes; at 184° , half-life 35.5 minutes. From this the temperature coefficient for 10° over the range considered is 1.85.

Discussion of Heterogeneous Reactions.

When a molecule is adsorbed by a surface the forces between it and the molecules constituting the surface modify the internal forces in a way which is at present quite incalculable and must be entirely specific. Generally speaking, it might be expected that the stability would be increased as often as it is decreased. Yet the accumulation of observations showing that almost any gas reaction takes place more readily on a given surface such as glass

than in the homogeneous phase raises the question whether the operation of some general cause is not superimposed on the various specific influences. In the case of combinations in which two or more molecules are involved the encounter of two types is obviously facilitated by the more or less prolonged sojourn of one of them on the surface, but this factor is inoperative in the case of the simple unimolecular decompositions. It seems relevant, therefore, to ask whether one universal factor may not be simply the second law of motion. Consider a molecule composed of two parts, A and B, the disruption of which constitutes the decomposition of the molecule. Let B receive an impact from another molecule which imparts to it momentum directed away from A. The small inertia of A, however, enables it to follow B, without the development of much strain between the two. If, however, A were firmly enough held to a surface, its inertia might be so great that the accelerating force, instead of drawing A after B, would cause the disruption of the "bond" between them. The reluctance of homogeneous gas reactions to proceed might thus be due to the small inertia of the different parts of the molecules rendering disruption by collision very improbable. This is only suggested as one of several possibilities. That it is a mechanical picture, whilst we now believe "activation" to consist in the passage of an electron to an orbit of higher quantum number, is not a relevant criticism, since the results of work on the collision of electrons with gas molecules show that a definite correlation exists between quasi-mechanical and quantum processes.

Summary.

The velocity of thermal decomposition of hydrogen peroxide and of sulphuryl chloride in the vapour state has been investigated. Both are found to be typical heterogeneous reactions taking place on the walls of the glass containing vessel, and following the unimolecular law. The heat of activation for the sulphuryl chloride reaction is calculated from the results.

It is pointed out that the almost universal occurrence of "wall" reactions makes some general explanation desirable. A possible factor is discussed in the explanation of the greater ease with which "wall" reactions as compared with homogeneous reactions occur in gases.

PHYSICAL CHEMISTRY LABORATORY,

BALLIOL COLLEGE AND TRINITY COLLEGE,

OXFORD.

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