

pressure for which the nozzle was designed, early condensation occurred. Undoubtedly the well known phenomenon called "compression shock" was brought about and, being highly irreversible, accounts for the early condensation observed.

Several excellent articles (12, 15, 24) have appeared recently which deal with gas bubble formation in a liquid. The approach is principally physical, with considerable attention given to the contact angle and surface cavities as sources of gas which serves as the nucleus for bubble formation. Bubble formation within the liquid with no ebullator is not treated.

The present discussion has been entirely thermodynamic, and the only assumption made regarding the bubble is that it must be spherical and that there may be a number of bubbles of the same size. It has been suggested (12, 31) that bubbles may form in various sizes, that only those larger than a critical size will grow, and that the smaller ones will condense. For such a system the superheat would be dependent upon the bubble size, and all sizes from the critical size to infinity would be possible, with no superheat necessary for the formation of bubbles sufficiently large. Experimental observations indicate that in the absence of nuclei very large degrees of liquid superheat are possible and that bubbles are very small initially, approaching molecular magnitudes (28). Condensation is a similar phenomenon, and initial drops observed are of molecular magnitude (31). The critical size hypothesis finds its basis in statistical mechanics which allows

for energy fluctuations, to be expected as one reduces the size of the system.

The above analysis makes no such allowance for fluctuations but assumes the energy of the liquid uniform throughout. On the basis of this assumption the results are reasonable. The single-molecule bubble may be difficult to imagine, but a molecule in the energy state required by a bubble of molecular size is not so difficult to imagine. It must possess the same energy as the vapor molecule although probably not the same kind (perhaps rotational and vibrational rather than translational).

An attempt has been made here to make it clear that, with bubbles of molecular magnitudes, nuclei of similar dimensions would be required. It is known that with crystalline solids interfacial energy and chemical reactivity differ for various faces of the unit crystal and may be a maximum at a corner where three faces intersect. Most solid surfaces are a composite of various faces, edges, and corners of crystals or broken crystals. Thus it is natural to assume that a property such as contact angle would not be sensitive to the variations of adhesion free energy that may actually exist. This assumption, coupled with roughness or curvatures of molecular or unit crystal magnitude, may explain why bubbles form at particular spots on a solid. There is probably also reason to believe that a bubble will preferentially form in a cavity of molecular magnitude, provided the adhesion tension there is a minimum or negative.

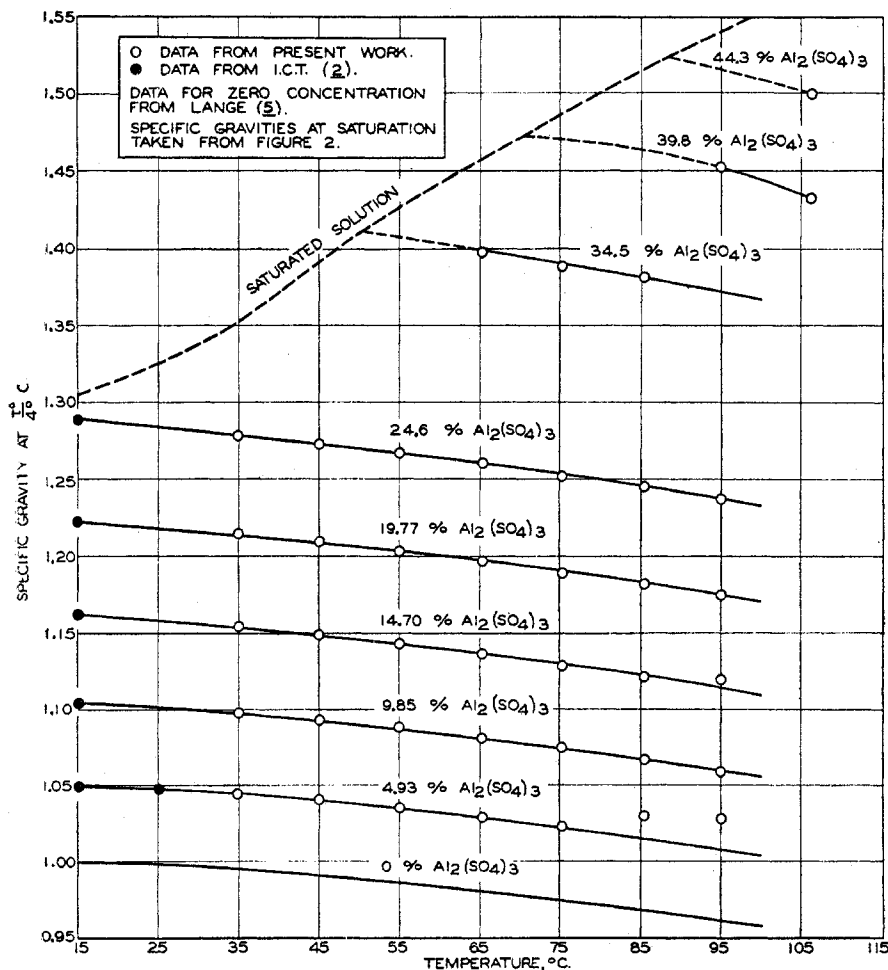


Figure 1. Experimental Values for Specific Gravity of Aluminum Sulfate Solutions

Specific Gravity of Aluminum Sulfate Solutions

Data on the specific gravity of aluminum sulfate solutions covering the temperature range 15° to 105°C. and concentrations from zero to saturation are presented. Specific gravity data for aluminum sulfate solutions above 45°C. or above 26% concentration were not available previously. The data are considered to be accurate within $\pm 0.25\%$ concentration.

**J. W. SILVA AND
J. E. CHENEVEY**

**Tennessee Valley Authority,
Wilson Dam, Ala.**

SPECIFIC gravity data, covering concentrations of aluminum sulfate solutions from 15° to 105° C., were needed in the development of an acid process for alumina from clay (8). The data were intended originally for pilot-plant work; therefore experimental methods were chosen to give only the precision necessary for such work. However, a review of the data indicated that they are of sufficient accuracy to be of general interest. International Critical Tables (2) give specific gravities at 15° C. for concentrations to 26% aluminum sulfate and at 25° C. for concentrations to 6%. The data in the handbooks are from this source. The specific gravities of Reuss, reported by Mellor (6), cover a temperature range of 15° to 45° C. for concentrations up to 25% aluminum sulfate. However, these data do not agree with those reported in International Critical Tables. Solubilities of aluminum sulfate are reported in International Critical Tables (4) and by Seidell (7), and boiling points of aluminum sulfate solutions are given by Badger and France (1) and in International Critical Tables (3). These data were used in the present investigation.

The specific gravity of aluminum sulfate solutions of known concentration was measured by standard 25-ml. pycnometers in a controlled-temperature bath. Reagent-grade aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ was used for the determinations. Separate solutions were made up to contain nominally 5, 10, 15, 20, 25, 30, 35, and 40% by weight of aluminum sulfate (the solutions above 25% were solid at room temperature). Determinations were made for each concentration, when possible, at approximately 35°, 45°, 55°, 65°, 75°, 85°, 95°, and 105° C. The concentration of each solution was checked by gravimetric determination of the aluminum content at the beginning, mid-point, and end of each series. The solutions were kept in glass-stoppered bottles in a constant-temperature oven, held a few degrees below the temperature at which the specific gravity was to be determined. The pycnometers were calibrated in the bath at the temperature to be used for every determination. Calibrations up to and including 85° C. were made with distilled water, and at the higher temperatures, with mercury. The specific volumes of water and mercury were taken from Lange (6). Temperature was measured by a thermometer checked by the National Bureau of Standards. The pycnometers were weighed to 0.1 mg., and all weights were corrected to vacuum. The specific gravities of the solutions were calculated with reference to water at 4° C. Some difficulties were experienced in keeping the solutions at constant concentration. The nominally 30% solution varied in concentration and resulted in unreliable determinations, and the entire series

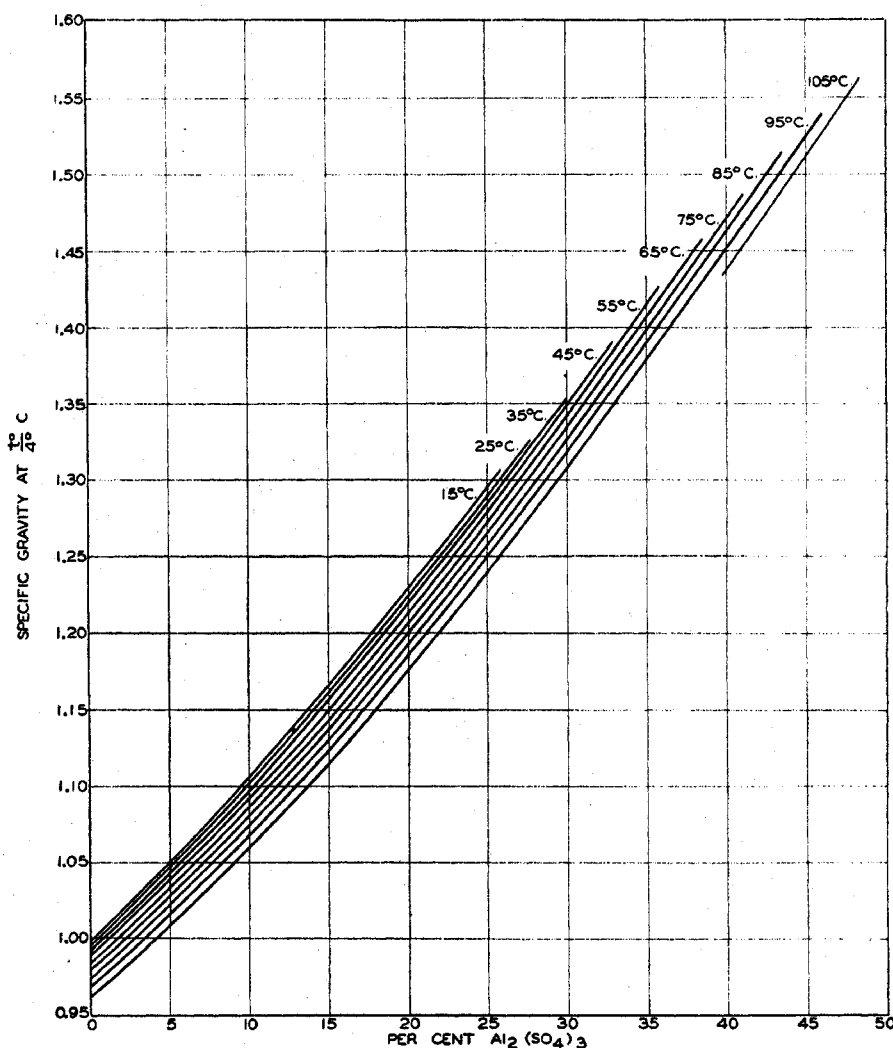


Figure 2. Isotherms of Aluminum Sulfate Solutions

was therefore discarded. The discrepancies for two points on the 5% curve and one point on the 15% curve (Figure 1) are probably also due to variations in concentration of the solutions.

The experimental data are presented in Table I and Figure 1. The points shown for 15° C. on Figure 1 were obtained by interpolation from data of International Critical Tables (2); these points are in excellent agreement with the experimental data. The values for specific gravity of water, included for comparison, were taken from Lange (5). The saturation line was taken from the upper ends of the isotherms of Figure 2. The extrapolations for the 34.5, 39.8, and 44.3% aluminum sulfate curves were also taken from Figure 2.

TABLE I. EXPERIMENTAL VALUES FOR SPECIFIC GRAVITY OF ALUMINUM SULFATE SOLUTIONS

| Temp., C. | d_s^0 at $\text{Al}_2(\text{SO}_4)_3$ Concentration of: | | | | | | | |
|--------------|---|--------|--------|--------|--------|--------|--------|--------|
| | 4.93% | 9.85% | 14.79% | 19.77% | 24.6% | 34.5% | 39.8% | 44.3% |
| 34.9 | 1.0440 | 1.0980 | 1.1539 | 1.2147 | 1.2785 | ... | ... | ... |
| 45.0 | 1.0399 | 1.0950 | 1.1484 | 1.2092 | 1.2726 | ... | ... | ... |
| 55.0 | 1.0347 | 1.0879 | 1.1426 | 1.2033 | 1.2666 | ... | ... | ... |
| 65.2 | 1.0288 | 1.0805 | 1.1361 | 1.1964 | 1.2603 | 1.3968 | ... | ... |
| 75.2 | 1.0222 | 1.0742 | 1.1281 | 1.1881 | 1.2513 | 1.3880 | ... | ... |
| 85.4 | 1.0296 | 1.0665 | 1.1213 | 1.1811 | 1.2446 | 1.3809 | ... | ... |
| 95.0 | 1.0288 | 1.0598 | 1.1206 | 1.1751 | 1.2381 | ... | 1.4542 | ... |
| 106.2 | ... | ... | ... | ... | ... | ... | 1.4332 | 1.5014 |

The curves of Figure 2 were derived from the curves of Figure 1. The upper limits of the isotherms represent the concentrations at saturation as given by Seidell (?). According to Badger and France (1), aluminum sulfate solution of 44% concentration boils at 105° C.; they state that their boiling point values are accurate to $\pm 1^\circ$ C., with results probably low rather than high. In the present work no sign of boiling was observed during the specific gravity determination for a 40% solution at 106° C.

The specific gravities determined in the present work and the values from International Critical Tables (2) do not agree with the data from Mellor (6).

Figure 2 was used extensively in pilot-plant control work. On the basis of the precision of the temperature measurements, weighings, and chemical analyses (Table I), the accuracy of the data is considered to be within $\pm 0.25\%$ concentration for pure solutions. The specific gravity of impure solutions, such as those obtained from the reaction between clay or bauxite and sulfuric acid, is influenced by the excess of either alumina or acid in the solution and by the presence of iron and other impurities. According to data from Mellor (6), solutions of commercial aluminum

sulfate have specific gravities lower than those of pure solutions of the same concentration.

ACKNOWLEDGMENT

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Vapor Pressure of Water Adsorbed on Dehydrated Eggs

BENJAMIN MAKOWER

Western Regional Research Laboratory,
U. S. Department of Agriculture, Albany, Calif.

Equilibrium pressure of water vapor over spray-dried whole eggs was determined at six temperatures varying from 17.1° to 70° C. and at moisture contents ranging from 0.5 to 5.5%. The results agreed well with similar data on eggs dried from the frozen state and with the less extensive data published by Gane (6). The results were analyzed by a graphical method suggested by Othmer (10), and from this analysis was derived the isosteric heat of adsorption of water on dried eggs at various moisture levels. The ratio of the isosteric heat to the latent heat of condensation of water vapor increases from 1.1 to 2.1 as the moisture content decreases from 5.5 to 0.5%. It was also shown that the adsorption isotherms can be represented, within certain limits, by the Brunauer, Emmett, and Teller theory (4) of adsorption of gases on solids.

KNOWLEDGE of the vapor pressure of water over dehydrated eggs is essential in the design of drying equipment for eggs and in the selection of packaging material for the dry product (11). The recent trend in drying toward lower moisture levels has brought about a need for vapor pressure data for eggs that contain less than 2% of water. The data in the literature for this moisture region are meager. Measurements previously obtained in this laboratory (9) and by Stuart *et al.* (14) were taken at one temperature only. Gane (6) measured the equilibrium moisture content at various temperatures and moisture levels, but the vapor pressure data derivable from his data do not adequately cover the region below 2% of water. As Gane points out, his results apply only to the sample of spray-dried eggs used. Vapor pressure may vary with different lots of eggs, as a result of differences in composition or differences in the method of drying or other treatment.

In the present investigation the measurements were extended to the low-moisture region and also repeated at the higher moisture levels, for the purpose of comparing materials prepared in different ways. A sample of dried whole eggs, prepared by drying from the frozen state (lyophilizing), was also included. In the latter method any deteriorative changes are likely to be minimized.

MATERIALS AND METHOD

Spray-dried eggs obtained from a commercial source contained initially about 5% of water. The lyophilized eggs prepared in this laboratory had a moisture content of about 2%. Ten samples of each kind of powder were adjusted to moisture contents covering a range from 0.5 to 5.5%. The samples were adjusted in one of two ways. One method involved addition of a known weight of water to a weighed sample that had been vacuum-dried at room temperature to a moisture level of about 0.2%. The water was evaporated from one vessel and adsorbed from the vapor phase by the powder in another vessel. The transfer was effected in a closed system, in the absence of air. The other method consisted in placing the sample in a vacuum desiccator that served as a constant-humidity chamber. The humidity was controlled by an aqueous sulfuric acid solution of known concentration (8). The sample either lost or gained water until equilibrium moisture content had been reached.

The moisture contents of the samples were determined by drying in a vacuum oven at 100° C. for 5 hours at a pressure of 2 to 5 mm. of mercury. This procedure is similar to the A.O.A.C. method (1) and is generally used in the industry. (Passage of dry air through the oven, as specified in the A.O.A.C. method, had no appreciable effect on results and was not included.) Vapor pressure measurements are expressed in terms of results obtained by this procedure, although actual water contents are believed to have been somewhat lower. When water contents of a number of samples were determined by drying to constant weight at room temperature (to minimize decomposition) in evacuated desiccators that contained magnesium perchlorate as the desiccant, it was found that the results were about 0.15% lower than those obtained by the vacuum-oven method. If it is as-