940. *The Reaction of Water Vapour with Liquid Sodium, Sodium Peroxide, Sodium Monoxide, and Sodium Hydride; Vapour Pressures in the Sodium Hydroxide–Water System.*

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Rates of reaction, and equilibrium pressures have been determined for the reaction between liquid sodium and water vapour at temperatures of 125—175°, and at initial water vapour pressures of 15—65 cm. of mercury. At initial pressures up to about 25 cm., reaction proceeds precisely according to the equation $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$. At higher pressures and low temperatures, some sodium hydride is formed also. At higher pressures and the higher temperatures, the sodium hydroxide film behaves as a separate phase, and forms an effective barrier between liquid sodium and water vapour at a pressure equal to the saturation vapour pressure of sodium hydroxide. These conclusions are supported by studies of the reactions of sodium peroxide, sodium monoxide, and sodium hydride with water vapour under the same experimental conditions. The technique used was found to be suitable for determinations of the vapour pressures of sodium hydroxide–water mixtures at 125—225°.

THE reaction between sodium and water is only violent when water is in the liquid state. With water vapour, the reaction proceeds quietly,[1-3] and reaction rates depend upon such factors as the temperature, the composition of gas phase, and the nature of the surface film formed. The reaction has already been studied by observing the rate of temperature rise in a sodium droplet held in a stream of moist argon,[4] or by measurement of the hydrogen produced in a stream of moist argon as it passes over a jet of liquid sodium–potassium alloy,[5] these investigations give only indirect evidence for the reactions involved. Some information on the reaction products is available from studies by Longton[6] and Furman.[7] Longton studied pressure changes in a closed system containing sodium and an initial water vapour pressure of 10 mm. Below 300°, the pressure decreased to half its initial value in a few hours, and was assumed to proceed according to the equation

$$Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2 \qquad (1)$$

Above 300°, sodium hydroxide reacts with sodium in one of the following ways[8]

$$NaOH + Na \longrightarrow Na_2O + \frac{1}{2}H_2 \qquad (2)$$

or

$$NaOH + 2Na \longrightarrow Na_2O + NaH \qquad (3)$$
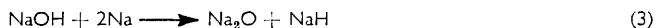
depending on whether the hydrogen pressure is greater or less than the dissociation pressure

[1] Bowrie, *J. Phys. Chem.*, 1931, **35**, 2964.
[2] Herrington, *J. Phys. Chem.*, 1934, **38**, 675.
[3] Woollen, Scott, and Dell, U.K.A.E.R.E., Rept. CE/R.2158.
[4] Corrsin, Steinmetz, and Marano, Nuclear Development Corporation Rept. NDA 84—19, 1959.
[5] Saltsburg, KAPL Rept. 1763, 1957.
[6] Longton, U.K.A.E.A. Rept. IGR–TN/C. 418, 1956.
[7] Furman, General Electric Company, Rept. GEAP–3208, 1959.
[8] Williams, N.R.L. Memo, 33, 1952.

of sodium hydride.[9] Under the conditions used by Longton, sodium hydride was not produced, and the overall reaction

$$2Na + H_2O \longrightarrow Na_2O + H_2 \qquad (4)$$

accounts for the observation that no pressure change occurred during reactions at temperatures of 300—500°. When the pressure of water vapour used is considerably reduced, this overall reaction is the only one observed at temperatures as low as 215°. Furman [7] passed a stream of helium, at 1 atm. pressure, containing 100—400 p.p.m. of water vapour, over liquid sodium and measured the hydrogen content ($H_2O + H_2$) of the effluent gas. No hydrogen was retained in the sodium sample at any temperature in the range 215—340°, and reaction (4) was taken to represent the overall reaction.

Since the reaction is a function of the gas pressure, it was of interest to extend these studies to higher pressures, and our results are described in the present Paper. Temperatures have been restricted to the range 125—175°, thus avoiding the sodium–sodium hydroxide reaction. Preliminary work indicated that the reaction of stationary liquid sodium with water vapour at 100—200° and atmospheric pressure proceeded smoothly. Under certain conditions, equilibrium was attained between excess of liquid sodium and a gas phase that still contained appreciable amounts of water vapour, so that one of the reaction products is able to act as an effective barrier between liquid sodium and water vapour. To identify this product, the pressure changes occurring when each of the possible products is exposed to water vapour have been examined under the same conditions as those used in the liquid sodium–water vapour reaction. The reaction of water vapour with sodium peroxide, sodium monoxide, and sodium hydride, and the sodium hydroxide–water vapour pressure, will be described first; the sodium–water vapour reaction will then be interpreted in the light of these observations.

EXPERIMENTAL

Sodium was purified as already described.[10] Sodium peroxide and sodium hydroxide were B.D.H. Analar grade. Sodium monoxide was prepared by the decomposition of sodium peroxide in an alumina crucible at 700° and 10^{-4} mm. Heating for 12 hr. gave a product 98·7% pure (determined by titration with hydrochloric acid). Sodium hydride was prepared as pure, white needles from sodium and hydrogen by a technique resembling that recently described.[9]

The apparatus used for the study of pressure changes is shown in Fig. 1. The glass vessel A (capacity 560 ml.) was attached to a spiral gauge S of sensitivity 90° per atmosphere pressure difference. The gauge was used for direct measurement of pressure by use of a spotlight, the mirror M and a calibrated scale 1 m. from M, which could be read with an accuracy of ± 1 mm. of mercury. The change in pressure was followed continuously by movement of the light spot on the scale. T was a two-way tap by means of which A could be opened either to the flask B (volume 25 ml.) containing distilled water, or to the vacuum connection C, or isolated. T had a hollow barrel, which permitted insertion of the capsule F. This consisted of a thin-walled tube blown out at the lower end to a fragile bulb, which held the sodium or one of its compounds; the tube F was sealed at the upper end, and a steel cap incorporated in the seal. The capsule was held in position by a permanent horseshoe magnet carrying a clip, which fitted over the key of tap T.

In a typical experiment, the apparatus was immersed in an oil thermostat containing 5 l. of Sternol, the temperature of which could be controlled to $\pm 1°$, and the oil level adjusted so that it was just below the top of tap T (Fig. 1). Tube D was opened to the vacuum frame, thus evacuating A (through C) and the outer case of the spiral gauge. Water was then placed in B, and allowed to boil until all the air was expelled from B and its connecting tubes. Tap T was then turned to allow water vapour from B to enter A; any required pressure of vapour in A could be obtained by observation of the spiral gauge. Tap T was then closed to isolate A, and the magnet removed; capsule F was thus released, and shattered on striking the bottom of A.

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[9] Addison, Pulham, and Roy, following Paper.
[10] Addison, Kerridge, and Lewis, *J.*, 1954, 2861.

The capsule was charged with the sodium compound under an atmospheric pressure of argon, and the free volume was less than 0·5 ml. This gave a pressure of 0·5 mm. in A, which was less than the experimental error. The presence of an argon pressure in the capsule had the practical advantage that, when F was broken in the vacuum, the sample was expelled by the gas, and none was retained in the narrow stem of the capsule.
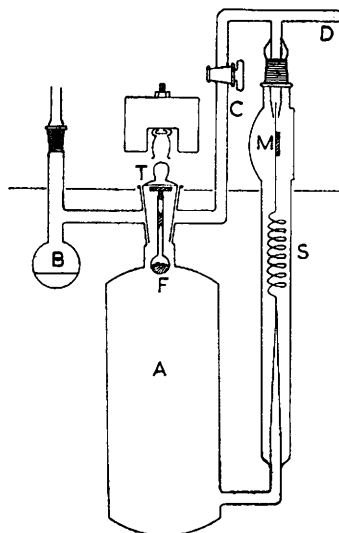

Fig. 1. Apparatus for study of pressure changes in reactions of water vapour with liquid sodium or sodium compounds.

By this method, the time at which reaction started could be sharply defined. The subsequent changes in pressure were followed until the equilibrium was established. The gaseous contents of A were then drawn into the vacuum line through a cold trap where any unreacted water vapour was condensed.
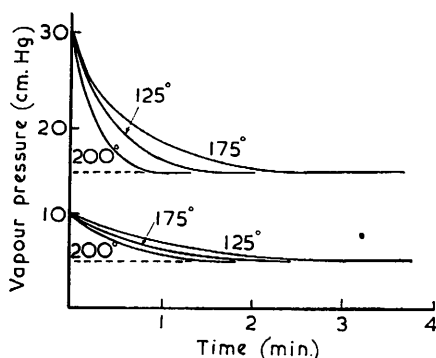

Fig. 2. Reaction of sodium peroxide with water vapour at initial pressures of 10 and 30 cm. Hg.
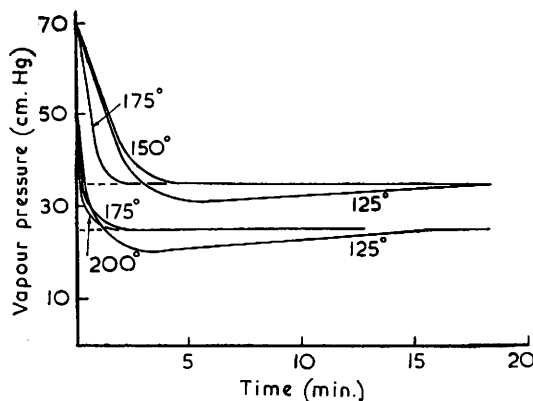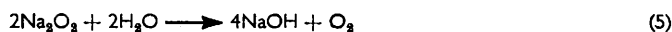
Fig. 3. Reaction of sodium peroxide with water vapour at initial pressures of 50 and 70 cm. Hg.

RESULTS AND DISCUSSION

Sodium Peroxide.—Water vapour pressures in the range 10—70 cm. of mercury have been used. In each experiment, the amount of sodium peroxide used was the stoichiometric amount according to the equation

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2 \qquad (5)$$

The variation in pressure with time is shown in Figs 2. and 3. In the stoichiometric reaction.

the final pressure is in all cases exactly one half of the initial water vapour pressure (P) in agreement with equation (5); no water vapour remained in the gas phase and no peroxide was present in the solid reaction product. Except for the 125° curves, the overall reaction is complete within 2—3 minutes. At the higher temperatures (150—200°), the reaction rate increases with temperature, and the results conform to a logarithmic rate law of the form $p = k \log (1 + \alpha t)$, where p is the pressure at time t. The 125° results are anomalous in apparent reaction rate and also because the pressure falls temporarily below 0·5 P. This behaviour is explained satisfactorily on the basis of the stepwise hydrolysis of sodium peroxide

$$Na_2O_2 + H_2O \longrightarrow NaO \cdot OH + NaOH \qquad (6)$$

$$NaO \cdot OH \longrightarrow NaOH + \tfrac{1}{2}O_2 \qquad (7)$$
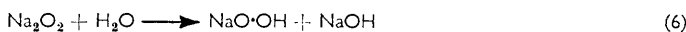
Sodium hydroperoxide is an unstable compound, and its thermal stability has not been studied in detail. It is unlikely to exist alone at these temperatures, whereas the $-O \cdot OH$ group appears to have a higher stability in admixture with sodium hydroxide. The formation of hydroperoxide in the stoichiometric reaction is a function of oxygen pressure and temperature. Thus, at an initial water vapour pressure of $P = 70$ cm., the effects of reaction (6) are evident. This reaction alone involves a more rapid decrease in pressure than does the overall reaction (5), and reaction therefore appears to proceed more rapidly at 125° than at higher temperatures, at which the hydroperoxide has only a transitory existence. At 125° also, the hydroperoxide is sufficiently persistent to cause the total (now oxygen) pressure to fall below 0·5 P. The subsequent evolution of oxygen from the solid reflects the operation of the slower reaction (7). At an initial pressure of 50 cm., similar behaviour is observed. At $P = 30$ cm., the decomposition of the hydroperoxide at 125° is still slow enough to give an anomalous rate of pressure decrease, but is not sufficiently slow to bring the pressure at any stage below 0·5 P. At $P = 10$ cm., decomposition is too rapid to be detectable in the pressure curves.

Sodium hydroperoxide is also stabilised in the presence of excess of sodium peroxide. The results of experiments identical with those shown in Figs. 2 and 3, except that amounts of sodium peroxide up to twice that required by equation (5) were used, are given in Table 1.

TABLE 1.

The reaction of water vapour with excess sodium peroxide (initial pressure $P = 37\cdot3$ cm. Hg. in all experiments).

Temp.	Ratio $\dfrac{Na_2O_2 \text{ used}}{Na_2O_2 \text{ (stoichiometric)}}$	Deviation below 0·5P (cm. Hg)	Mole % NaO·OH in product	Temp.	Ratio $\dfrac{Na_2O_2 \text{ used}}{Na_2O_4 \text{ (stoichiometric)}}$	Deviation below 0·5P (cm. Hg)	Mole % NaO·OH in product
125°	1·50	0·90	1·9	150°	1·51	2·30	4·9
,,	1·65	1·95	3·9	,,	1·74	4·30	8·4
,,	1·90	3·00	5·5	,,	1·89	6·05	11·2
150	1·24	0	0	175	1·65	1·75	3·5
,,	1·48	3·35 (reverting to zero)	0	,,	2·00	2·60	4·6

With sufficient excess of sodium peroxide, equilibrium pressures lower than 0·5 P were obtained at each temperature, so that the hydroperoxide is more stable in a sodium peroxide–hydroxide lattice than it is in sodium hydroxide alone.

Sodium Monoxide.—Water vapour at pressures of 20 and 45 cm. of mercury was allowed to react with stoichiometric quantities of sodium monoxide at 150°. The pressure fell to near zero in 1·5 and 5 minutes, respectively, in agreement with the equation

$$Na_2O + H_2O \longrightarrow 2NaOH \qquad (8)$$

and there was no evidence for the presence of sodium hydride or sodium hydroperoxide in the product.

Sodium Hydride.—Experiments with water vapour pressures in the range 7 to 75 cm. of mercury, and stoichiometric quantities of sodium hydride according to the equation

$$NaH + H_2O \longrightarrow NaOH + H_2 \qquad (9)$$

showed no pressure variations whatsoever at 125°. The experiments supported equation (9), and confirmed the absence of any intermediate stages involving pressure changes. Three minutes after the capsule was broken no water vapour remained in the gas phase. In experiments with excess of water vapour, the final pressure was precisely the sum of the pressure of hydrogen produced, and the equilibrium vapour pressure of the sodium hydroxide solution.

Vapour Pressures in the Sodium Hydroxide–Water System.—Although sodium hydroxide acts as a drying agent at room temperature, this is certainly not characteristic of its behaviour at higher temperatures. However, published data on vapour pressures are concerned almost entirely with solutions containing up to 40% of sodium hydroxide, at temperatures up to about 70°, and it was necessary to determine the water-vapour pressures corresponding to hydroxide-rich mixtures at the higher temperatures. Finely ground
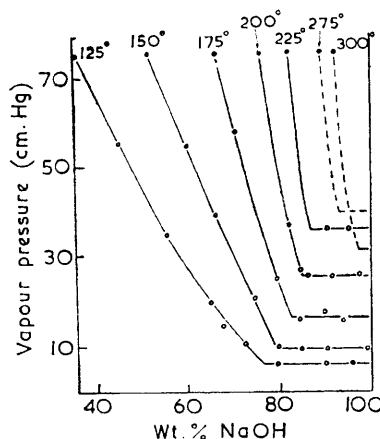

Fig. 4. Equilibrium vapour pressures in the sodium hydroxide–water system.

samples of hydroxide were exposed to known pressures of water vapour, when the pressure decreased steadily over a few minutes to a limiting value representing the equilibrium vapour pressure. From the pressure decrease, the NaOH : H₂O ratio in the condensed phase could be calculated; the results are given in Fig. 4. For each temperature, there is a particular concentration above which the equilibrium vapour pressure is constant. Over this region, the condensed phase consists of a saturated solution at that temperature, together with the solid anhydrous hydroxide, and the observed pressure is thus the saturation vapour pressure. The lower limit of these regions represents the solubility of sodium hydroxide which, from the phase diagram,[11] has the values given in Table 2. The positions of the

TABLE 2.

The two-phase region for sodium hydroxide and water.

Temp.	125°	150°	175°	200°	225°	275°	300°
Solubility (wt. % NaOH)	79	81	83	85	86	92	98
Saturation vapour pressure (cm.)	6·0	9·1	17·5	26·0	36·0	[40·5]	[32·0]

breaks in the vapour pressure curves are near to the solubility values. Although pressure equilibrium is achieved rapidly with pure sodium hydroxide and water vapour, it is very slow when approached from the opposite direction. When the vessel was evacuated after equilibrium had been initially established, the saturation pressure was restored, but only

[11] von Antropoff and Sommer, *Z. phys. Chem.*, 1926, **123**, 161.

over periods of many hours. This reflects the reluctance of sodium hydroxide to crystallise from these concentrated solutions.

Below the solubility composition, the vapour pressures increase rapidly towards limiting values at one atmosphere derived from the boiling points of these solutions.[11] For comparison, calculated values for 275 and 300° are included as broken lines in Fig. 4. These pressures were determined from the positions of the Dühring lines on the phase diagram that Standiford and Badger [12] derived from the boiling point data of von Antropoff and Sommer [11] by extrapolation to very high sodium hydroxide concentrations. The phase change from α to β-NaOH, which occurs at 300°, gives rise to a saturation vapour pressure at 300°, that is rather lower than that for 275°.

In the present context, the feature of major significance is that in the temperature range used (which is also the range used in the liquid sodium–water vapour experiments), solid sodium hydroxide can exist in equilibrium with a vapour pressure of water of up to half an atmosphere. It follows that, if pure sodium hydroxide is brought into contact with water vapour below the saturation pressure, absorption of water vapour is negligible. In a typical experiment, a capsule of pure sodium hydroxide was broken in water vapour at 200° and 25 cm.; no absorption of vapour could be detected. A cohesive film of sodium hydroxide formed on the surface of liquid sodium could therefore act as an effective barrier preventing reaction with water vapour. In their studies of the reaction of sodium monoxide with less than the stoichiometric amount of water at 300°, Kay and Gregory [13] suggested that a film of sodium hydroxide might form a barrier to the reaction between sodium oxide and water.

It should be emphasised that the above discussion is only relevant to temperatures below 322°, the melting point of sodium hydroxide.[14] The physical properties of the water–molten hydroxide system are likely to be quite different.[8,15]

Liquid Sodium.—When capsules of liquid sodium were broken in water vapour, the sodium was spread in the form of droplets on the sides of the vessel. The method has advantages in that the time at which reaction starts is clearly defined, and clean sodium surfaces are initially formed. Identical quantities of sodium in different experiments give similar, but not identical, surface areas; visual observation of droplet sizes indicated that general comparisons between different experiments that assumed the same degree of dispersion were justified, but that the calculation of thermodynamic properties based on precise comparisons of reaction rates were not justified. When liquid sodium came into contact with water vapour at 175° and 65 cm. pressure, there was a momentary flash of flame. At 40 cm. pressure, a transient glow appeared on the sodium droplets; this is probably the " pre-ignition glow " observed by Corrsin, Steinmetz, and Marano.[4] These effects vanished within two seconds and, when the sodium droplets struck the walls of the vessel their temperature was rapidly restored to that of the thermostat. Subsequent variations in pressure are shown in Fig. 5; an excess of sodium was used in all the experiments. The main reaction is $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$ and, if the sodium hydroxide film did not exert any independent influence on the reaction, the pressure should fall to half its initial value in all cases. In fact, deviations from the half-pressure value do occur, and can be related directly to the properties of sodium hydroxide already discussed; these are collected in Table 3, which includes some additional measurements of pressure deviations. At initial pressures below about 25 cm., the reaction was entirely regular. The reaction rate increased with temperature; the pressure fell to precisely half the initial value in all cases (expts. 7—9, Fig. 5), so that reactions that produce sodium oxides can be eliminated; no water vapour remained in the gas phase. Using pressures of about 1 cm., Longton [6]

[12] Standiford and Badger, *Ind. Eng. Chem.*, 1954, **46**, 2400.
[13] Kay and Gregory, *J. Amer. Chem. Soc.*, 1958, **80**, 5648.
[14] Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Suppl. II, Longmans, 1961, p. 670.
[15] Galinker and Korabkov, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 407.
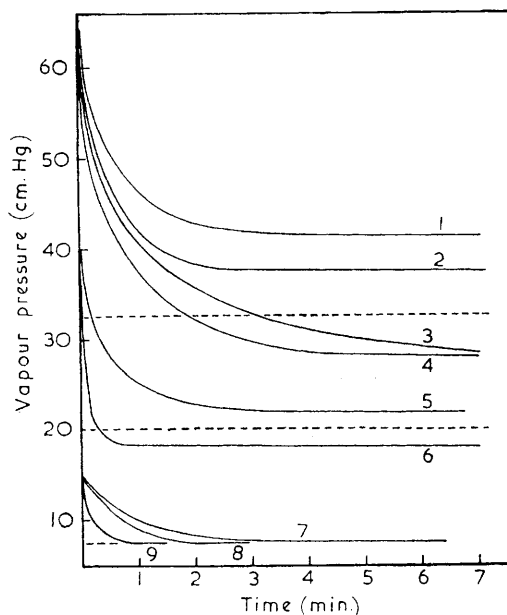
FIG. 5. Pressures changes in the liquid sodium–water vapour reaction.

Expt. No.	Initial pressure (cm.)	Temp.	Wt. of sodium (g.)	Mole ratio Na : H_2O
1	65	175°	0·641	2·20
2	65	150	0·758	2·45
3	65	125	0·496	1·51
4	65	125	0·900	2·74
5	40	175	0·548	3·02
6	40	125	0·790	3·90
7	15	125	0·520	6·84
8	15	150	0·522	7·33
9	15	175	0·554	8·22

found this behaviour to occur at temperatures up to 300°. The film is sufficiently thin to be permeable to water, and cannot maintain a water-vapour pressure characteristic of sodium hydroxide as a separate phase. The film is presumably permeable to hydrogen also, but at these lower pressures the rate of hydride formation is too slow to be detectable.

At initial pressures above about 25 cm., deviations do occur; these are now highly temperature-dependent, being negative at 125° and positive at 175° (Table 3). The results at 125° (Table 3) show that the negative deviation increases with initial pressure, and thus with the final hydrogen pressure. In spite of the fact that the film now present is

TABLE 3.

Influence of pressure and film thickness on the liquid sodium–water vapour reaction.

Temp.	Initial pressure P (cm.)	Deviations in equilibrium pressure from $0.5P$ (cm.)	Temp.	Initial pressure P (cm.)	Deviations in equilibrium pressure from $0.5P$ (cm.)
125°	15	0	175°	15	0
,,	25	0	,,	40	+2·2
,,	40	−1·5	,,	50	+5·5
,,	65 (Na : H_2O ratio 1·51)	−4·3	,,	65	+9·4
,,	65 (Na : H_2O ratio 2·74)	−4·7			
150	15	0			
,,	25	0			
,,	40	0			
,,	50	+1·7			
,,	65	+4·5			

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thicker, it is still permeable to hydrogen, and the higher hydrogen pressure introduces some sodium hydride into the film. No water vapour remained in the gas phase. The quantity of hydrogen dissolved in the free sodium is less than 0.3%,[9] and the two experiments at $125°$ and 65 cm. pressure, in which different amounts of sodium were used (Table 3), gave similar negative deviations. The negative deviation is therefore a direct consequence of the presence of sodium hydride in the film.

At the highest temperatures and pressures used, deviations become positive, and at the same time water vapour is detected in the gas phase at equilibrium. The results can be interpreted quantitatively on the assumption that the film is sufficiently thick (owing to the high pressure of water vapour) and cohesive (because of the higher temperature) to become impermeable to hydrogen. No hydride is formed, and the pressure of the water vapour retained in the gas phase is that which is characteristic of sodium hydroxide when acting as a separate phase. The pressure values in Table 4 are calculated on the basis of these assumptions, which are supported by the close agreement between calculated and observed pressures. As the initial pressure decreases, these assumptions become less valid. Thus, at $175°$, the calculated differs from the observed final pressure by -0.6, $+3.2$, and $+6.5$ cm. for initial pressures of 65, 50, and 40 cm., respectively.

TABLE 4.

Comparison of calculated and observed equilibrium pressures.

	150°	175°
Temperature	150°	175°
Initial H_2O pressure (cm.)	65	65
NaOH–H_2O saturation vapour pressure (cm.)	9·1	17·5
Water vapour absorbed in reaction (cm.)	55·9	47·5
Equilibrium H_2 pressure (cm.)	27·9	23·8
Final pressure (H_2O + H_2, cm.) calculated	37·0	41·3
,, ,, ,, observed	37·0	41·9

Rate Laws.—Reactions that proceed by diffusion through a continuous film normally follow a parabolic rate law,[16,17] which in this case can be expressed as $\Delta p = kt^{\frac{1}{2}}$; Δp is the fall in pressure at time t, and $2\Delta p$ represents the quantity of water vapour consumed in
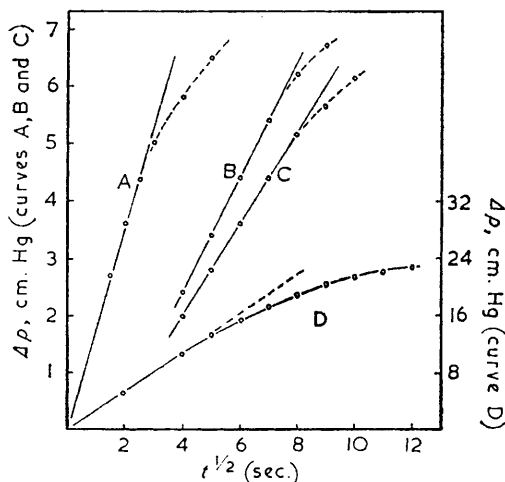

FIG. 6.   Application of parabolic rate law to liquid sodium–water vapour reactions (Temperatures: A, 175°; B, 150°; C, 125°; D, 175°.   Initial pressures A, 15 cm.; B, 15 cm.; C, 15 cm.; D, 65 cm.).

the reaction. It is of interest to examine the reaction rates in this light (Fig. 6). At 15 cm. initial pressure, the parabolic law is followed for a major part of the reaction period, which is consistent with the postulate that this film is permeable to water vapour and hydrogen throughout the reaction. At $175°$ (Curve A, Fig. 6) reaction is rapid, and the film becomes continuous almost immediately. The $\Delta p - t^{\frac{1}{2}}$ line, on extrapolating, therefore passes

[16] Evans, *Trans. Electrochem. Soc.*, 1943, **83**, 335.
[17] Epstein, General Electric Company Rept. GEAP-3272, 1959.

through the origin; at **125** and **150°** (Curves B and C), the corresponding lines do not pass through the origin. At these temperatures reaction is much slower, and there is probably an initial period during which a free metal surface is available, and the reaction would follow the linear law. At **175°** and **65** cm. pressure (Curve D), where the water-vapour pressure in the gas phase shows clearly that diffusion through the film does not occur, the reaction begins according to the parabolic law, but departure from the law becomes pronounced as reaction proceeds.

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