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Report

THE BEHAVIOUR IN THE ATMOSPHERE OF THE AEROSOL FROM A SODIUM FIRE

W. S. CLOUGH J. A. GARLAND

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Health Physics and Medical Division,
Atomic Energy Research Establishment,
Harwell, Berkshire.

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1. Introduction

If an accidental release of radioactive material should occur from a sodium cooled fast reactor any resulting radiation hazard would be determined by the physical and chemical forms of the aerosols. In this paper an attempt is made to forecast the nature of such an aerosol. Radioactive aerosols released from a sodium cooled reactor are unique in that the activity will probably be firmly associated with the sodium from the beginning of the release and interactions with adventitious atmospheric aerosols or trace impurities (e.g. organic materials) will be excluded at least during the early stages. However the sodium, which forms the great majority of the mass of the aerosol is very reactive towards some of the major constituents of the atmosphere - notably oxygen, water and carbon dioxide. The nature of the chemical reactions which follow the release of a sodium aerosol into the atmosphere is considered in this paper. It is shown that hygroscopic products result and the consequent changes in particle size and atmospheric deposition characteristics of the aerosol are discussed.

2. The chemical form of sodium in the atmosphere

2.1 Reaction with oxygen

Thermochemical data can be used to predict the stable states which are formed when sodium reacts with oxygen and water vapour in the atmosphere. In an environment containing an excess of sodium (e.g. in a reactor containment) oxygen reacts with sodium according to the reaction.

$$Na_{(c)} + 1/4\ O_{2(g)} \rightarrow \tfrac{1}{2}\ Na_2O_{(c)} \quad \Delta H_{298} = -49.7 \text{ Kcal/mole}$$

However, in the excess of oxygen which is eventually present in the case of sodium release to the atmosphere the above reaction is less favourable than

$$Na_{(c)} + \tfrac{1}{2}\ O_{2(g)} \rightarrow \tfrac{1}{2}\ Na_2O_{2(c)} \quad \Delta H_{298} = -60.3 \text{ Kcal/mole}$$

or

$$Na_{(c)} + O_{2(g)} \rightarrow NaO_{2(c)} \quad \Delta H_{298} = -61.9 \text{ Kcal/mole}$$

and the formation of a mixture of peroxide and superoxide is expected.

2.2 Reaction with water vapour

Neither sodium peroxide nor the superoxide are stable with respect to water - each reacts to give sodium hydroxide according to the reactions

$$Na_2O_{2(c)} + H_2O_{(g)} \rightarrow 2NaOH + \tfrac{1}{2}\ O_2 \quad \Delta H_{298} = -26.27 \text{ Kcal/mole}$$

and

$$2NaO_{2(c)} + H_2O_{(g)} \rightarrow 2NaOH + \tfrac{3}{2}\ O_2 \quad \Delta H_{298} = -23.07 \text{ Kcal/mole}$$

Thus the enthalpy calculations suggest that a sodium aerosol released into the atmosphere would be converted to the form of sodium hydroxide. Standard state free energy changes for the above reactions (from which equilibrium constants could have been calculated) have not been calculated due to the absence from the literature of some of the basic data for the oxides of sodium. However experience indicates that the reactions predicted by the enthalpy changes do in fact occur, for sodium is known to react rapidly with oxygen and the resulting oxides remove water vapour from the atmosphere to form sodium hydroxide. The kinetics of the reaction of oxygen and water vapour in the atmosphere with sodium have not been investigated experimentally but a small piece of sodium exposed in air forms a pool of hydroxide solution within minutes and the reaction would be expected to be even faster in the case of a finely divided aerosol. The sodium hydroxide which is formed is hygroscopic and will condense more water forming a droplet the dimensions of which will to a large extent determine the physical behaviour of the aerosol.

2.3 Reaction with carbon dioxide

The atmosphere normally contains carbon dioxide at a partial pressure of about 0.00033 atm. The reaction between carbon dioxide and sodium hydroxide is energetically favourable

$$2NaOH_{(c)} + CO_{2(g)} \rightarrow Na_2CO_{3(c)} + H_2O_{(1)} \quad \Delta G^{o}_{298} = -30.4 \text{ Kcal/mole}$$

and the reaction has been used in the industrial préparation of sodium carbonate.

Continued absorption of carbon dioxide into a droplet of sodium hydroxide will lead to the formation of a solution which at equilibrium will be a mixture of carbonate and bicarbonate. The position of the equilibrium has been investigated by McCoy and Smith (1903) who showed the effect of total sodium concentration (C), solubility of carbon dioxide (S gram mole/litre at 1 atm. pressure) and partial pressure of carbon dioxide (P atmospheres) on the fraction of sodium present in the form of the bicarbonate (X). Harte et al. (1933) extended the work to include a term for the effect of temperature (t) and developed from experimental results the expression

$$\frac{X^2 \quad C^{1.29}}{SP\ (1-X)(185-t)} = 10$$

This expression has been used to calculate the results shown in Fig. 1 for the percentage of bicarbonate present as a function of normality for the range of temperature shown at a fixed CO_2 pressure of 0.00033 atmospheres. The effect of variation in the ambient partial pressure of carbon dioxide is also shown in Fig. 1. The change in X for a 15% variation in carbon dioxide pressure at $10^{0}C$ is shown. The ambient carbon dioxide pressure does not usually change by more than 10%.

It should be noted that all the above calculations are applicable to the behaviour of sodium in the atmosphere only if chemical equilibrium is achieved in a time which is short compared to the residence time of the sodium in the atmosphere. While this assumption is probably reasonable for the formation of oxides, hydroxide and carbonate, it may not be true for the equilibrium between carbonate and bicarbonate. This point will be further dealt with in section 5.

3. Physical changes affecting the sodium compounds exposed to a humid atmosphere

When crystals of a deliquescent material are exposed to a humid atmosphere they absorb water, so that a solution is formed. Absorption of water continues until the solution has been diluted to such an extent that it is in equilibrium with the air above it. Subsequent changes in the humidity of the air cause further condensation or evaporation of water. The equilibrium relative humidity for a saturated solution of a given solute is critical: if the relative humidity is below this value no condensation will take place on crystals of the solute, but once the critical value of the relative humidity is exceeded condensation of water will occur and a solution will be formed. However it has been observed (Dessens, 1949) that small droplets may remain as supersaturated solutions for periods of minutes or even hours when the relative humidity falls again.

Several authors (e.g. Wright (1936), Mason (1957), and recently Garland (1969)) have indicated how the equilibrium size of droplets containing deliquescent materials may be calculated. In the present paper the equilibrium radius, r, was found by solving the following equation:

$$H = H^1 \exp\left(\frac{2 \gamma M}{\rho R T r}\right)$$

where H is the relative humidity of the air

H^1 is the relative humidity in equilibrium with a flat surface of solution of the same concentration and temperature as the droplet,

γ is the surface tension of the droplet solution,

ρ is the density of the droplet,

R is the gas constant,

T is the absolute temperature,

M is the molecular weight of water.

Solving the equation is not simple since γ, ρ and H^1 are all functions of the concentration of the droplet solution and therefore of the mass of solute and the droplet radius. Therefore a computer programme was written to solve the equation by a successive approximation method.

Previous authors used Raoult's law to calculate H^1. In the case of electrolyte solutes this involves a knowledge of van't Hoff's factor. However McDonald (1952) has shown that this factor varies with concentration and the present authors prefer to use experimental values for H^1. Tabulated values for this quantity, for γ and for ρ were obtained from International Critical Tables, and linear interpolation was used for intermediate values.

Calculations for sodium hydroxide and sodium carbonate were carried out for a wide range of particle masses at 10°C. The shape of the curves is expected to depend only slightly on temperature but the solubility and therefore the relative humidity at which droplets form may change with temperature. The graphs (Figs. 2 and 3) show the results. The size of the dry particle is also shown and a scale at the top of each graph allows the mass of sodium present in each particle to be read off, by comparison with the dry particle size.

One of the most significant differences between the results is in the relative humidity at which the particles dissolve. The hydroxide particles are present as solution drops whenever the relative humidity is above 35% (except for very small particles) but the carbonate does not dissolve until the humidity reaches 95%. The comparable figure for sodium bicarbonate is 92%.

It was not possible to perform the calculations accurately for sodium bicarbonate solutions because of lack of data on H^1 and γ. However calculations of H^1 from Raoult's law indicates that the true values are likely to be close to those for sodium hydroxide. As γ is not expected to differ greatly between hydroxide and bicarbonate solutions the graph for the equilibrium droplet size for sodium bicarbonate is likely to be similar to that for sodium hydroxide shown in Fig. 2. The major difference is that the bicarbonate particles will not begin to grow as droplets until the relative humidity is higher than 92%.

Although no large change in droplet size is expected to accompany the conversion of carbonate to bicarbonate, a decrease in pH from 11 to 8 will occur. The resulting sodium bicarbonate will still be basic with respect to vegetation generally (pH usually < 6) but the effect of any change in pH on the absorption and wash off characteristics remains speculative. The results from the calculation of the equilibrium between carbonate and bicarbonate (see section 3) have been included in Fig. 3. The areas marked on the graph show the range of sodium concentrations for which the equilibrium composition is either greater than 90% carbonate or greater than 90% bicarbonate at 10°C.

4. Rates of reactions

4.1 The reaction with oxygen and water vapour

The chemical rate of reaction of metallic sodium with oxygen and water vapour is known to be very rapid and the limitation on the rate of reaction is likely to be the physical access of the reacting gas to the sodium surface. In the case of massive pieces of sodium the reaction with oxygen eventually becomes slow due to formation of a protective layer. However reaction with the first millimeter depth of a clean sodium surface can be seen to be very rapid and it seems unlikely that the oxide layer formed is impervious enough to prevent rapid total oxidation of aerosols of sodium with diameters up to several tens of microns. In the case of water vapour the reaction product, sodium hydroxide, is soluble in the water vapour which will be condensed from the atmosphere so that a fresh surface of sodium oxide will be continuously exposed.

4.2 The reaction rate of carbon dioxide with droplets of sodium hydroxide

The chemical rate of reaction between carbon dioxide and hydroxyl ions has been shown to be very high and the rate of formation of carbonate in a droplet of sodium hydroxide will be controlled either by the gas phase diffusion rate of CO_2 to the droplet surface or the liquid phase diffusion rates of the reactants in the droplet.

In the case of gas phase diffusion of carbon dioxide to a droplet of sodium the rate can be calculated from the equation derived by Chamberlain et al. (1960) from Fuchs' theory of evaporation of droplets

$$\frac{da}{dt} = \frac{4\,r\,\pi\,DC}{\frac{D}{rv\alpha} + \frac{r}{r+\Delta}}$$

where a is the number of molecules absorbed in time t

D is the diffusion coefficient in air

C is the concentration in the gas phase

r is the radius of the droplet

$\nu = (RT/2\pi M)^{\frac{1}{2}}$ is a quarter of the mean kinetic velocity of the molecule

α = the accommodation coefficient for capture of the molecule at the droplet surface

Δ = a length of the order of the mean free path of the molecule.

For a given mass of dry sodium aerosol the equilibrium droplet size of sodium hydroxide can be calculated at any given relative humidity (see previous section). For the known mass of sodium the number of moles of sodium hydroxide in the droplet can be calculated and using the above equation the time required for the diffusion to the droplet of enough carbon dioxide to react with all the hydroxyl ions can be calculated. Some examples of the results of such calculations are shown in Table 1.

Table 1

Mass of Sodium g.	R.H. %	Equil. NaOH Droplet Radius µm	Reaction Time secs
7×10^{-17}	99	0.1	10^{-5}
5×10^{-14}	99	1	10^{-3}
5×10^{-11}	99	10	10^{-1}
1×10^{-15}	40	0.1	10^{-4}
1×10^{-12}	40	~ 1	10^{-2}
1×10^{-9}	40	10	1

The calculations are approximate in so far as they assume $\alpha = 1$ and no allowance has been made for the change in droplet size as the reaction proceeds. In a large sodium release the carbon dioxide and water vapour pressures at the centre of the plume could be less than those for ambient conditions which has been assumed above. However the method is probably sufficiently accurate for the order-of-magnitude results quoted above and to allow a comparison of gas phase and liquid phase diffusion rates to be made.

The rate of diffusion of carbon dioxide within a droplet can be estimated using the equation for the rate of diffusion along the radius given by Crank (1956)

$$Qt = 4\pi Dt \frac{ab}{b-a} (C_2 - C_1)$$

Where Qt = the amount diffusing in time t

D = diffusion coefficient

a = radius of sphere to which the molecule diffuses

b = total radius of the droplet

C_2 = concentration at surface of droplet

C_1 = concentration at surface of sphere of radius a.

C_2 can be calculated for CO_2 from Henries law, C_1 is assumed to be zero when $a = \frac{b}{10}$.

Using the above equation the time required for diffusion of sufficient CO_2 into the droplet to react with all the hydroxide present can be calculated. Some examples of the results of such calculations are shown in Table 2.

Table 2

Mass of Sodium g.	R.H. %	Equil. NaOH Droplet Radius µm	Reaction Time secs.
7×10^{-17}	99	0.1	10^{-4}
5×10^{-14}	99	1.0	10^{-2}
5×10^{-11}	99	10	1
1×10^{-15}	40	0.1	10^{-2}
1×10^{-12}	40	1.0	1
1×10^{-9}	40	10	100

The reaction times calculated are probably best regarded as an upper limit because the method of calculation contains the assumption that the CO_2 diffuses a distance b-a before reacting. In fact reaction will occur at all points along b but the more complex calculation for this case is probably not justified because the enthalpy change, possible mixing within the droplet and change of droplet size during the course of the reaction introduce large uncertainties which are not allowed for in the calculation.

Comparison of Table 1 and Table 2 shows that over the whole range of droplet sizes and relative humidities considered the reaction rate will be controlled by diffusion of carbon dioxide in the liquid phase and the reaction time for complete conversion of a sodium hydroxide droplet to a sodium carbonate droplet is in all cases likely to be less than a few minutes.

4.3 The reaction rate of carbon dioxide with sodium carbonate solutions

The literature on the rate of attainment of the equilibrium between carbon dioxide, carbonate and bicarbonate is extensive, usually from industrial sources, and often contradictory. It seems certain, however, that the rate depends on a chemical rate constant which will be slow compared to diffusion of CO_2 in the liquid or gas phase but may be increased by the presence of catalysts. McCoy et al. (1903) give the time for attainment of equilibrium for ambient air bubbled through sodium carbonate solutions as about 70 hours but this figure can only be regarded as an approximate guide to the reaction rate of CO_2 with a sodium carbonate aerosol because of the very different and variable conditions in the aerosol case.

5. Discussion

Ettinger, Moss and Busey (1967) report the results of an experimental investigation into the size distribution of the smoke which results when sodium metal burns in air and other oxygen-nitrogen mixtures. Large numbers of submicron particles were found, but most of the mass was associated with larger particles, the mass median diameters ranging from 0.5 to 16.17 μ. These sizes are very much larger than those reported for plutonium fires in the same paper. Several of the samples were collected from fires in humid air. In these cases the particles collected were presumably of sodium hydroxide. However, droplets would have evaporated before examination in the electron microscope and the sizes reported are dry sizes.

Although the results of individual experiments are too variable to justify a detailed analysis, it is of interest to consider what changes might occur when particles of sodium oxide in the size range indicated by these results escape into the atmosphere. Table 3 gives some of the expected properties of the aerosol particles at the different stages considered below.

The first change which occurs is the conversion to sodium hydroxide. This is expected to occur rapidly, and in the case of a large fire the time taken will probably be determined by the time taken for turbulent mixing and diffusion to bring sufficient water vapour into the cloud of combustion products. The thermal rise of the cloud may be expected to assist this mixing, and the time is not likely to be more than a few minutes, even for a massive cloud. Similarly, condensation of water vapour with dissolution of the particles to form droplets will occur as the water vapour becomes available and the relative humidity exceeds the critical value of 35%.

The expected growth of the droplets to their equilibrium size at the ambient relative humidity will probably be prevented by the formation of sodium carbonate, proceeding simultaneously. At low humidities (below 35%) the particle will remain dry at all stages and the chemical conversion to the final form (sodium carbonate) will proceed slowly, and perhaps incompletely, because of the lack of an aqueous phase. Under most conditions however (35% < RH < 92%) the droplet of sodium hydroxide will dry out rapidly as carbon dioxide is incorporated, the final product being a particle of hydrated carbonate. At higher humidities a relatively large droplet of carbonate solution will be produced.

Further uptake of carbon dioxide to form sodium bicarbonate will probably progress slowly and rather incompletely except at very high humidities. Raoult's law suggests that a small increase in droplet size will accompany the chemical change as the number of ions in solution increases from three to four for each two sodium atoms. Available evidence suggests that conversion to bicarbonate will take place to a substantial extent only if the relative humidity approaches or exceeds 99%.

Table 3 presents information on the size and deposition velocity attained by particles of a number of different sodium contents at the various stages discussed above and under a number of relative humidities. Deposition velocities were estimated using the results discussed by Chamberlain (1967). For several of the particle sizes in the range of the results of Ettinger et al. the deposition rate is increased by about an order of magnitude when the relative humidity becomes large. The hygroscopic growth of the particles will also have an appreciable effect on deposition in rain. Results quoted by Chamberlain (1967) show that 30 micron particles are removed almost completely from the atmosphere by an hour or so of moderate rain (2 mm/hr). The rate increases rapidly with particle size and is about ten times slower for particles around 5 microns diameter.

Clouds of particles with such wide size distributions (e.g. geometric standard deviation up to 3.25) as those found by Ettinger et al. (1967) must be expected to change in physical characteristics during their travel through the atmosphere. The larger particles (> 10 μ diameter) will deposit much more rapidly than the submicron particles. If the mixing depth of the atmosphere is taken as 1 km the relaxation time for deposition (height divided by deposition velocity) will be seen to be a few hours for these particles when the humidity is high. If substantial amounts of activity are released in this size range considerable contamination over a range of a few hundred kilometers downwind might be expected. Rain falling through the cloud may remove practically all the larger sizes within an hour or

Table 3

Examples of particle size and deposition velocity attained by sodium particles under various atmospheric conditions

Mass of sodium particle g	Particle as sodium hydroxide								Particle as sodium carbonate decahydrate					
	Dry		70% R.H.		90% R.H.		99% R.H.		Dry*		95% R.H.		99% R.H.	
	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}	Radius µm	Deposition velocity cm sec^{-1}
5.10^{-14}	0.3	3.10^{-2}	0.41	3.10^{-2}	0.55	3.10^{-2}	1.1	4.10^{-2}	0.37	3.10^{-2}	0.60	3.10^{-2}	1.0	4.10^{-2}
2.10^{-12}	1.0	4.10^{-2}	1.4	5.10^{-2}	1.8	7.10^{-2}	3.8	0.3	1.2	4.10^{-2}	2.0	7.10^{-2}	3.3	0.2
5.10^{-11}	3.0	0.15	4.1	0.4	5.5	0.7	11	2	3.7	0.3	6.0	0.8	10	0.1
2.10^{-9}	10	1.5	14	2	18	3	40	6	12	2	20	3	33	4
5.10^{-8}	30	4	42	6	55	9	120	35	37	5	65	12	110	30

Deposition velocities are based on experimental results of Chamberlain (1967) and apply to a wind speed of 7 m/sec^{-1} (25 mk/hr) over grass of height 10 cm. The experiments were carried out with dry particles and there was some evidence that droplets, which would adhere to the grass, would have deposition velocities a few times greater.

*Lower states of hydration than the decahydrate are stable at relative humidities smaller than about 80%. The particle size will then be slightly smaller.

so leading to more concentrated local contamination. Only the particles smaller than a few microns would then be left suspended. Washout and deposition of these particles will be much slower and will normally be spread over a much larger area.

6. Conclusions

The chemical form and physical size of the particles or droplets formed when sodium is released into the atmosphere will be modified by the presence of oxygen, water vapour and carbon dioxide in the atmosphere. The chemical form under various conditions has been predicted and the equilibrium droplet size for a given sodium compound has been calculated as a function of sodium mass and relative humidity. The formation of sodium carbonate from sodium hydroxide droplets is controlled by liquid phase diffusion of reactants in the drop and probably occurs in times less than a few minutes. The formation of sodium bicarbonate from sodium carbonate droplets is much slower and delays of tens of hours may elapse before equilibrium is achieved.

At high relative humidities the final state will certainly be a droplet of solution. At humidities below 95% the final state will be a particle of sodium carbonate, although droplets of hydroxide solution may be present for a time of the order of 1 minute or less. The appreciable changes in size consequent upon changes in relative humidity may lead to important changes in the residence time and deposition of the particles in the atmosphere.

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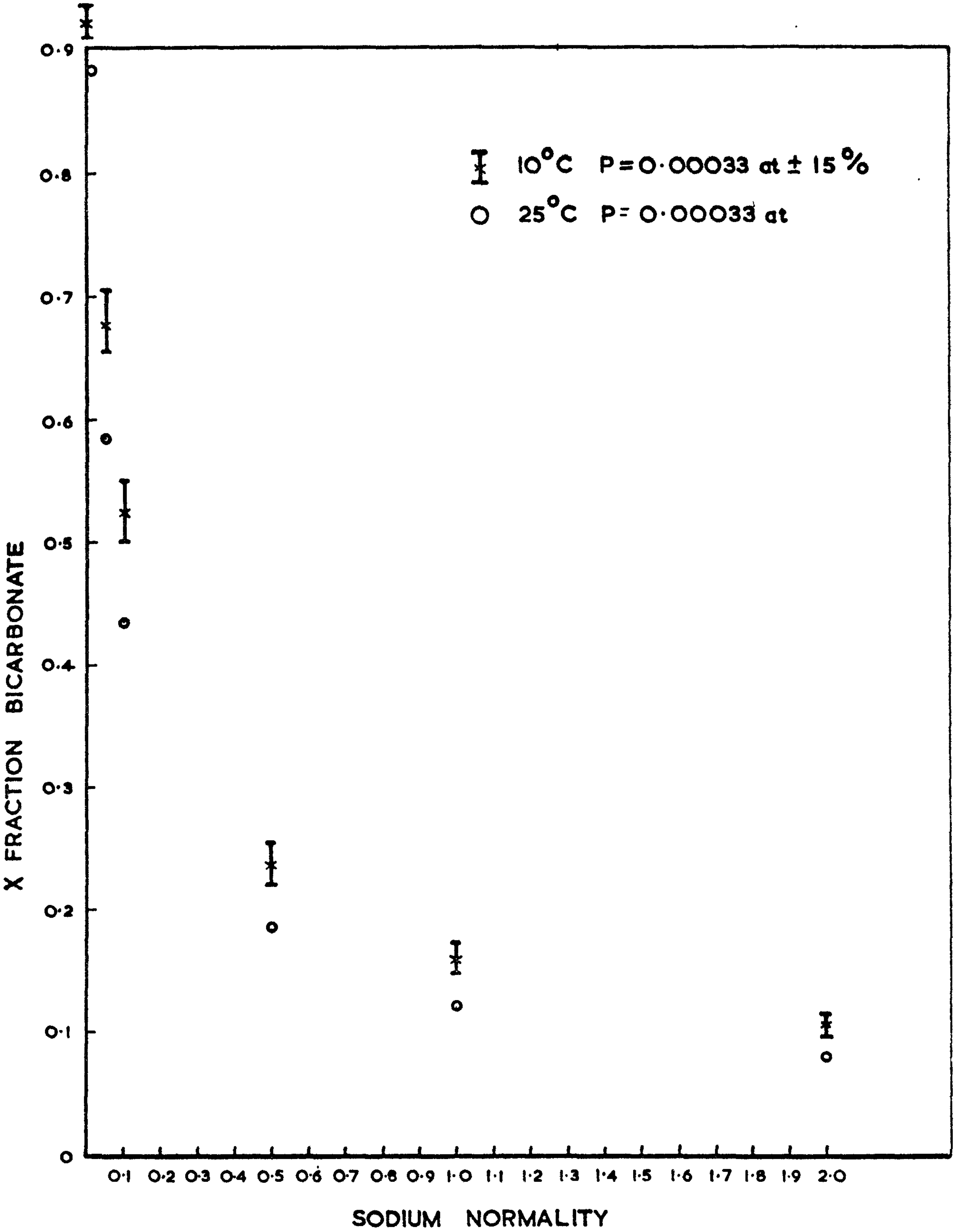
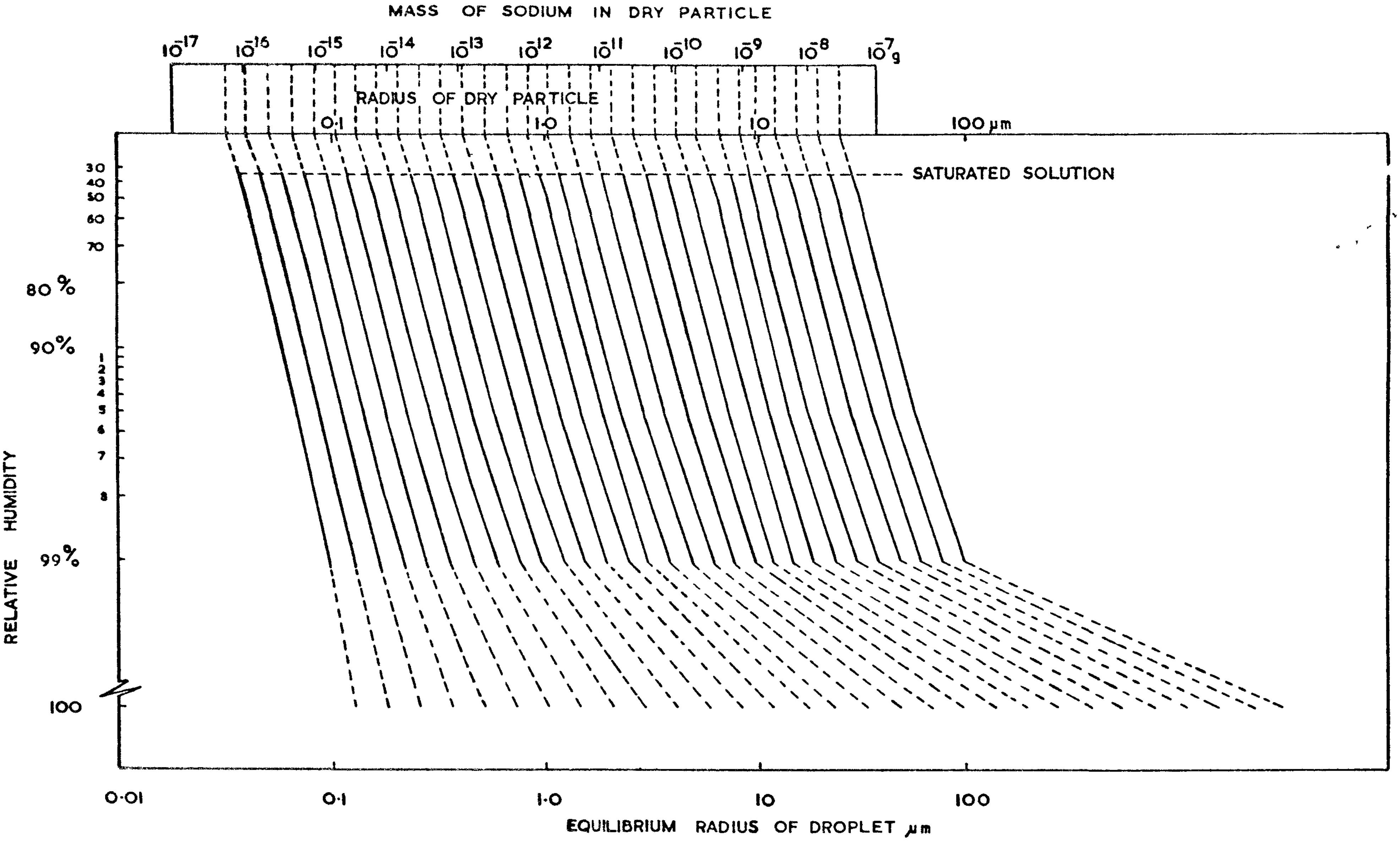
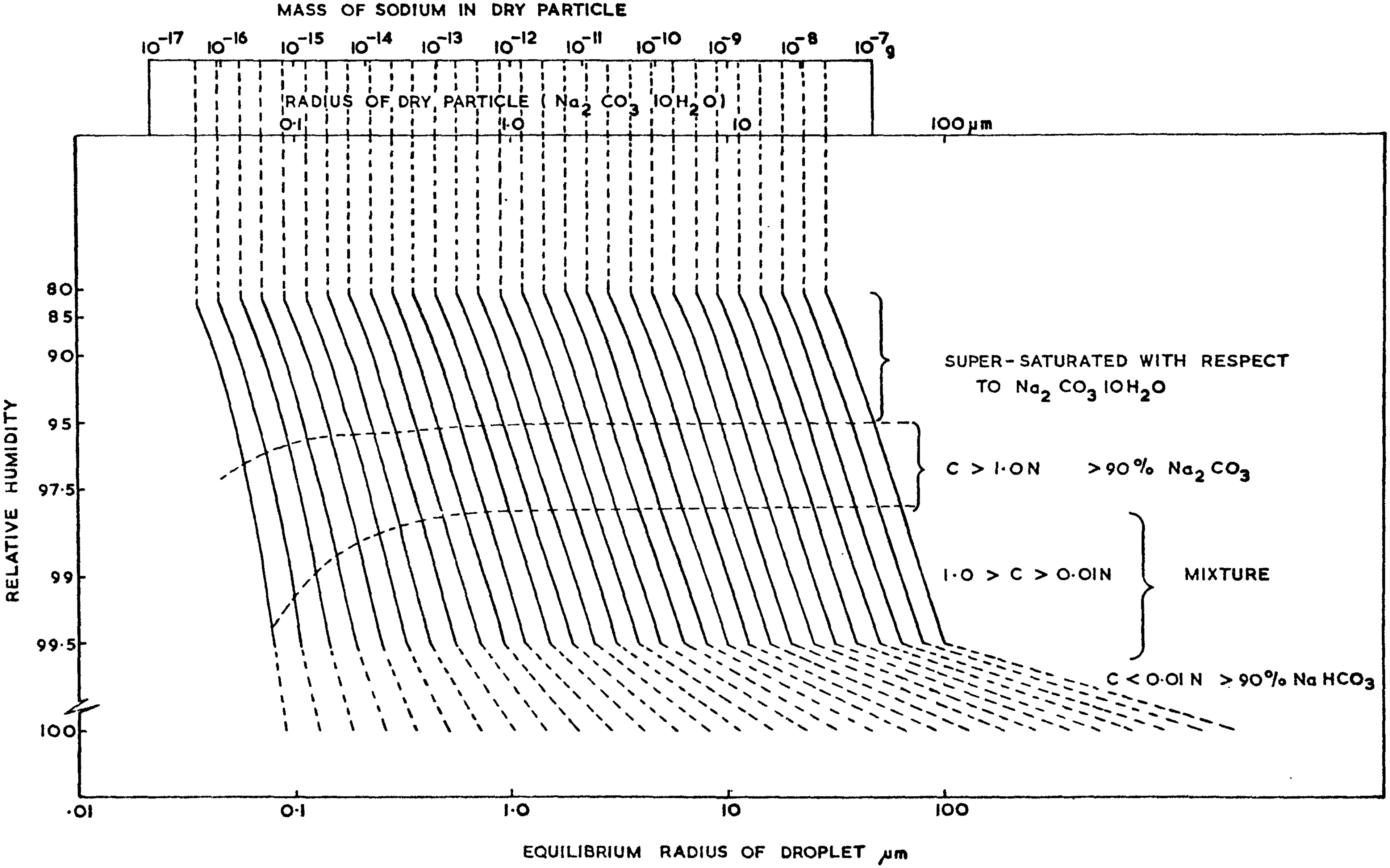


A.E.R.E. R.6460 FIG.1. THE EQUILIBRIUM BETWEEN SODIUM CARBONATE AND BICARBONATE.



A.E.R.E. R6460 FIG 2 THE SIZE OF DROPLETS OF SODIUM HYDROXIDE SOLUTION
AS A FUNCTION OF SODIUM CONTENT AND RELATIVE HUMIDITY



A.E.R.E. R.6460 FIG.3 THE SIZE OF SODIUM CARBONATE DROPLETS AS A FUNCTION OF SODIUM CONTENT AND RELATIVE HUMIDITY