surface of the vessels. A heterogeneous reaction of some magnitude has, however, been observed, but it is confined to the surface of the sulphur, its velocity being proportional to the area thereof.

At 760 mm., in pure hydrogen, when precautions were taken to keep a uniform pool of sulphur in the reaction vessel, the dynamic method, in our hands, gave a practically straight $\log d$ [H_2S]/dt against $1/T$ plot between 265° and 350° The velocities were unaffected by an increase in the surface/volume ratio of 500 per cent, but were appreciably altered by changes in the area of liquid sulphur; in the latter case, within certain limits, the temperature coefficient of the total reaction was not sensibly changed, provided the particular areas were kept constant throughout the temperature range. The introduction of nitrogen resulted in a curve, similar in form, and close in actual position, to that of Norrish and Rideal, and the velocities were somewhat higher than was warranted by the partial pressure of hydrogen employed.

A study of the gas reaction was made, statically, in bulbs, wherein the amount of sulphur was always more than twenty times that converted to the hydride, but was, nevertheless, insufficient to allow of any liquid being present. The surface/volume ratio and the pressure of hydrogen were varied, and the results showed that the velocity of hydrogen sulphide formation was: (1) proportional to the concentration of hydrogen; (2) proportional to the square root of the concentration of sulphur; (3) independent of the area of the glass surface.

The plot of $\log d$[H_2S]dt against $1/T$ was perfectly straight, and gave a temperature coefficient of 1·94. With the same partial pressure of hydrogen, in the presence of nitrogen, $\log d$ [H_2S]dt against $1/T$ was decidedly curved, and the velocities were appreciably greater than with pure hydrogen. The difference, brought about by the nitrogen, points to a chain mechanism, and the investigation is proceeding with the substitution of helium for nitrogen, and with the limitation of the space for chain formation. The gaseous reaction proceeds in accordance with the equation,

$$d\ [H_2S]/dt = K\ [H_2] \times \sqrt{[S]}.$$

Two or three forms of chain mechanism suggest themselves, but we hesitate to differentiate between these in the absence of other data which are at present being sought.

By a modification of the shapes of the bulbs, whereby three pools of liquid sulphur, of different sizes, were exposed to the action of hydrogen, the composite reaction, in the presence of known areas of sulphur, was investigated. The velocity of the surface reaction was computed by deducting that of the homogeneous one from the composite figure, and its temperature coefficient was estimated from the results obtained. The reaction at the surface of liquid sulphur proved to be: (1) proportional to the area of the liquid exposed; (2) proportional to the pressure of hydrogen. It gave a straight $\log d$ [H_2S]/dt against $1/T$ plot, from which a temperature coefficient of 1·85 was calculated. The surface reaction proceeds in accordance with the equation,

$$d\ [H_2S]/dt = K \times \text{area of liquid sulphur} \times [H_2].$$

Although Bodenstein failed to recognise the composite nature of the reaction between hydrogen and sulphur, first suggested by Norrish and Rideal, he evidently believed it to have the characteristics of the gaseous reaction here described, in spite of the fact that his analytical results did not entirely confirm this view. His approximate methods also obscured the effect of the heterogeneous reaction occurring at the sulphur surface and prevented its detection.

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[1] Z. phys. Chem., 29, 315; 1899.
[2] J. Chem. Soc., 123, 696; 1923.

Variation Problems for a Symmetrical Region

IN a review in NATURE[1] it is stated that the equation of conduction of heat can be regarded only as a limiting case of an equation arising in the calculus of variations. A successful attempt has been made, however, to derive the equation directly from a variation problem of an unusual type.

It is found that if we write

$$u = F\ (x,\ t),\ v = F\ (x,\ -t)$$

and integrate

$$\frac{\delta u}{\delta x}\frac{\delta v}{\delta x} \times v\ \frac{\delta u}{\delta t}$$

over a region bounded by the lines $x = \pm a, t = \pm b$, requiring F to be zero on the boundary, the variation of the resulting integral I gives rise to the differential equation

$$\frac{\delta^2 u}{\delta x^2} = \frac{\delta u}{\delta t}.$$

A physical meaning for I has not yet been found. A variation problem for a symmetrical domain usually gives rise to a functional equation such as $F''\ (t) = n^2\ F\ (-t)$. A solution $F\ (t) = A \cosh\ (nt) - B \sin\ (nt)$ of this equation may be found by splitting $F\ (t)$ into its even and odd parts, a device that is often useful.

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[1] NATURE, 129, 850, June 11, 1932.

IF, in Prof. Bateman's example, we take

$$F\ (x,\ t) + F\ (x,\ -t) = 2\ \varphi\ (x, t),$$
$$F\ (x,\ t) - F\ (x,\ -t) = 2\ \psi\ (x, t),$$

then φ and ψ may be regarded as independent of each other, and the variational equations are

$$\frac{\delta \varphi}{\delta x^2} = \frac{\delta \psi}{\delta t}, \qquad \frac{\delta^2 \psi}{\delta x^2} = \frac{\delta \varphi}{\delta t}.$$

It is true that the equation $\dfrac{\delta^2 u}{\delta x^2} = \dfrac{\delta u}{\delta t}$ can be derived by adding these two equations, but it represents only a *part* of the variational system: the *whole* set consists of the above two equations, which when we eliminate ψ give

$$\frac{\delta^4 \varphi}{\delta x^4} = \frac{\delta^2 \varphi}{\delta t^2},$$

and I regard this as the true differential equation arising in Prof. Bateman's problem.

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