High-temperature Hydrolysis of Sodium Chloride

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The hydrolysis of sodium chloride according to the reaction

$$NaCl(s,l)+H_2O(g) = NaOH(s,l)+HCl(g)$$

has been investigated over the temperature range 600-950°C using a dynamic method. A mathematical model describing the hydrolysis reaction is derived which is in good agreement with the experimental data. Because of the solid-solid and liquid-liquid solubility of sodium hydroxide in sodium chloride, the activity of the sodium hydroxide is much less than unity and consequently the equilibrium partial pressures of hydrogen chloride generated are much greater than otherwise expected. The activity coefficient of sodium hydroxide in sodium chloride is evaluated and shown to be temperature-dependent, with a sharp discontinuity at the melting point of sodium chloride. It is further demonstrated that equilibrium is established very rapidly, even at temperatures where the sodium chloride is in the solid phase.

The high-temperature hydrolysis of sodium chloride in the presence of additives such as silica and alumina is a subject which has received much attention, but recently few investigations have been reported. Earlier studies were largely concerned with ways of producing cheap silicates for the glass industry, or of producing hydrochloric acid.[1-4] Consequently, information on the more fundamental aspects of the pure hydrolysis reaction is scanty.

The work reported here is mainly concerned with chemical equilibria, though certain kinetic aspects are also considered. It was initiated as a result of similar studies on the hydrolysis of sodium chloride in the presence of silica and other siliceous materials. The latter was of interest because of its importance in the chemistry of segregation,[5] on which the recently developed TORCO process [6] for the treatment of refractory copper ores, depends. However, in order to gain a proper understanding of the $NaCl+SiO_2+H_2O$ system, it was first necessary to examine pure sodium chloride reacting with water vapour at high temperatures. This apparently simple system is more complex than expected.

EXPERIMENTAL

APPARATUS

The apparatus used for following the course of the hydrolysis reaction is shown in fig. 1. Essentially, this consisted of a gas flow system which passed water vapour through a charge of sodium chloride contained in a high-temperature platinum reator. The effluent gases, including the hydrogen chloride produced by the reaction, were passed into an absorption vessel where the evolved hydrogen chloride was continuously monitored.

A flow controller provided a constant flow of dry, high-purity nitrogen to the system and, when desired, this carrier gas could be humidified by passing it through two wash bottles containing water, immersed in a thermostatically-controlled water bath. The partial pressure of water vapour in the inlet gas could thus be accurately varied. The gas mixture then passed via a heated tube (to prevent condensation) directly to the reactor. This consisted of a 1.5 cm diam. platinum tube, at the centre of which was welded a fine platinum gauze to support the charge. The reactor was heated by means of a temperature controlled (±3°C) tube furnace. The exhaust gases were led, again via a heated tube, into a specially designed absorption vessel whose temperature was maintained constant at 20°C. The latter contained a solution with a pre-set pH value. Electrodes in the absorption vessel were connected to a pH meter and titration unit, so that any change in the pre-determined pH was corrected for by the addition of sodium hydroxide titrant from an automatic burette.

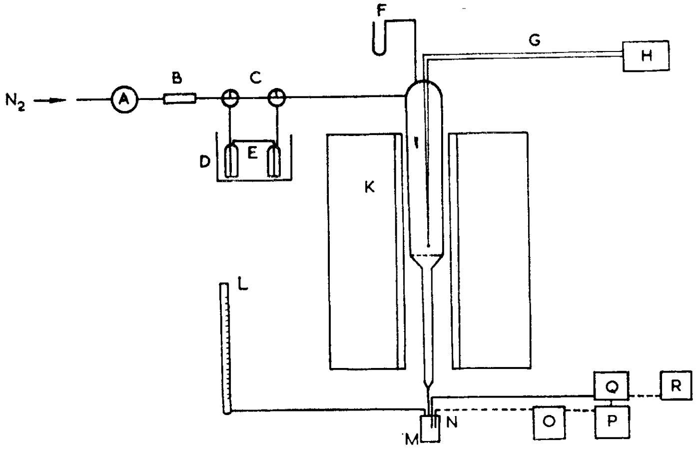

FIG. 1.—Schematic diagram of experimental apparatus: A, flow controller; B, drying tube; C, 3-way stop-cocks; D, thermostatically controlled water bath; E, wash bottles; F, manometer; G, Pt/13 % Rh-Pt thermocouple sheathed with 13 % rhodium-platinum; H, temperature recorder; I, platinum reactor; K, temperature-controlled furnace; L, soap-bubble flow-meter; M, constant temperature absorption vessel; N, glass-calomel electrode; O, pH-meter; P, automatic titrator; Q, automatic burette; R, titrant recorder.

The latter incorporated a digital counter, permitting readings to within 0.001 ml, and was coupled to a recorder to provide continuous monitoring of hydrogen chloride production. The flow rate of the nitrogen carrier gas leaving the absorption vessel was accurately measured with a soap-bubble flow-meter. In experiments at temperatures below the melting point of sodium chloride, the gas stream was usually passed downwards through the reactor, while for temperatures above the melting point, the direction of flow was reversed in order to keep the molten charge suspended above the platinum mesh.

PROCEDURE

The charge was inserted into the reactor and heated to the required temperature in a stream of dry nitrogen. After temperature equilibrium had been attained, the nitrogen was humidified to the appropriate extent. The hydrogen chloride produced dissolved in the solution in the absorption vessel, the consumption of titrant being recorded as a function of time. Only analytical reagent sodium chloride, dried at 120°C, was used in the experiments. This was crushed and screen sized. In most tests the minus 48 mesh +65 mesh (Tyler) fraction was used.

RESULTS AND DISCUSSION

The hydrolysis of sodium chloride at high temperatures may be described by the general equation:

$$\mathrm{NaCl}(s,l)+\mathrm{H_2O}(g) = \mathrm{NaOH}(s,l)+\mathrm{HCl}(g). \qquad (1)$$

The phase diagram of the NaCl+NaOH system [7] indicates limited solid-solid solubility of sodium hydroxide in sodium chloride. Since in the present investigation the amounts of sodium hydroxide produced at temperatures below the melting point of sodium chloride are very small, this condition would apply. Therefore, in the following calculation the data for the unstable sodium hydroxide solid is used, since in solid solution it would not have the mobility and hence the entropy of the liquid phase.

In this case the free energy change of eqn (1) at around 1000 K is then given by *

$$\Delta G(s)[\text{cal}] = 36\,267 - 4.577\,T \qquad (2)$$

$$= -RT \ln K(s), \qquad (3)$$

where

$$K = a_{\text{NaOH}}p_{\text{HCl}}/a_{\text{NaCl}}p_{\text{H}_2\text{O}}, \qquad (4)$$

where a and p refer to the activity and the equilibrium partial pressure of the specified component, T is the absolute temperature, and K is the equilibrium constant for reaction (1) with sodium chloride and sodium hydroxide in the solid state.

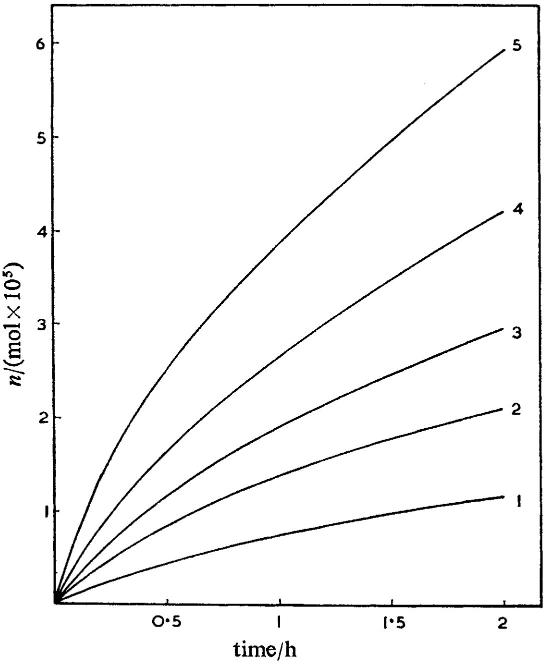

FIG. 2.—Effect of nitrogen flow rate on the hydrolysis of sodium chloride. Charge, 10 g NaCl; reaction temperature, 700°C; $p_{\text{H}_2\text{O}}$, 266 Torr; nitrogen flow rates at room temperature and atmospheric pressure were for curves 1 to 5 respectively 20, 40, 80, 160, 320 ml/min.

Above the melting point of sodium chloride, complete liquid-liquid solubility occurs and eqn (2) becomes

$$\Delta G(l)[\text{cal}] = 31\,043 - 0.842\,T \qquad (5)$$

$$= -RT \ln K(l) \qquad (6)$$

Preliminary experiments showed that evolution of hydrogen chloride occurs at temperatures well below the melting point of sodium chloride. The (gas evolution, time) curves have a characteristic shape, as shown in fig. 2, the rate of hydrogen

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* All thermodynamic values used in this paper were taken or derived from *JANAF Tables*.[8]

chloride evolution being high at the start of the reaction and decreasing progressively with time. Since, for any particular curve, both p_{H_2O} and the total gas flow are effectively constant, p_{HCl} decreases in similar fashion with time. Fig. 2 also shows that, under otherwise constant conditions, the extent of hydrolysis increases with carrier gas flow rate. Analogous sets of curves were obtained by systematically varying p_{H_2O} and the mass of the charge, and these also showed that p_{HCl} increased with increasing charge mass and increasing p_{H_2O}.

The general pattern of behaviour discussed above can be explained qualitatively in terms of eqn (4), if the following assumptions are made: (i) since sodium chloride is in large excess, its activity remains effectively constant and equal to unity; (ii) since solid-solid (or liquid-liquid) solubility exists, the activity of the sodium hydroxide is proportional to its mol fraction in the system; (iii) the sodium hydroxide formed is uniformly distributed in the sodium chloride. Thus, for given experimental conditions, the product $a_{NaOH}p_{HCl}$ in eqn (4) is constant, i.e., at the start of the reaction, when little sodium hydroxide has been formed and a_{NaOH} is small, p_{HCl} is high; as the reaction proceeds and a_{NaOH} increases, p_{HCl} must correspondingly decline, as was indeed observed. A more quantitative interpretation is now discussed. Let

F = total gas flow rate [mol/h],
p = total gas pressure in reaction zone [atm],
p_{HCl} = equilibrium partial pressure of hydrogen chloride [atm],
n = number of moles of sodium hydroxide produced in time t (equivalent to the number of moles of hydrogen chloride produced in time t),
N = number of moles of sodium chloride in reactor,
γ = activity coefficient of sodium hydroxide in sodium chloride,

then the rate of hydrogen chloride or sodium hydroxide production is

$$\mathrm{d}n/\mathrm{d}t = Fp_{HCl}/p. \tag{7}$$

Since $a_{NaOH} = \gamma n/(N+n) \simeq \gamma n/N$ with $a_{NaCl} = 1$, and assuming that equilibrium conditions between gaseous and condensed components obtain, eqn (4) gives

$$K \simeq \gamma n p_{HCl}/N p_{H_2O}. \tag{8}$$

From (7) and (8), integration yields

$$n = [2FNp_{H_2O}K/p\gamma]^{\frac{1}{2}}t^{\frac{1}{2}}, \tag{9}$$

or

$$\log n = \tfrac{1}{2}\log(2FNp_{H_2O}K/p\gamma)+\tfrac{1}{2}\log t, \tag{10}$$

Thus, a plot of n against $\sqrt{t}$ should yield a straight line passing through the origin or, alternatively, a (log n, log t plot) should be linear with slope $\frac{1}{2}$. Likewise, if equilibrium between gaseous and condensed phases is maintained, then at a given temperature and reactor pressure, n, after a given time, should be the same for all experiments for which the product ($Fp_{H_2O}N$) has the same value. Assumption (iii) implies instantaneous diffusion of the sodium hydroxide into the sodium chloride and, since this condition is more likely to be approached above the melting point of sodium chloride, this situation is examined first.

Fig. 3 shows the results of hydrolysis experiments carried out at temperatures above 800°C. In all cases the (n, $\sqrt{t}$) plots are linear throughout most of the range but none intersect the origin. Corresponding (log n, log t) plots are also linear, with slopes varying from about 0.58 at 850°C down to 0.54 at 950°C. In table 1 experimental data taken at 850°C are tabulated. The results show that in a given time the number of moles of hydrogen chloride evolved is constant for a given value of the product ($Fp_{H_2O}N$).

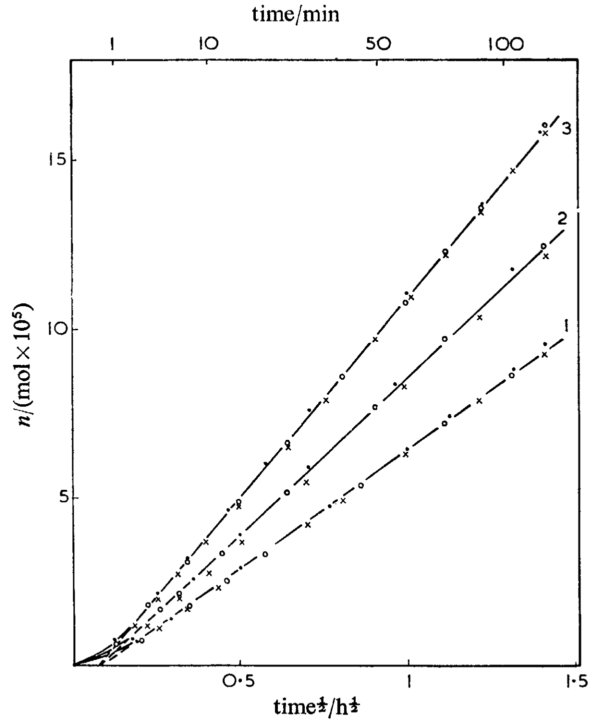

FIG. 3.—Effect of temperature on the hydrolysis of sodium chloride above its melting point. Curve 1, 850°C; curve 2, 900°C; curve 3, 950°C;

	F_{av}/(mol h^{-1})	p_{H_2O}/atm	N/mol	$F_{av}.p_{H_2O}N \times 10^3$ (atm mol^2 h^{-1})
•	0.206	0.108	0.0428	0.952
○	0.103	0.216	0.0428	0.952
×	0.103	0.108	0.0856	0.952

TABLE 1.—COMPARISON OF SODIUM HYDROXIDE PRODUCED AT 850°C WHEN VARYING F, N, p_{H_2O} WHILE MAINTAINING THE PRODUCT (FNp_{H_2O}) CONSTANT

t h	F mol h^{-1}	N mol	p_{H_2O} atm	$p_{H_2O}FN \times 10^3$ atm mol^2 h^{-1}	$n \times 10^5$ mol
0.5	0.103	0.0428	0.216	0.952	4.28
0.5	0.103	0.0856	0.108	0.952	4.21
0.5	0.208	0.0428	0.108	0.961	4.39
1.0	0.103	0.0428	0.216	0.952	6.41
1.0	0.103	0.0856	0.108	0.952	6.30
1.0	0.208	0.0428	0.108	0.961	6.43
1.5	0.103	0.0428	0.216	0.952	8.02
1.5	0.103	0.0856	0.108	0.952	7.89
1.5	0.208	0.0428	0.108	0.961	8.07
2.0	0.103	0.0428	0.216	0.952	9.35
2.0	0.103	0.0856	0.108	0.952	9.28
2.0	0.208	0.0428	0.108	0.961	9.60

From the results of fig. 3 and table 1 the model provides a reasonable representation of the hydrolysis at temperatures above the melting point. From the slopes of the (log n, log t) plots, the degree of fit improves with increasing temperature. However, when an attempt was made to apply the model at temperatures below the melting point, severe divergences were apparent at short times, as is evident in fig. 4.

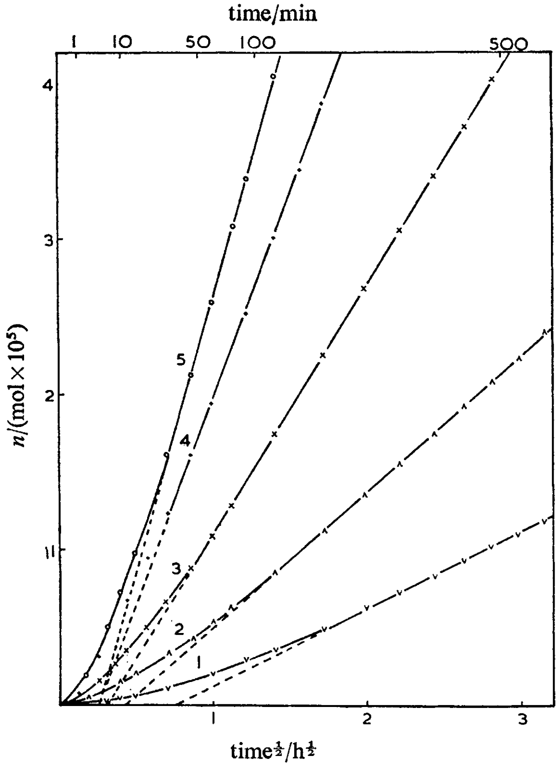

FIG. 4.—Effect of temperature on the hydrolysis of sodium chloride below its melting point. N, 0.856 mol ; p_{H_2O}, 0.216 atm ; F_{av}, 0.206 mol h^{-1}. Curve 1, 600°C ; curve 2, 650°C ; curve 3, 700°C ; curve 4, 750°C ; curve 5, 780°C.

The most likely cause is that diffusion to give sodium hydroxide homogeneously dispersed in the sodium chloride requires a finite time. In fact, there is some evidence that diffusion does play a role, especially during the initial stages of hydrolysis. This is demonstrated by the results of fig. 5 which show that hydrogen chloride evolution increases with decreasing particle size of sodium chloride.

An attempt was therefore made to formulate a rigorous model incorporating diffusion but the resulting differential equations proved intractable. Accordingly, a simpler empirical approach was adopted. At the start of the reaction the rate of water vapour attack on the sodium chloride surface is very rapid resulting in a high concentration at, or near the surface, of sodium hydroxide. Consequently, the probability of water molecules reacting with molecules of sodium chloride decreases and becomes dependent upon the rate of diffusion of sodium hydroxide into the sodium chloride mass. Broadly therefore, it can be supposed that at the start of the reaction N_{eff}, the effective number of moles of sodium chloride available for reaction, is much less than N, the total number of moles of sodium chloride present.

Accordingly a_{NaOH} must be greater than previously assumed and consequently p_{HCl} is less than predicted by the original model. As reaction proceeds, the rate decreases and diffusion does not become such a limiting factor. Essentially, therefore, N_{eff} approaches N with increasing reaction time. A simple function which would reasonably describe the variation of N_{eff} with time is given by

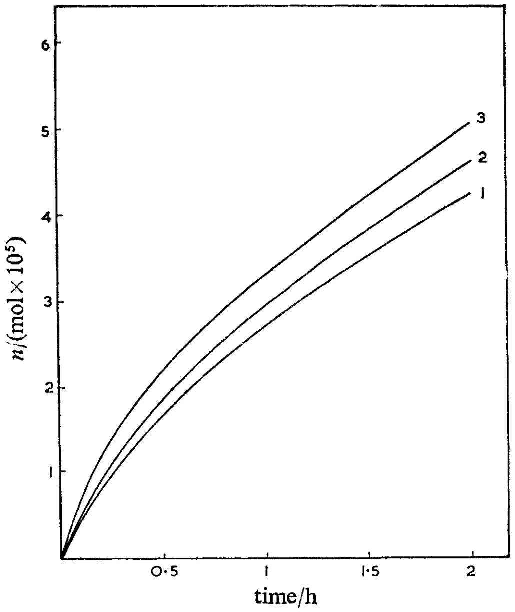

FIG. 5.—Effect of particle size on the hydrolysis of sodium chloride. Charge, 10 g NaCl; reaction temperature, 700°C; p_{H_2O}, 266 Torr; nitrogen flow rate at room temperature and atmospheric pressure, 160 ml/min. Curve 1, −35+65 mesh; curve 2, −65+100 mesh; curve 3, −100 mesh.

$$N_{eff} = N[1-\exp(-t/\lambda)]\,^* \qquad (11)$$

λ is equivalent to a " time constant " which, in the present case, is a measure of the time required for diffusion limitations to become small, i.e., it corresponds approximately to the time at which deviation from linearity occurs in the (n, $\sqrt{t}$) plot. Clearly λ would be expected to decrease with increasing temperature and fig. 4 suggests that it does.

In terms of this more refined model eqn (9) now becomes

$$n = [2Fp_{H_2O}KN/p\gamma]^{\frac{1}{2}}\{t+\lambda[\exp(-t/\lambda)-1]\}^{\frac{1}{2}}, \qquad (12)$$

or

$$\log n = \tfrac{1}{2}\log[2Fp_{H_2O}KN/p\gamma)+\tfrac{1}{2}\log\{t+\lambda[\exp(-t/\lambda)-1]\}. \qquad (13)$$

If this model is correct, and if the appropriate value of the time constant is used, a plot of log n against log $\{t+\lambda[\exp(-t/\lambda)-1]\}$ should give a straight line with slope $\frac{1}{2}$. Approximate values of λ can be obtained from fig. 3 and 4, by inspection. However, a better method of evaluating λ is as follows. Referring to eqn (13) when t is large

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* A more precise description would be $N_{eff} = N(1-\exp(-t/\lambda)+N_0/N)$, where N_0 is the number of sodium chloride molecules available for reaction at $t = 0$. However, as there is no way of determining N_0, and since its inclusion would complicate the mathematics without significant interpretational benefits, the simpler expression is justified for most practical purposes.

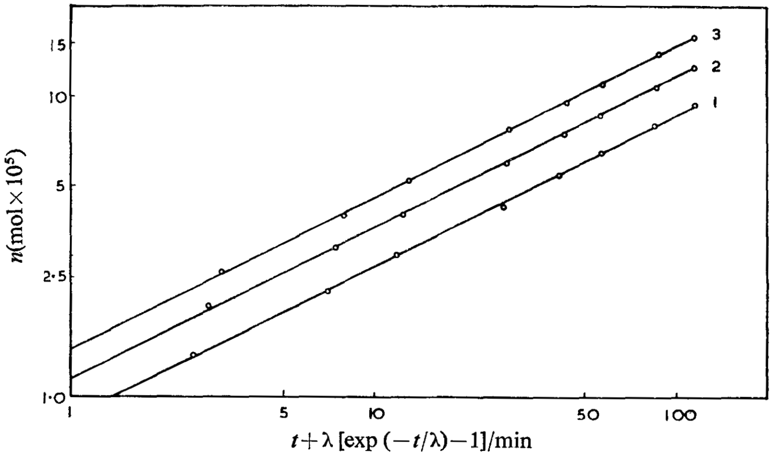

FIG. 6.—Plot of log n against log $[t+\lambda(\exp(-t/\lambda)-1)]$.

curve	1	2	3
temp./ °C	850	900	950
λ/min	3.0	2.5	2.0

the second bracket reduces to $[t-\lambda]$ or, if $\lambda \ll t$ to t, which is an equivalent situation to eqn (10). By using the approximate value of λ an experimental point with very large t is plotted on the log n against log $\{t+\lambda[\exp(-t/\lambda)-1]\}$ graph and through this point is drawn a line of slope $\frac{1}{2}$. A second experimental point with small t is then chosen such that it also falls on the line of slope $\frac{1}{2}$, when the correct value of λ* is inserted into the term $\{t+\lambda[\exp(-t/\lambda)-1]\}$. Using this accurate value of λ the remaining experimental points may be plotted on the log n against log $\{t+\lambda[\exp(-t/\lambda)-1]\}$ graph. As is shown in fig. 6 and 7 good fits are achieved.

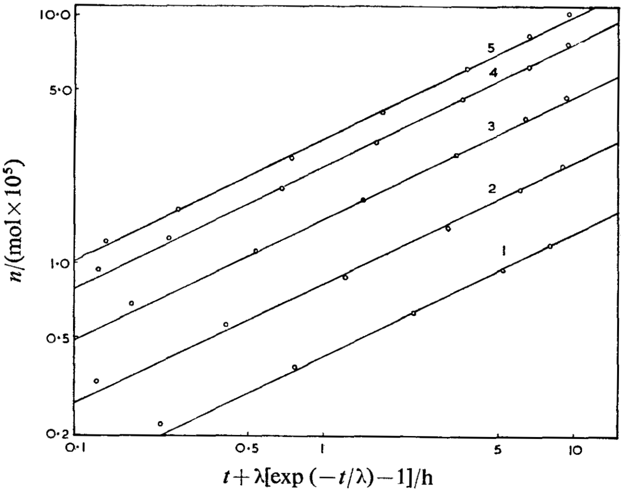

FIG. 7.—Plot of log n against log $[t+\lambda(\exp(-t/\lambda)-1)]$.

curve	1	2	3	4	5
temp./°C	600	650	700	750	780
λ/h	1.9	0.85	0.55	0.32	0.28

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* λ can now be evaluated by back calculation using a trial and error approach.

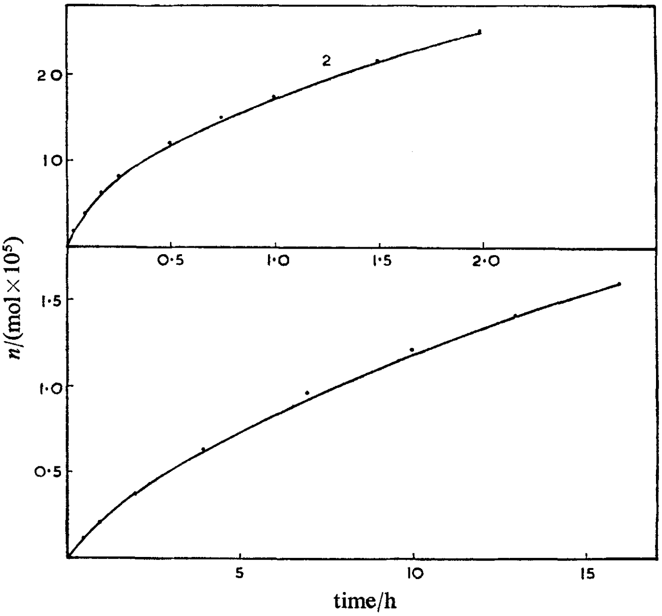

FIG. 8.—Comparison of experimental curves with the curves predicted by the model. Solid line, experimental; dots, predicted.

curve	1	2
temp./°C	600	900
λ	*1.9 h*	*2.5 min*

Fig. 8 shows comparisons of actual and predicted behaviour of hydrogen chloride evolution at 600 and 900°C. With the correct choice of λ excellent agreement is obtained between theory and practice.

When $\{t+\lambda[\exp(-t/\lambda)-1]\} = 1$, eqn (13) reduces to

$$n^2 = 2Fp_{H_2O}KN/p\gamma. \tag{14}$$

This equation can be solved for K/γ since the remaining quantities are all known. Fig. 9 shows a plot of log (K/γ) against $1/T$ which may be compared with the variation of the

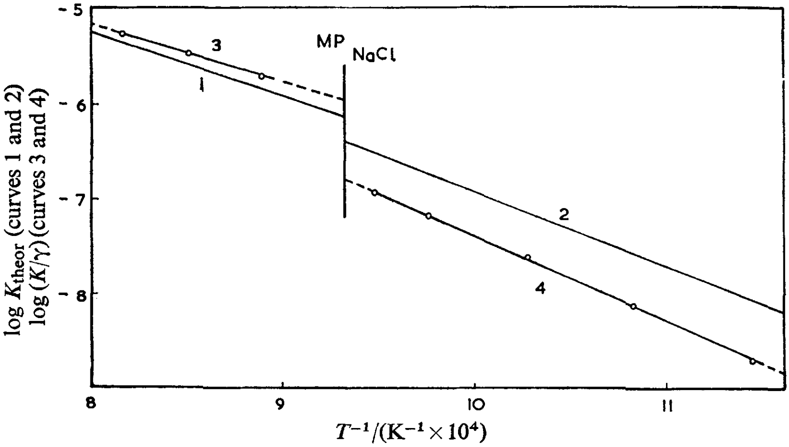

FIG. 9.—Variation of K/γ and $K_{theor.}$ with temperature.

theoretical equilibrium constant with temperature. From the figure, below the melting point the activity coefficient γ is greater than 1 and above the melting point it is less than 1. Furthermore, γ is slightly temperature dependent in each region. The relationship, derived from a least squares fit of the experimental data and from the variation of the theoretical equilibrium constant with temperature, is

$$\log \gamma = 0.392 - 608/T \qquad (15)$$

above the melting point of sodium chloride; and

$$\log \gamma = -0.580 + 1038/T \qquad (16)$$

below the melting point of sodium chloride.

A point which has already been mentioned in relation to table 1, namely that the system is in equilibrium, requires further amplification. If the data of fig. 2 are considered and values of n after a given time (say, 120 min), are compared with corresponding values of F, then the following relationship, derived from eqn (13), should apply if λ is constant:

$$n_1/n_x = (F_1/F_x)^{\frac{1}{2}}, \qquad (17)$$

where $n_{1 \ldots x}$ refers to the number of moles of hydrogen chloride produced in different runs after time t at flow rates of $F_{1 \ldots x}$, respectively. This relationship has been evaluated in table 2 using data from fig. 2. The results indicate that λ must be reasonably constant. Furthermore, implicit in the results of table 2 is the fact, that in spite of a large variation in gas flow rate, equilibrium is maintained at a temperature well below the melting point of sodium chloride. At the higher flow rates used, the contact time of the water vapour in the gas stream with the charge of sodium chloride was only a fraction of a second, which emphasizes how rapidly equilibrium conditions are attained. This fact has important implications for the kinetics [9] of the TORCO process.

TABLE 2.—EVALUATION OF THE RELATIONSHIP $n_1/n_x = (F_1/F_x)^{\frac{1}{2}}$ FOR THE CURVES OF FIG. 2

	F ml/min	$n_x \times 10^{-5}$ [mol HCl at t = 120 min]	$(F_1/F_x)^{\frac{1}{2}}$	n_1/n_x
1	320	5.92	1.00	1.00
2	160	4.20	1.41	1.41
3	80	2.96	2.00	2.00
4	40	2.10	2.82	2.82
5	20	1.18	4.00	5.02

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