Salts in Porous Aluminosilicates. Part I. Sodium Chlorite, Chlorate, Perchlorate, and Azide

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Solid solutions of $NaClO_4$, $NaClO_3$, and $NaClO_2$ + NaCl in sodalite hydrate and of NaN_3 in cancrinite hydrate have been prepared and some properties examined. The isotherms of salt uptake are continuous functions of salt concentration in the synthesis mixtures. Thermogravimetric and differential thermal analyses of the oxo-salt sodalites and of the sodium azide–cancrinite have been made and interpreted. The kinetics of release of oxygen from the oxo-salt and of nitrogen from the azide solid solutions have been measured as functions of temperature, and, in the case of the oxo-salts, as functions of the oxo-salt concentrations. In the case of azide the curves of nitrogen evolution show an inflexion. The kinetics have been considered for the oxo-salts in terms of the probable reaction mechanisms.

SODALITE and cancrinite form solid solutions with numerous salts during hydrothermal crystallisation from alkaline gels containing the salt.[1-3] The salts are trapped within the cavities and channels found in the aluminosilicate frameworks. Sodalite[4,5] is composed of tetradecahedral cages of free diameter *ca.* 6.6 Å, and one molecule of salt, two of NaOH, or four of water fill a cavity.[2] In an ideal cancrinite wide channels circumscribed by 12-rings [*i.e.* rings made from 12 joined $(Al,Si)O_4$ tetrahedra] run parallel to the *c* axis.[6] They are surrounded by columns of undecahedral cavities (cancrinite cages). These columns are also parallel to the *c* axis and are linked to each other. The wide channels appear however to be blocked either by stacking faults or by some adventitious anions such as silicate incorporated during synthesis.

In both cancrinite and sodalite the limiting unit-cell composition for salt inclusion is $6(NaAlSiO_4)\cdot 2NaX$ where X is one equivalent of an anion; NaX may be replaced in varying proportions by water and by NaOH, yielding compositions $6(NaAlSiO_4)\cdot 2(1-x-y)NaX\cdot 4yNaOH\cdot 8xH_2O$. Usually the amount of NaOH is not large, and NaX may be totally replaced by water. Continuous isotherms of salt uptake plotted against the salt concentration in the aqueous synthesis magma have been reported.[2] Some of the salts of interest ($NaClO_4$, $NaClO_3$, and $NaClO_2$) should act, on heating the salt–sodalite solutions, as safe reservoirs of oxygen released in a controllable way according to the temperature. Sodium azide–cancrinite should serve as a similar reservoir of Na and N_2. Because these 'packaged' salts have different local environments from those of the same salts in bulk, it was of interest to examine the properties and reactivities of the salts in the form of their solid solutions in the aluminosilicate matrices.

EXPERIMENTAL

The sodalites and cancrinites were normally made from mixtures of NaOH (32 g), metakaolin (2 g), and distilled water (200 cm³) to which the desired amount of the salt ($NaClO_4$, $NaClO_3$, $NaClO_2$, or NaN_3) was added. In other syntheses the amount of NaOH added was systematically varied. The reaction occurred in polypropylene bottles rotating at 80 °C for 6 d.

The crystals were examined by *X*-ray powder photography, thermal gravimetric analysis (t.g.a.), and differential thermal analysis (d.t.a.). The thermal decomposition of the intracrystalline salts was followed by measuring the oxygen (oxo-salts of chlorine) or nitrogen (sodium azide) evolved on heating. The furnace had a large heat capacity and was controlled to within ±0.5 °C. It was raised quickly (by a rack and pinion unit) around the small silica reaction bulb. As much zeolitic water as possible was removed by prior outgassing at temperatures below those at which any gas evolution could be detected (300 °C for $NaClO_4$– and 200 °C for $NaClO_3$– and $NaClO_2$–sodalites and for NaN_3–cancrinite). During the subsequent thermal decomposition of the salts a trap cooled by liquid nitrogen condensed any residual water evolved at higher temperatures. Liquid nitrogen and furnace levels were kept fixed. The total oxo-salt or azide content of crystals was estimated by measuring the total gas evolved up to 690 °C. The initial time delay in establishing the steady furnace temperature when the furnace was first raised around the reaction bulk was *ca.* 4 min.

RESULTS

The Salt–Felspathoid Complexes.—In agreement with earlier results[2] it was found that with $NaClO_4$, $NaClO_3$, $NaClO_2$, and NaCl, or in the absence of salts, sodalite crystallised, but at higher azide concentrations cancrinite formed. The oxo-salts changed the yields of oxo-salt–sodalite complex which crystallised, as shown in Figure 1(*a*) for the weights obtained from parent mixtures containing 2 g of metakaolinite. The isotherms for uptake of $NaClO_4$ and of $NaClO_3$ are shown in Figure 1(*b*). The reaction mixtures were such that the amounts of salt taken up were small relative to the amounts initially present in the mixture.

If the rather small[2] content of NaOH guest molecules in the crystals is neglected, the unit-cell compositions may be written as $6(NaAlSiO_4)\cdot 2(1-x)NaX\cdot 8xH_2O$ ($X = ClO_4^-$ or ClO_3^-). For the maximum salt uptakes of Figure 1(*b*) for $NaClO_4$ and $NaClO_3$, $x = 0.129$ and 0.085. Thus 87 and 91.5% of the cavities have an $NaClO_4$ or an $NaClO_3$ occupant. With these compositions 100% yields from 2 g of metakaolinite would correspond to 3.25 and 3.18 g for $NaClO_4$– and $NaClO_3$–sodalite respectively. For sodalite hydrate ($x = 1$) 100% yields would be 2.99 g. Comparison of these figures with

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[1] St. J. Thugutt, *Z. anorg. Chem.*, 1892, **2**, 65.

[2] R. M. Barrer and J. F. Cole, *J. Chem. Soc.* (*A*), 1970, 1516.

[3] R. M. Barrer, J. F. Cole, and H. Villiger, *J. Chem. Soc.* (*A*), 1970, 1523.

[4] L. Pauling, *Z. Krist.*, 1930, **74**, 213.

[5] J. Lons and H. Schultz, *Acta Cryst.*, 1967, **23**, 434.

[6] O. Jarchow, *Z. Krist.*, 1965, **122**, 407.

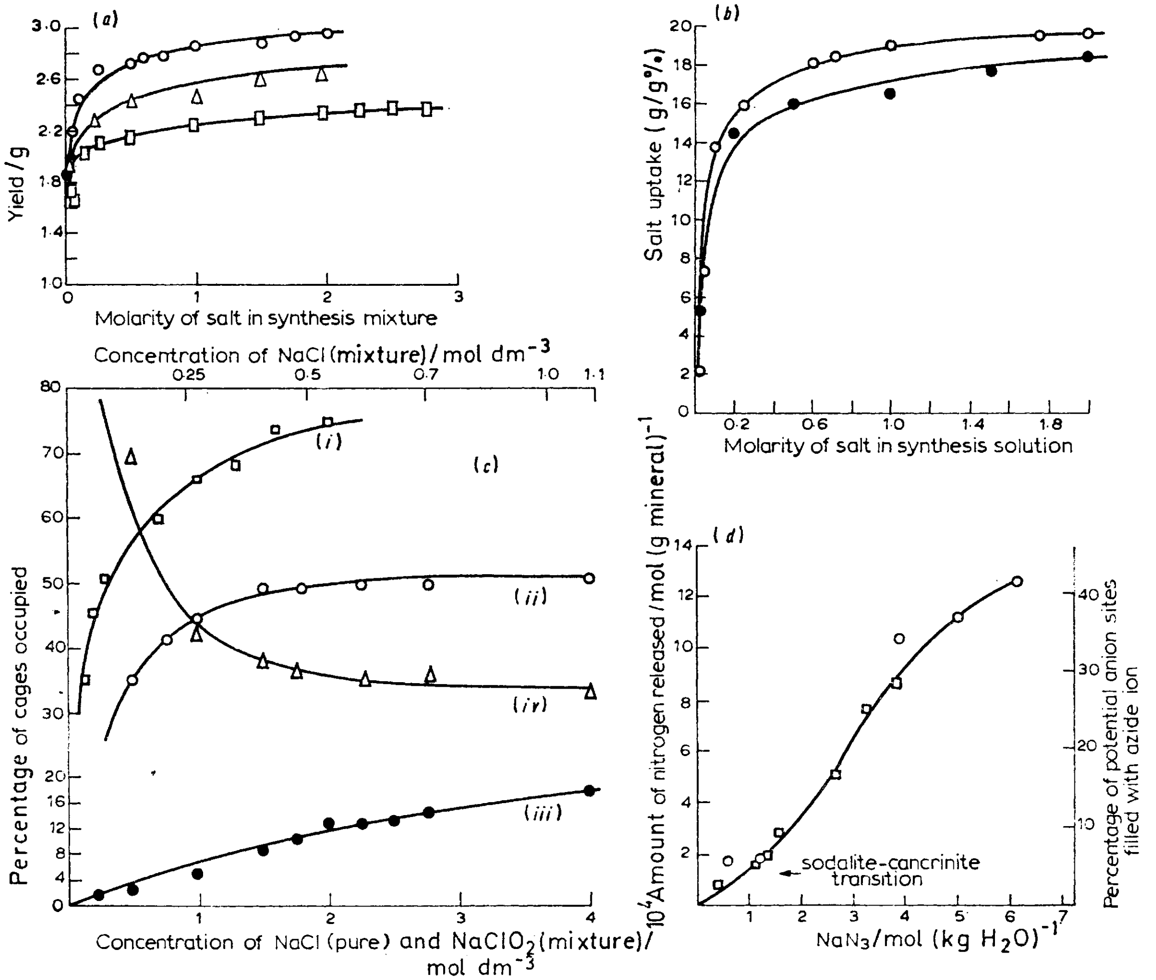

FIGURE 1 (a) Effect of oxo-salt concentration on the yield of oxo-salt–sodalite solid solution: (○) $NaClO_4$; (△) $NaClO_3$; (□) $NaClO_2$; (●) basic sodalite. (b) Isotherms of salt uptake against salt concentration: (○) $NaClO_4$; (●) $NaClO_3$. (c) Isotherms of mixed $NaClO_2$–NaCl uptakes: (i) for NaCl in the absence of $NaClO_2$; (ii) NaCl in mixture with $NaClO_2$; (iii) $NaClO_2$ in mixture with NaCl; (iv) the decrease in zeolitic water for increasing uptake of NaCl + $NaClO_2$. (d) Isotherm for NaN_3 in sodalite (for low azide concentration) and in cancrinite (for larger azide concentrations): (○) synthesis series 1; (□) synthesis series 2

the largest weights formed [Figure 1(*a*)] gives maximum yields as follows:

	Yield (%)
$6(NaAlSiO_4)\cdot1.7NaClO_4\cdot1.03H_2O$	92
$6(NaAlSiO_4)\cdot1.83NaClO_3\cdot0.68H_2O$	85
$6(NaAlSiO_4)\cdot8H_2O$	62

Thus strong oxo-salt solutions considerably improve the yields.

The isotherms for inclusion of $NaClO_2$ and NaN_3 are shown in Figures 1(*c*) and 1(*d*). The parent $NaClO_2$ contained 14% by weight of NaCl and a little $NaClO_3$ (*ca.* 1.9%). Accordingly the $NaClO_2$–sodalites were analysed, and the isotherm for NaCl was also found [curve (*ii*)]. The isotherm[2] for the uptake of NaCl during crystallisation in the absence of $NaClO_2$ is shown as curve (*i*). The solid was analysed by breaking down the crystals with 1 mol dm^{-3} H_2SO_4, reducing oxo-salt to Cl^-, and determining total Cl^-. The oxo-salt content was found from the total oxygen evolved on heating to 690 °C. Interpretation of the results to give the $NaClO_2$ content assumed negligible intracrystalline $NaClO_3$.

The isotherm for NaN_3 showed an inflexion in the region where azide–sodalite was being replaced by azide–cancrinite, and can be attributed to this fact. The maximum azide uptake corresponds to *ca.* 40% of the value appropriate to the formula $6(NaAlSiO_4)\cdot2NaN_3$.

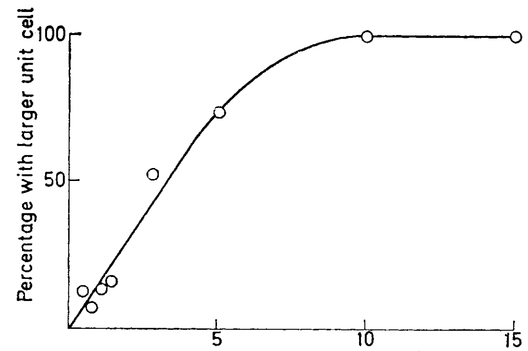

FIGURE 2 Estimated proportion of the $NaClO_4$–sodalite having the larger *d* spacings

X-*Ray Diffraction*.—In some sodalite hydrates *X*-ray powder photographs indicated line splitting suggesting two cubic phases with slightly different cell edges. This behaviour was observed in syntheses using 6 and 10 N NaOH 6 N NaOH. The splitting was reduced when samples were dried at 45 °C, and disappeared on drying at 100 °C. Thus the behaviour appeared to depend on the condition of drying.

Splitting of certain lines was also observed with some NaClO$_4$–sodalites. By means of a densitometer, and using one of the split lines for reference, the proportion of the form having the larger unit cell was estimated as a function of the concentration of NaClO$_4$ (Figure 2). Line splitting did not depend upon the drying temperature but was a function

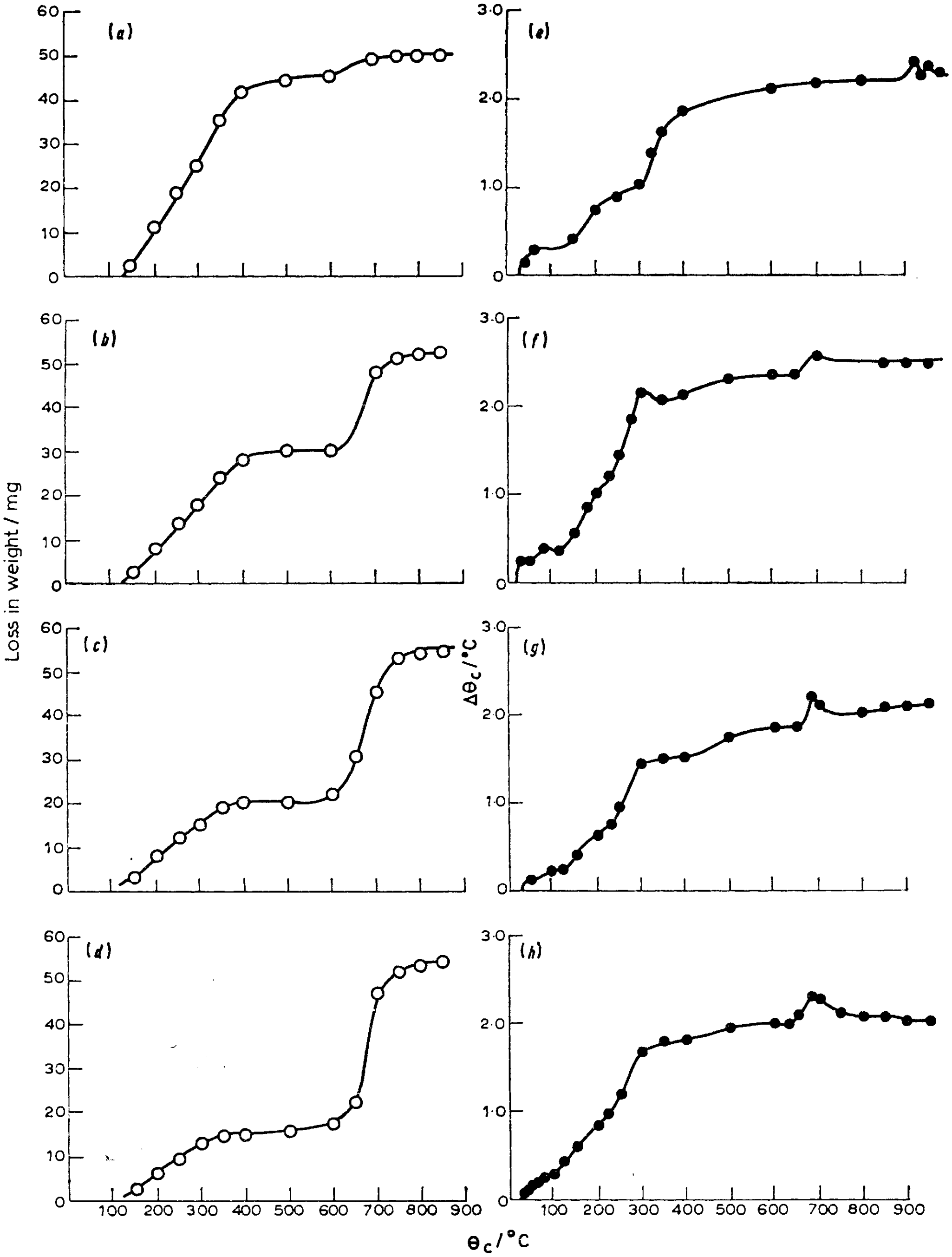

FIGURE 3 T.g.a. [(*a*)—(*d*)] and corresponding d.t.a. curves [(*e*)—(*h*)] for some NaClO$_4$-sodalites with different NaClO$_4$ contents. Weight % of oxygen evolved = 1.14 (*a*), 5.01 (*b*), 7.74 (*c*), and 8.88 (*d*)

but not 4 N alkali.[7] Syntheses of basic sodalite were repeated with 4, 6, 8, and 10 N NaOH at 80 °C for 5 d. Line splitting occurred in the air-dried products especially with

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[7] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 2534.

of the concentration of $NaClO_4$. The behaviour could be due to co-existence of a sodalite phase richer in water and one richer in $NaClO_4$.

Barrer and Cole[2] synthesised a sodium carbonate–sodalite with a doubled unit cell of 17.709 ± 0.007 Å. If there is Na_2CO_3 in every alternate tetradecahedral cage and 4 H_2O in each of the others, the ordering in the distribution of the guest molecules could then result in the doubled cell.

Differential Thermal and Thermogravimetric Analysis.—The oxo-salt–sodalites. In d.t.a. and t.g.a. the heating rate was 10 °C min^{-1}; in d.t.a. *ca.* 25 mg of sample was taken and in t.g.a. *ca.* 500 mg. Examples of some of the curves for $NaClO_4$– and $NaClO_3$–sodalites are shown respectively in Figures 3 and 4. In t.g.a. the first region of weight loss represents evolution of zeolitic water. As expected this loss becomes greater the lower the oxo-salt content. The

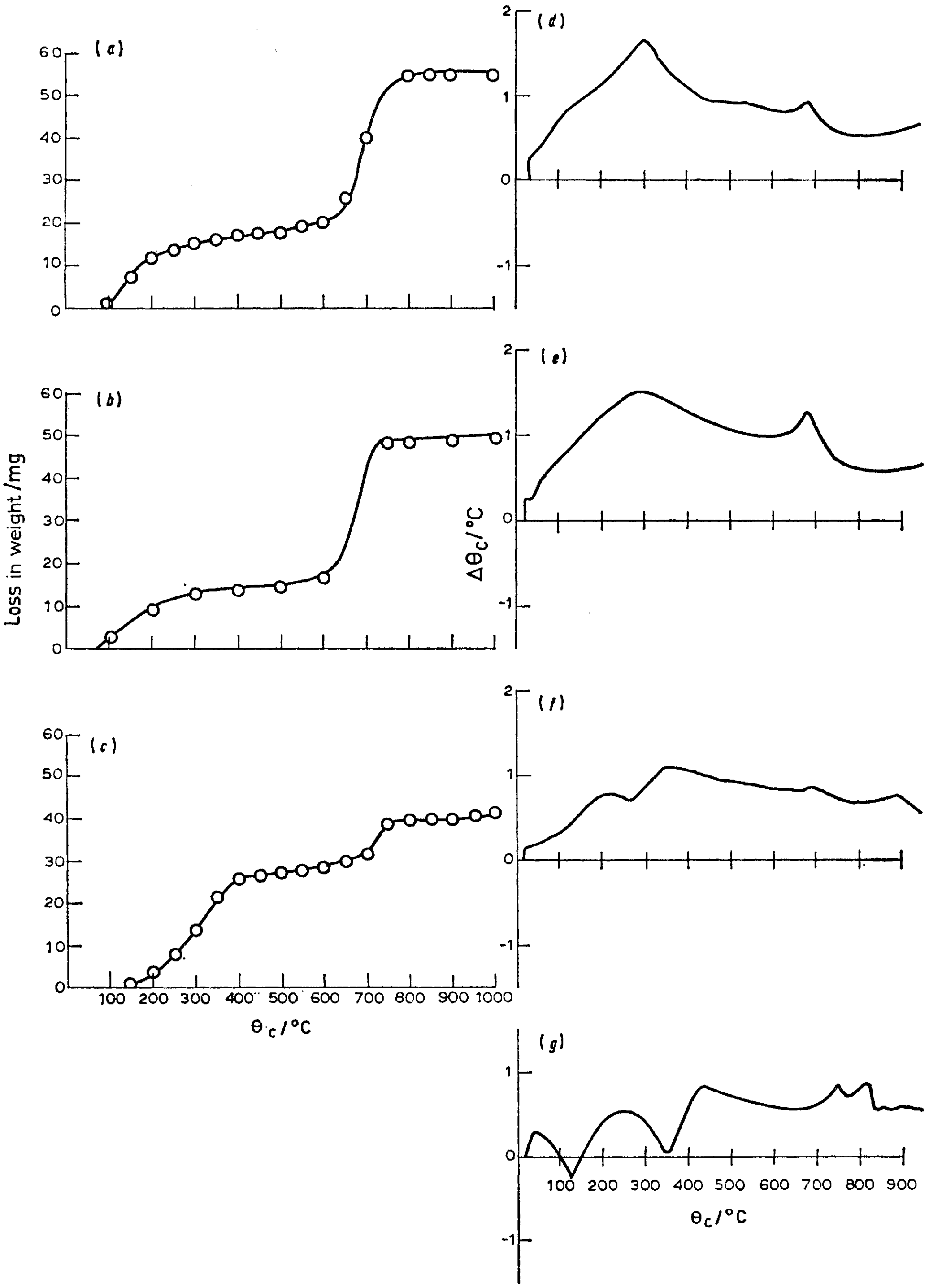

FIGURE 4 T.g.a. [(*a*)—(*c*)] and corresponding d.t.a. curves [(*d*)—(*f*)] for some $NaClO_3$–sodalites with different $NaClO_3$ contents. Curve (*g*) is for basic sodalite. Total weight % of oxygen evolved = 7.4 (*a*), 6.6 (*b*), and 2.45 (*c*)

second region of weight loss represents evolution of oxygen. For high $NaClO_3$ loadings oxygen evolution was first detectable at *ca.* 350 °C; as the chlorate content declined this temperature increased to *ca.* 500 °C. With $NaClO_4$–sodalite the corresponding temperatures were *ca.* 450 and *ca.* 600 °C. With $NaClO_2$–sodalite there was some overlap in the two regions of water loss and oxygen evolution.

The d.t.a. curves for the three oxo-salt–sodalites were very different from that of salt-free sodalite hydrate [curve (*g*), Figure 4]. Sodalite hydrate showed exotherms at *ca.* 750 and *ca.* 820 °C. All $NaClO_3$–sodalites gave a low-temperature exotherm and a second exotherm at *ca.* 670 °C. Thus there is thermal evidence of a two-stage breakdown of the oxo-salt. The low-temperature peak occurred at *ca.* 300 °C for highly loaded $NaClO_3$–sodalite and at *ca.* 350 °C for the sodalite with the lowest loading in $NaClO_3$ [5.32 g per g (%)]. When d.t.a. was conducted in a nitrogen atmosphere instead of air the low-temperature peak was observed at *ca.* 400 °C but the high-temperature one remained at *ca.* 670 °C. The two stages in $NaClO_3$–sodalite were demonstrated by measuring the d.t.a. curves of samples pre-heated at *ca.* 575 °C respectively for 3, 10, and 27 min and until all the oxygen was evolved [Figure 5(*a*)]. The low-temperature exotherm quickly disappeared but not that at 670 °C, except in the sample from which all the oxygen had been evolved. The probable stages are therefore: at *ca.* 350 °C, disproportionation of $NaClO_3$ to $NaClO_2$ and $NaClO_4$ and breakdown of $NaClO_2$ to NaCl and O_2; and, at the higher temperature (exotherm at *ca.* 670 °C), decomposition of $NaClO_4$ to $NaClO_2$ and O_2 and of the resulting $NaClO_2$ to NaCl and O_2.

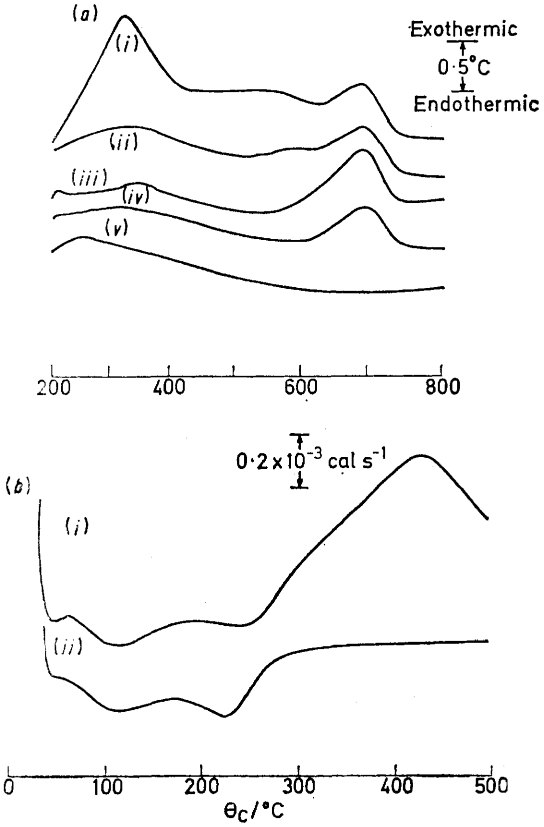

FIGURE 5 (*a*) Effect of pre-heating on the d.t.a. curves of a $NaClO_3$–sodalite with 7.1% of oxygen: (*i*) no pre-heating; (*ii*) 3 min at 575 °C; (*iii*) 10 min at 575 °C; (*iv*) 27 min at 575 °C; (*v*) pre-heated until no more O_2 was evolved. (*b*) Differential scanning calorimetry of NaN_3–cancrinite: (*i*) heating in air; (*ii*) heating in nitrogen. The sample contained 4.8 weight % of NaN_3

The $NaClO_2$ loading was never large [Figure 1(*c*)]. No exotherm at *ca.* 670 °C was observed so that thermal breakdown of $NaClO_2$ to NaCl and O_2 did not generate enough $NaClO_4$ (by the reaction $O_2 + NaClO_2 \longrightarrow NaClO_4$) to be detectable. The absence of the 670 °C exotherm also suggests that the amount of entrained $NaClO_3$ arising from the $NaClO_3$ impurity in the $NaClO_2$ must be low. A rather small exotherm at *ca.* 400 °C for samples most heavily loaded with $NaClO_2$ was not observed for those of lowest $NaClO_2$ content.

At the high-temperature end of the d.t.a. runs further exotherms occurred at temperatures which depended on the $NaClO_2$ content and which decreased as this content decreased. These exotherms were also observed with very lightly loaded $NaClO_4$– and $NaClO_3$–sodalites and are attributed to aluminosilicate-lattice breakdown. The dependence on temperature is determined by the amounts of the NaCl left in the sodalite framework when all oxo-salt has decomposed, and which stabilise the sodalite. The lowest recrystallisation exotherms were thus found with salt-free sodalite hydrate with peaks at *ca.* 750 and *ca.* 820 °C (Figure 4). The sodalites richest in original oxo-salt and hence, finally, in NaCl did not show a recrystallisation exotherm even at the highest accessible temperature (Figures 3 and 4).

Azide–cancrinite. Differential scanning calorimetry (d.s.c.) of the azide–cancrinite containing *ca.* 5.5 g per g (%) of azide gave the curves of Figure 5(*b*), for a heating rate of 10 °C min^{-1} in air [curve (*i*)] and in nitrogen [curve (*ii*)]. The strong exotherm in curve (*i*) at *ca.* 420 °C is missing from (*ii*) and is therefore attributed to a reaction with O_2. In both curves endothermal minima appeared at *ca.* 120 °C, and at *ca.* 250 [curve (*i*)] and *ca.* 220 °C [curve (*ii*)].

Bulk NaN_3 has a decomposition temperature of *ca.* 275 °C and the bulk reaction (1) is exothermic with ΔH *ca.* −43 kJ

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g) \qquad (1)$$

mol^{-1}. The decomposition of intracrystalline azide is therefore probably also exothermic so that the endotherms are not explained as azide decomposition but as loss of zeolitic water. The exotherm at *ca.* 420 °C in air could arise from reaction of oxygen either directly with azide or with the Na released by reaction (1). For oxidations (2) and (3)

$$2\,NaN_3 + O_2 \longrightarrow Na_2O_2 + 3\,N_2 \qquad (2)$$

$$2\,Na + O_2 \longrightarrow Na_2O_2 \qquad (3)$$

occurring in the bulk phases the heats are −550 and −505 kJ mol^{-1} respectively, and so they will also be strongly exothermic in the azide–cancrinite.

Kinetics of Release of Gas from Salt-Felspathoids.—The influence of temperature and, in the case of the oxo-salts the influence of salt concentration, were investigated.

Influence of temperature: azide–cancrinite. A notable feature of the release of nitrogen from azide–cancrinite is the two-stage nature of the rate curves [Figure 6(*c*)]. It has been stated that bulk azide (NaN_3) also decomposes in two stages, each with a distinct energy of activation.[8] In

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[8] Supplement II to 'Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry,' vol. 8, 'Nitrogen Part II,' Longmans, 1967, p. 43 and Tables IV and V.

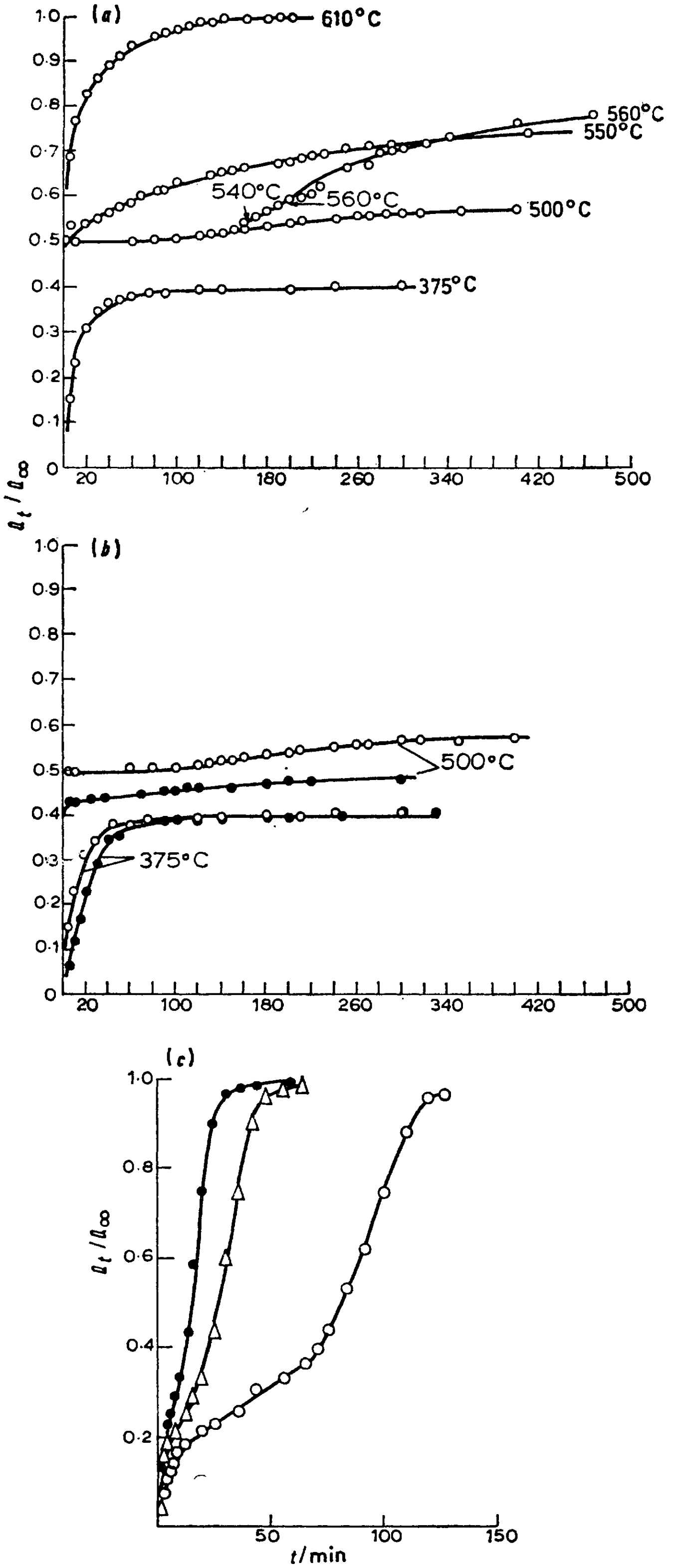

FIGURE 6 (*a*) Evolution of oxygen at different temperatures from $NaClO_2$–sodalite containing 3.14% by weight of $NaClO_2$. (*b*) Evolution of oxygen at different temperatures from two $NaClO_2$–sodalites containing 3.14 (○) and 1.5% by weight of $NaClO_2$ (●). (*c*) Evolution of nitrogen at different temperatures from NaN_3–cancrinite containing 5.5% by weight of NaN_3 at 550 (○), 575 (△), and 600 °C (●)

cancrinite the azide is in undecahedral cages, in the wide channels parallel to the *c* axis [Figure 1(*b*)] or in both. It is possible that when the Na released by azide decomposition reaches a critical concentration it begins to catalyse decomposition of the remainder of the azide. Figure 6(*c*) also shows the large temperature coefficient of the rate of nitrogen release. The form of the kinetic curves precludes activated diffusion of nitrogen as the only rate-determining step.

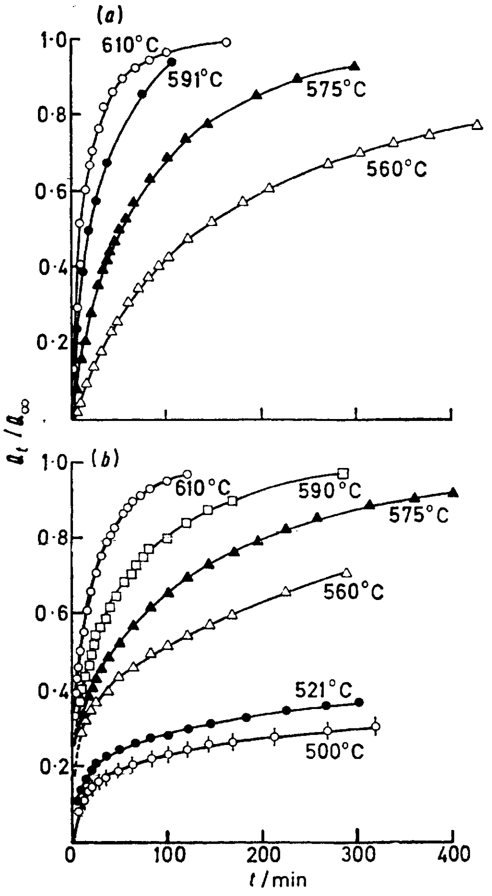

FIGURE 7 Evolution of oxygen at different temperatures from (*a*) $NaClO_4$–sodalite containing 18.1% by weight of $NaClO_4$, and (*b*) $NaClO_3$–sodalite containing 17.3% by weight of $NaClO_3$

Apparent energies of activation, E, were determined from expression (4) where t_1 and t_2 are the times required to reach

$$E = 19.2\,[T_1T_2/(T_1-T_2)]\,\log_{10}\,(t_2/t_1) \qquad (4)$$

the same value of Q_t/Q_∞ at each of two temperatures T_1 and T_2; Q_t and Q_∞ are the amounts of gas released at time t and

TABLE 1

Values of E (kJ mol^{-1}) derived from equation (4) for N_2 evolution from NaN_3–cancrinite

Q_t/Q_∞	T_1/K	T_2/K	E
0.4	873	848	153
	848	823	256
0.6	873	848	140
	848	823	256
0.8	873	848	140
	848	823	239

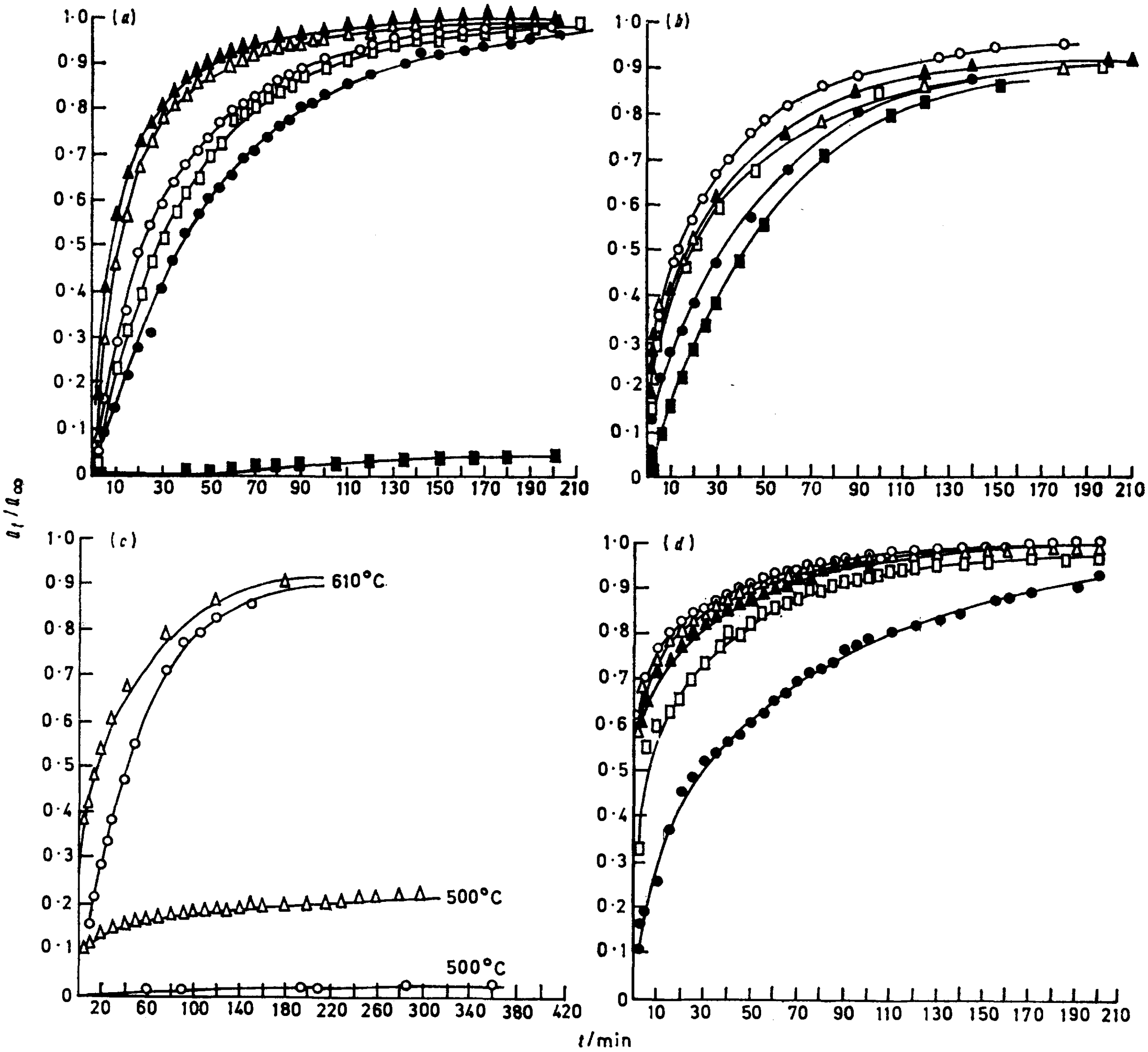

FIGURE 8 Concentration dependences of the fractional rates of oxygen release, Q_t/Q_∞. (*a*) $NaClO_4$–sodalite at 610 °C. Weight % of $NaClO_4$ = 19.5 (▲), 19.0 (△), 13.8 (○), 8.0 (□), and 2.0 (●) respectively. The curve (■) is for the 19.5 weight % sample at 490 °C. (*b*) $NaClO_3$–sodalite at 610 °C. Weight % of $NaClO_3$ = 18.5 (○), 17.8 (▲), 16.5 (□), 16.0 (△), 14.6 (●), and 5.23 (■) respectively. (*c*) $NaClO_3$–sodalite at 610 and 500 °C: (△) 16.5%; (○) 5.2% $NaClO_3$ by weight. (*d*) $NaClO_2$–sodalite at 610 °C. Weight % of $NaClO_2$ = 3.1_9 (○), 2.5 (△), 2.2_5 (▲), 1.5 (□), and 0.33 (●)

when the evolution of gas is complete and all the salt is therefore decomposed. The values of E (Table 1) show a strong dependence on temperature, but not on Q_t/Q_∞ in the range $0.4 \leqslant Q_t/Q_\infty \leqslant 0.8$. This range lies within the second stage of the reaction kinetics [Figure 6(*c*)].

When azide–cancrinite was first outgassed at 200 °C to remove as much zeolitic water as possible and was then heated *in vacuo* to 675 °C to release all the nitrogen, the product was bluish grey, a colour ascribed to sodium in the cancrinite. The e.s.r. spectrum of the product showed a very broad line (*g ca.* 2.0_9) which could be due to Na atoms. The colour recalls the black, purple, and blue sodalite–sodium complexes formed by heating outgassed sodalite hydrate in Na vapour and then progressively reducing the Na content by heating *in vacuo*.[9]

Influence of temperature: oxo-salts–sodalite. The kinetics of oxygen evolution from $NaClO_2$–sodalite are shown in Figure 6(*a*) and 6(*b*), and those for $NaClO_4$– and $NaClO_3$–sodalite in Figure 7(*a*) and 7(*b*). Apparent activation energies, E, were evaluated from equation (4). The results (Table 2) show that for $NaClO_3$ the apparent E tends to

TABLE 2

Values of E (kJ mol^{-1}) from equation (4)

$NaClO_4$–Sodalite				$NaClO_3$–Sodalite			
Q_t/Q_∞	T_1/K	T_2/K	E	Q_t/Q_∞	T_1/K	T_2/K	E
0.4	848	833	376	0.2	794	773	220
0.6	848	833	398	0.4	848	833	252
	864	848	352	0.6	848	833	312
					863	848	310
0.8	883	848	288		883	863	258
				0.8	883	848	318

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[9] R. M. Barrer and J. F. Cole, *J. Phys. and Chem. Solids*, 1968, **29**, 1755.

increase with Q_t/Q_∞ as would be expected for at least two consecutive reactions of which the last had the highest activation energy. The dependence of E on Q_t/Q_∞ was less marked with $NaClO_4$. Chemical steps compatible with the above behaviour and with the d.t.a. and t.g.a. curves (Figures 4 and 5) are given below:

$NaClO_3$–sodalite

$$2\,NaClO_3 \longrightarrow NaClO_2 + NaClO_4 \qquad (5)$$

$$NaClO_2 \longrightarrow NaCl + O_2 \qquad (6)$$

$$NaClO_4 \longrightarrow NaClO_2 + O_2 \qquad (7)$$

followed by reaction (6) again

$NaClO_4$–sodalite

(7) followed by (6)

Reactions (5) and (6) occur at lower temperatures in d.t.a. and t.g.a. than (7). It is thus expected that reaction (7) has the highest value of E, as shown in Table 2 for $NaClO_4$–sodalite. With $NaClO_3$–sodalite processes (5) and (6) occur most readily and are reflected in the lower E for smaller Q_t/Q_∞. Over the later stages, *e.g.* with $Q_t/Q_\infty = 0.8$, E approaches the value for $NaClO_4$–sodalite because reaction (7) is now involved [followed rapidly by (6)]. An overall influence of activated diffusion of oxygen is not ruled out and is considered later.

Oxygen evolution from $NaClO_2$–sodalite was incomplete at low temperatures [Figure 6(*a*) and 6(*b*)]. Reaction commenced readily at *ca.* 375 °C and then ceased. Further reaction began above 500 °C [Figure 6(*a*)]. By 610 °C the overall reaction was rapid and did not differentiate the above two stages. After virtual cessation at 500 °C *ca.* 50% of the total oxygen had been evolved. Figure 6(*a*) shows a run at 500 °C, and a second at 500 °C with a rise after 160 min to 540 °C and finally to 560 °C. The behaviour suggests that O_2 released at these lower temperatures by reaction (6) cannot readily escape, and may in part reverse (7), according to reaction (8) for which[10] $\Delta H = -81.6$ kJ mol^{-1}. Sodium perchlorate in sodalite did not release

$$NaClO_2 + O_2 \longrightarrow NaClO_4 \qquad (8)$$

appreciable amounts of O_2 at 500 °C so that the two stages of oxygen evolution are understandable. However, at 610 °C reaction (8) is not important since all the oxygen is readily evolved. In d.t.a. of $NaClO_2$–sodalite no evidence was obtained of the exotherm at *ca.* 670° C characteristic of reaction (7) followed at once by (6). The $NaClO_2$ content of the $NaClO_2$–sodalites is always low [Figure 1(*c*)] and that of any $NaClO_4$ resulting from reaction (8) must be still lower.

Concentration dependence: oxo-salt–sodalites. For all three oxo-salts ($NaClO_4$, $NaClO_3$, and $NaClO_2$) the quotients Q_t/Q_∞ depend on oxo-salt concentration in the sodalite structure [Figure 8(*a*)—8(*d*)]. In $NaClO_3$-sodalite evidence for reactions (5) and (6) follows from consideration of the times, $t_{0.8}$, for Q_t/Q_∞ to reach 0.8 (Table 3). Reactions (5) and (6) together release a third of the total oxygen. The $NaClO_4$ formed in reaction (5) subsequently liberates two thirds of this oxygen. Thus $t_{0.8}$ is likely to be more characteristic of the concentration of $NaClO_4$ formed in reaction (5) than of the $NaClO_3$ initially present. Table 3 gives $t_{0.8}$ at 610 °C and the oxo-salt contents for the $NaClO_2$–, $NaClO_3$–, and $NaClO_4$–sodalites. Values of $t_{0.8}$ in columns 3 and 6 of Table 3 may be compared with the perchlorate contents (columns 5 and 7). In accordance with the above expectation, for comparable perchlorate contents the values of $t_{0.8}$ for $NaClO_3$– and $NaClO_4$–sodalites are not very different.

TABLE 3

Values of $t_{0.8}$ (min) for oxygen release from oxo-salt–sodalites at 610 °C

$NaClO_2$–Sodalite		$NaClO_3$–Sodalite			$NaClO_4$–Sodalite	
$t_{0.8}$	$NaClO_2$ (10^2 g/g)	$t_{0.8}$	$NaClO_3$ (10^2 g/g)	$NaClO_4$ formed (10^2 g/g)	$t_{0.8}$	$NaClO_4$ (10^2 g/g)
16.5	3.1	54.5	18.45	11.3	28.5	19.5
19	2.5	70	17.84	10.9	34.3	19.1
25.5	2.2_5	80.5	16.53	10.1	72	13.8
43.3	1.5	80.5	16.00	9.2	79	8.0
109	0.33	91	14.60	8.5	100	2.0
		105.5	5.23	3.0		

The $t_{0.8}$ values for oxygen release from $NaClO_2$-sodalite are increased because of the small $NaClO_2$ concentration. However, at the most nearly comparable oxo-salt contents (the first or second lines in Table 3 for $NaClO_2$–sodalite and the last lines for $NaClO_4$– and $NaClO_3$–sodalites), $t_{0.8}$ is much less for $NaClO_2$ than for the other two oxo-salts. This supports the view that reaction (6) occurs more rapidly than (7), and that $NaClO_2$ in the crystal matrix is thermally less stable than $NaClO_4$.

DISCUSSION

Thermochemical Considerations.—For the bulk-phase reactions involving pure oxo-salts one has[10] $\Delta H_1 = 27.8$, $\Delta H_2 = -105$, and $\Delta H_3 = 81.6$ kJ mol^{-1} for reactions (5)—(7). The signs of each of these heats should be the same in the sodalite matrix as for the corresponding bulk-phase reaction. If reactions (5) and (6) overlap the nett process is exothermic in accord with the low-temperature exotherm of $NaClO_3$-sodalite (Figure 4). Similarly if reactions (6) and (7) overlap the high-temperature exotherm at *ca.* 670 °C follows (Figure 3 and 4). Finally the exotherm for $NaClO_2$-sodalite at *ca.* 400 °C is also understood according to the sign of the heat of reaction (6).

Concentration Dependence of Q_t/Q_∞.—The rate of evolution of oxygen may be controlled by chemical steps, by diffusion, or by both. This control may be considered in the light of the increase in Q_t/Q_∞ at a given time with initial oxo-salt content.

For control by chemical steps the simplest case is provided by $NaClO_2$-sodalite [equation (6), k_2 is the rate constant]. At 610 °C reaction (8) need not be considered and so we obtain expression (9) and Q_t/Q_∞ cannot depend

$$Q_t/Q_\infty = 1 - \exp(-k_2 t) \qquad (9)$$

at time t on the initial oxo-salt content. For the decomposition of $NaClO_4$ at 610 °C the reactions are (7) (rate

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[10] Nat. Bur. Stand. Circular 500, 1952, pp. 451—452.

constant k_3) and (6). For these consecutive reactions expression (10) applies which again makes Q_t/Q_∞ at

$$Q_t/Q_\infty = 1 - \tfrac{1}{2}\exp(-k_3t) - \frac{[k_2\exp(-k_3t) - k_3\exp(-k_2t)]}{2(k_2 - k_3)} \quad (10)$$

given t independent of initial $NaClO_4$ content. Only for $NaClO_3$ in sodalite, where the first postulated step (5) is bimolecular, would Q_t/Q_∞ increase with the initial $NaClO_3$ concentration. However, as this was the case with all three oxo-salts (Figure 8), purely chemical control does not seem possible.

For diffusion control from equal spheres of radius r_0 in which D is the constant diffusion coefficient of oxygen we obtain expression (11), again making Q_t/Q_∞ at time t

$$Q_t/Q_\infty = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp - \frac{Dn^2\pi^2t}{r_0^2} \quad (11)$$

independent of the initial oxo-salt content. However, three conditions could alter this conclusion. (*i*) The greater the oxo-salt concentration the more fully are the diffusion paths of escaping O_2 molecules obstructed by oxo-salt or by NaCl formed from it. This would make D, and Q_t/Q_∞ at time t, decrease as the oxo-salt concentration increased, the opposite to the behaviour shown in Figure 8. (*ii*) The greater the oxo-salt concentration the higher the local concentration (c) and activity (a) of the O_2 formed. This would presumably increase the term $d\ln a/d\ln c$ in expression (12) where B denotes the mobility.

$$D = B\, d\ln a/d\ln c \quad (12)$$

If the decrease in B due to (*i*) is more than offset by $d\ln a/d\ln c$ as oxo-salt concentration increases, an increase of Q_t/Q_∞ at time t with oxo-salt content could be expected. (*iii*) If the effective radius r_0 of the crystals grown became smaller the larger the oxo-salt content, D/a^2 in equation (11), and so Q_t/Q_∞ at given t, would increase. Crystallisation yielded clusters and spherulitic growths to which it was difficult to ascribe values of r_0, and so decrease of r_0 with increasing oxo-salt content cannot be ruled out.

Since (*ii*) and (*iii*) seem the only simple ways of explaining the apparent concentration dependence of Q_t/Q_∞ at time t, it is suggested that the kinetics are controlled either by diffusion or by combined diffusion and chemical reaction, but not by chemical reaction alone. Finally it is noted that for the ideal unit-cell compositions $6(NaAlSiO_4)\cdot 2NaX$ ($X = ClO_4$, ClO_3, or ClO_2) the oxidising power corresponds to 81, 62, and 43 cm^3 of O_2 per g of reagent at s.t.p.

E. A. D. thanks the British Council, and G. A. M. the Wolfson Foundation, for support.

[6/181 *Received, 27th January, 1976*]