parallel crystallite formation referred to in (*b*). Thus, in creep, the polycrystalline specimen had deformed like a single crystal.

It should be added that when the tensile specimen after unloading was held at the elevated temperature for the same time as the creep specimen, no appreciable recovery in structure occurred.

The effect is illustrated in Figs. 1, 2, 3 and 4. Fig. 1 is a back-reflexion photograph from the metal in the initial state; the sharp (420) reflexion spots indicate perfect strain-free grains. Fig. 2 is from the tensile specimen after extension; the transition from reflexion spots to an almost continuous ring indicates the extensive nature of the breakdown to the random crystallite formation even after only 0·9 per cent extension. Fig. 3 is from the creep specimen, and shows that the reflexions are still relatively sharp spots, indicating a minimum disturbance of the internal structure of the grains. Fig. 4 is from the extended tensile specimen after it had been heated at 300° for 1 hour, and shows that no appreciable recovery or recrystallization has taken place.

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## Standard Entropy of Adsorption

WE have recently shown[1], by a thermodynamical procedure, how the standard free energy of adsorption of a solute on to a solution/air interface ($\Delta G^\circ$) may be obtained from the limiting slope $\alpha$ at low concentrations of the surface tension-concentration curve. This is given by the equation

$$\alpha = \delta RT \exp. (-\Delta G^\circ/RT) \quad . \quad . \quad (1)$$

where $\alpha$ is $-(d\gamma/dc)_{c=0}$ and $\delta$ is the thickness of the surface layer, which was identified with the most probable length of the adsorbed molecule. The standard states in bulk and on the surface are hypothetical states in which the solute is at unit activity in each (activity is expressed in molality units), but essentially have all the properties of infinitely dilute solutions.

It is possible to obtain the standard entropy of adsorption ($\Delta S^\circ$) from this. Differentiation of equation (1) with respect to $T$ gives

$$\Delta S^\circ = -\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\frac{\Delta G^\circ}{T} + \frac{RT}{\alpha}\frac{d\alpha}{dT} - R \quad . \quad (2)$$

In the derivation of equation (2), the entirely justifiable assumption is made that $\delta$ does not vary appreciably with temperature within any reasonable range of temperature. Unfortunately, little experimental work has been carried out on the variation of $\alpha$ with temperature. The only available data are from measurements by Rehbinder[2] of the surface tensions of solutions of fatty acids of various chain-lengths at different temperatures and concentrations. The accuracy of these determinations is not high, but they allow a systematic series of values of $d\alpha/dT$ to be calculated. If these values are used in conjunction with the more accurate values of $\alpha$ at 20° C. recently given by one of us (A. F. H. W.)[3], it is possible to arrive at a numerical estimate of $\Delta S^\circ$ for the adsorption of some members of the fatty acid series at an aqueous surface. These values of $\Delta S^\circ$ calculated by means of equations (1) and (2) are shown in the accompanying table.

| Solute | $\Delta G^\circ$ kcal./mole | $\Delta S^\circ$ cal./° C. mole | $\Delta H^\circ$ kcal./mole |
|---|---|---|---|
| Propionic acid | −1·63 | −14·4 | −5·9 |
| *n*-Butyric acid | −2·45 | − 6·2 | −4·3 |
| *n*-Valeric acid | −3·18 | + 1·1 | −1·8 |
| *n*-Caproic acid | −3·72 | + 6·6 | −1·7 |
| *n*-Heptoic acid | −4·52 | + 7·2 | −2·4 |

The data for *n*-caproic and *n*-heptoic acids are likely to be less accurate, since with chains of this length the time-dependence of surface tension becomes important and Rehbinder's method[2] was not suitable to take account of this. The apparent falling off in the $\Delta H^\circ$ values for these two compounds may be illusory, and more account should be taken of the increasing trend shown by the lower members of the series.

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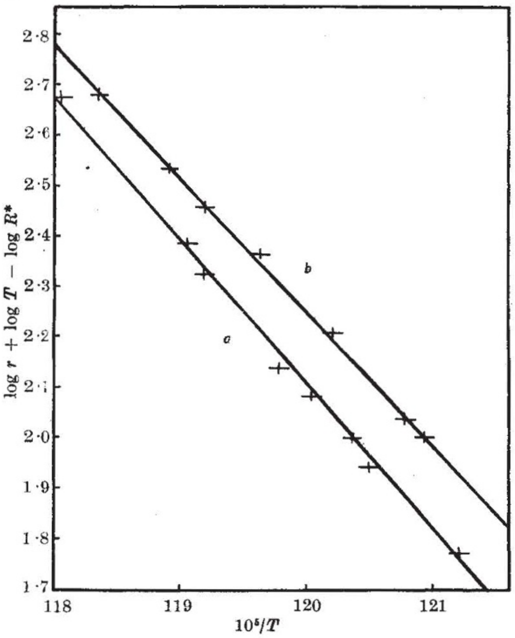
## Chain-initiating Process in the Reaction between Hydrogen and Oxygen between the Second and Third Explosion Limits

THERE has been much discussion concerning the reaction responsible for the initiation of chains, in the thermal reaction between hydrogen and oxygen, in the non-explosive region between the second and third explosion limits[1]. In their early work[2], Lewis and von Elbe favoured the thermal dissociation of hydrogen, but in a later paper[3] they reject this view because their value of the overall activation energy is "of the order of only 100 K-cals" which they regard as the sum of the activation energies of the chain-initiating and chain-propagating steps, and hence conclude that the energy of activation of the initiating reaction is less than 100 kcal. This value excludes the dissociation of hydrogen (and, of course, oxygen, but the thermal dissociation of this molecule is not considered for valid kinetical reasons) as the chain-initiating reaction, and to meet these conditions, these authors postulate the dissociation of hydrogen peroxide according to $H_2O_2 \rightarrow H_2O +$ O or 2OH, without being very precise about the origin of the hydrogen peroxide, other than assuming that the reaction $H_2 + O_2 \rightarrow H_2O_2$ may play a part initially. Recently, Willbourn and Hinshelwood[4] have made a fresh experimental study of the third limit and the slow reaction at lower pressures and, in contrast to Lewis and von Elbe, conclude that the initiation reaction is probably $H_2 + M \rightarrow 2H + M$.

A choice between these two mechanisms is possible if the energy of activation of the initiation process is carefully determined. Accordingly, we have obtained pressure-time records at many temperatures within the range 555°–575° C. at pressures equivalent to: (*a*) 200 mm. $H_2$ + 110 mm. $O_2$ at 577° C. and (*b*) 300 mm. $H_2$ + 150 mm. $O_2$ at 577° C., under conditions approximating as closely as possible to those of Willbourn and Hinshelwood. A cylindrical silica vessel coated internally with potassium chloride and held in a thermostatically controlled horizontal electric furnace was used as reaction vessel and a mirror type Foord gauge used as a manometer. The rest of the apparatus was of conventional design. The reproducibility of the results was good.



Under steady state conditions when the chains are terminated linearly, the rate of a chain reaction is the rate of initial production of centres divided by the net branching factor and multiplied by the reciprocal of the mean life of the centres[5]. The denominator in the expression can be evaluated in terms of the experimental variables from studies of the adjacent explosion boundary, at all points on which, provided thermal influences are absent in the explosion, the denominator is zero[5]. Using such reasoning, Willbourn and Hinshelwood write $r$ (the rate of pressure change in mm. Hg min.$^{-1}$) $= f_1 R^*/$ (constant) $T$, where $f_1$ is the rate of the initiating reaction, the contant is independent of temperature, and $R^*$ is a function of temperature and concentration of reactants which can be calculated from the experimental data on the third limit. The energy of activation of the initiation reaction can then be obtained from the slope of the curve obtained by plotting ($\log r + \log T - \log R^*$) against $T^{-1}$. The figure shows the results obtained in our experiments. They are linear in confirmation of the general validity of Willbourn and Hinshelwood's mechanism; and lead to values of the activation energy for the initiation reaction of 134 ± 4 and 123 ± 3 kcal. for (*a*) and (*b*) respectively: thus virtually excluding the initiation reaction proposed by Lewis and von Elbe and affording additional evidence for the thermal dissociation of hydrogen as this process.

Since $M$ in this reaction includes oxygen molecules, a corollary to this conclusion is that a collision between highly energized hydrogen and oxygen molecules can, and often does, result in dissociation of the hydrogen rather than in reactions of the type: $H_2 + O_2 \rightarrow H_2O_2 +$ 35 kcal., or $H_2 + O_2 \rightarrow 2HO - 20$ kcal. (the heats given apply to molecules in their ground states)[6]. This result would not have been anticipated and is rather surprising on theoretical grounds.

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[1] The explosion limits are here numbered in order of increasing pressure. See also refs. 3 and 4 where the same convention is used.

[2] Lewis and von Elbe, "Combustion, Flames and Explosions of Gases", 39 (Cambridge, 1938).

[3] Lewis and von Elbe, *J. Chem. Phys.*, **10**, 376 (1942).

[4] Willbourn and Hinshelwood, *Proc. Roy. Soc.*, A, **185**, 353 (1946).

[5] For elaboration of this, see Dainton, *Trans. Farad. Soc.*, **38**, 227 (1942).

[6] Assuming the value of $Q_a$ for $H_2O_2$ of 255·7 kcal. mole$^{-1}$ given by Skinner, *Trans. Farad. Soc.*, **41**, 645 (1945), and Dwyer and Oldenberg's value of 100 kcal. for the bond energy in the OH radical (*J. Chem. Phys.*, **12**, 351 (1944)).