Evaporation and Drying of Drops in Superheated Vapors

A. M. TROMMELEN and E. J. CROSBY

University of Wisconsin, Madison, Wisconsin

The evaporation of pure liquid drops and the drying of drops containing suspended and dissolved solids in an atmosphere of superheated vapor were studied. Changes in the weight and temperature of approximately 2 μliter drops of four food products, five miscellaneous materials, and pure water were measured as evaporation and drying proceeded at different drying temperatures. Evaporation of water was found to take place more slowly in superheated steam than in air. However, the medium, in which faster drying occurred, depended upon the material being dried. No major differences between the final products were observed for these two drying media except that some materials yielded denser particles in superheated steam than in air.

The potential of superheated vapors, which are chemically identical to the moisture being removed from a solid, as a drying medium has long been recognized (*7*). The number of commercial applications has, however, been somewhat limited (*2, 4, 11, 23*). Drying with superheated vapors has numerous advantages over drying with gases, and that advantage most often cited is the considerable improvement in thermal efficiency (*4, 7, 22*). Chu et al. (*4*) pointed out that the problem of dust collection is considerably simplified when the excess vapors to be removed from the system are passed through a total condenser. It was also noted that drying with superheated vapors provides an inert environment in which to process materials which are readily oxidized and that, when dealing with flammable solvents, the danger of an explosion within the dryer is eliminated. Walker et al. (*23*) illustrated the use of superheated vapors as an effective drying medium when the material being dried is a poor conductor of heat. Also, the volume of the exhaust from a drying system will be much smaller for superheated vapor than for gases. A major disadvantage in using superheated vapors is the difficulty in handling solids which are sensitive to temperatures above the boiling point of the solvent at the pressure existing in the dryer. The practical limitation of constructing and financially justifying satisfactory equipment in which condensation will not occur and from which the dry product can be removed without loss of the vapors (*14*) also exists.

A pure liquid which evaporates into a gas or dissimilar vapor attains dynamic equilibrium at a temperature somewhat below the dry bulb temperature because of the combined resistances to heat and mass transfer in such a drying medium. When the liquid evaporates into a medium of its own vapor, the resistance to mass transfer becomes vanishingly small, and the temperature of the liquid then approximates that of its saturated vapor at the ambient pressure (*4, 5, 21, 24*). Similar thermal effects would be expected during the first period of drying when dissolved solids are present. This has been observed for the drying of single drops in air (*3, 15 18*), even though the length of this period of drying may indeed be very short.

Numerous experimental studies of the rates of heat and mass transfer to and from spherical bodies in an extensive fluid, where the interface was immobile and surfactants were absent, have been carried out. Critical reviews of these investigations have recently been made (*10, 12, 16*), and Hughmark (*10*) concluded that, for $1 < N_{Re} < 450$ and N_{Sc} or $N_{Pr} < 250$, the following correlation is applicable:

$$(N_{Nu} \text{ or } N_{Sh}) = 2.0 + 0.6\, N_{Re}^{1/2}\, (N_{Pr} \text{ or } N_{Sc})^{1/3} \quad (1)$$

Equation (1) is based on data where the continuous phases were air and various liquids. Toei et al. (*21*) investigated the evaporation of water drops into superheated steam and mixtures of steam and air. For $9 < N_{Re} < 120$ and $0.7 < N_{Pr} < 1.0$, these investigators determined that

$$[N_{Nu} \text{ or } N_{Sh}(p_{Bm}/P)^{-0.20}] = 2.0 + 0.65\, N_{Re}^{1/2}(N_{Pr} \text{ or } N_{Sc})^{1/3} \quad (2)$$

which is in good agreement with Equation (1). Lee and Ryley (*13*) studied the evaporation of nonspherical drops of water into superheated steam and reported the empirical factor in Equation (1) to be 0.74 instead of 0.6. A similar comparison is possible only for flow parallel to a flat surface (*4, 5, 17, 22*), where the drying of sand and evaporation of water with air and superheated steam were investigated. For this geometry, there is very poor agreement between experimental data from one study to another of the variation in construction of equipment. Only Chu et al. (*5*) and Wenzel and White (*24*) studied both drying media, and their results also suggest a common correlation of heat transfer coefficients for both gases and superheated vapors.

In order to understand better the manner in which drops containing solids dry in superheated vapors as compared with gases, single drops of several aqueous solutions and suspensions were dried in both superheated steam and air. Of primary importance was the determination and comparison of the drying rates in these two media under similar conditions of drying. Also of major interest was the nature of the final particles produced from initially identical drops when dried in different environments.

EXPERIMENTAL PROCEDURE

Apparatus

The experimental equipment consisted of a vaporizer connected to a vertically oriented superheater at the top of which was located a convergent nozzle with an attached drying chamber. A 25-gal., steam jacketed, glass lined, reaction vessel served as the vaporizer, and the rate of flow to the superheater was monitored with an orifice meter connected to a mercury manometer. The transfer line between the vaporizer and the superheater was traced with electrical heating tape to prevent condensation. The superheater, which also acted as the heater for the air, was the same as that described by Downing (*6*). Rotameters were used to measure the flow of air which was taken directly from the supply of compressed air in the laboratory. The convergent nozzle, used to produce a flat velocity profile, was of the same design as that used by

---

A. M. Trommelen is with Unilever Research Laboratorium, Vlaardingen, Nederland.

Ranz and Marshall (*15*).

Details of the drying chamber and the manner in which the drop was suspended and weighed are shown in Figure 1. The experimental procedure was similar to that followed by Sano and Nishikawa (*18*) which, in turn, was based on the technique developed by Charlesworth and Marshall (*3*). The drop was suspended at the junction of a chromel-constantan thermocouple which itself was affixed to the end of a Salvioni balance (*1*). Simultaneous measurement of the temperature of the drop together with its weight allowed a good check on the identical nature of the numerous initial drops needed to obtain a reliable history of a drop's weight during drying.

The balance proper was a filament of Pyrex glass, drawn from 6-mm. stock, whose length was 55 cm. and whose diameter varied from 0.5 mm. at the fixed end to 0.25 mm. at the free end. The deflection of the filament varied according to the weight of the drop and was measured by the distance over which the fixed end had to be moved so as to maintain the free end at its initial position. This particular balance had a deflection of 11 mm./mg. The thermocouple wires, whose diameters were 0.051 mm., were attached to the filament with minute quantities of paraffin at 3-cm. intervals. For that part of the balance which was exposed to the hot gases or vapors, a silicone cement was used for the attachment. In order to facilitate easier suspension of the drop from the thermocouple, the last 3 cm. were composed of wire whose diameter was 0.076 mm. All connections were silver soldered, and the junction, from which the drop was suspended, was given the form of a small bead. The filament was encased in a U shaped channel to protect it against air currents existing or generated near the balance. A small clamping device was used to anchor the free end of the filament to maintain the drop in a stationary position while the drying medium passed through the nozzle.

A slide valve for rapid diversion of the drying medium was attached directly to the convergent nozzle and acted as the support for the drying chamber. The drying chamber, a double walled Pyrex cylinder, shielded the drying medium as well as the end of the balance, thermocouple, and drop from drafts in the laboratory. Hot air was passed between the inner and outer wall to prevent condensation of the vapors in preference to the use of insulation with imbedded electrical tracing (*21*). The balance entered through a slot in the side of the chamber, with the annular space being sealed off at this point. Two coplanar, flat windows located in the inner and outer walls allowed an undistorted view of the drying drops. The drops were located about 3 to 4 cm. above the nozzle during drying. A port, which was easily closed off, in the side of the chamber opposite the balance made the junction of the thermocouple easily accessible for suspension and removal of the drops. The drops were formed at the end of a squarely honed, 30-gauge (O.D. = 0.30 mm. and I.D. = 0.15 mm.) hypodermic needle with a microsyringe having a volume of 10 μliter and calibrated in units of 0.1 μliter.

Certain of the drying sequences were recorded photographically with a NIKON-F 35-mm. reflex camera equipped with a motor drive and timer to facilitate time-lapse photography. A combination of back and front lighting was used. Photographs were taken through a microscope with an approximately 17X magnification, and the total magnification for the system was 8.3X.

Measuring Techniques

Only when drops containing solids dry very slowly is it possible to obtain a complete history of the drying from a single drop (*3, 18*). When the temperature of the drying medium is relatively high, drying takes place quite rapidly, even when the drop is in a field of negligible velocity. Consequently, a number of identical drops were each dried for different lengths of time, with the weight of each drop yielding one point on the drying curve. The instantaneous weight of each drop at the end of its drying period was obtained by extrapolating numerous weighings obtained under the mildest of drying conditions to zero time of weighing as follows. Once the balance was zeroed, it was clamped into position for actual drying. With the slide valve closed, a drop was formed and suspended from the themocouple. Immediately thereafter, the slide valve was opened, and a chromometer was simultaneously started. After a desired period of exposure to the drying medium, the slide valve was closed, and the balance was unclamped. The fixed end of the balance was moved until the balance was again zeroed, at which time both the displacement of the balance and the reading of the chromometer were recorded. As the drop slowly and continuously changed weight, the balance required continuous zeroing, and a series of three to five consecutive readings of displacement and cumulative time was made. The recorded displacements and cumulative times less the drying time were then plotted and extrapolated to zero time. This gave the deflection of the balance corresponding to the instantaneous weight of the drop. The weights of a drop for other periods of drying were similarly determined.

The thermocouple wires were, via a cold junction, connected to a Bausch and Lomb recording potentiometer whose lowest full scale range of 10 mv. was used and whose chartspeed ranged up to 20 in./min. For voltages greater than 10 mv., the zero point of the potentiometer was electrically biased. During the accumulation of data for a complete history of drying, the temperature of the drop was monitored at a low chart speed for purposes of control only. After these measurements were completed, an identical drop was completely dried with the recorder operating at the highest chart speed so as to obtain a detailed account of the thermal history of the drop.

Accuracy of Measurements

The major sources of error in determining the drying histories of the drops were in the actual measurement of a drop's weight and the transfer of a drop from the microsyringe to the thermocouple junction. The Salvioni balance was calibrated against a Cahn, Model M-10, electrobalance for which the sensitivity was 0.001 mg. and the precision was ± 0.005 mg. for a full scale reading of 10 mg. The accuracy of the calibration was then no better than ± 0.006 mg. Protection of the glass filament from ambient air currents with the U shaped channel did not completely eliminate random movement, and the reproducibility of measuring the deflection of the filament was ± 0.2 mm. which corresponded to ± 0.02 mg. As this lack of reproducibility was present during both the zeroing of the balance and the actual weighing of a drop, an accuracy of ± 0.04 mg. resulted for the balance. The error involved in the formation and transfer of the drops was more difficult to access. Drops were formed with a precision of better than ± 0.05 μliter or about ± 0.05 mg. However, in spite of precautions, the liquid tended occasionally to wet and climb up the outside of the hypodermic needle. Also, as might be expected, some liquid always remained on the tip of the needle after the drop was transferred to the thermocouple. The time which lapsed between the formation and ultimate suspension of a drop varied somewhat, and a slight amount of evaporation took place during this period. Finally, the time necessary to open and close the slide valve, although small, also affected the accuracy of the measurement. As the drops studied had an initial volume of at least 1.5 μliters, the accuracy of the drying histories was estimated to be within ± 10 %.

The recording potentiometer registered the output of the thermocouple with an accuracy of ± 0.05 mv. This corresponded to an accuracy in the measured temperature of ± 0.75°C. As there were many times small fluctuations in the recorded output of the potentiometer, the accuracy of the temperature was taken as ± 1.5°C. Above 153°C, the recorder was electrically biased, and the inaccuracy of the measured temperature was then doubled.

Heat Transfer to Supported Drops

For the experimental procedure used in this study, heat was transferred to the drops by convective transfer directly from the drying medium, by radiative transfer from the surrounding enclosure, and by conductive transfer along the thermocouple. The rate at which heat was transferred to the drop by convection was determined from

$$Q_c = Ah^{\bullet}(T_g - T_d) \tag{3}$$

where

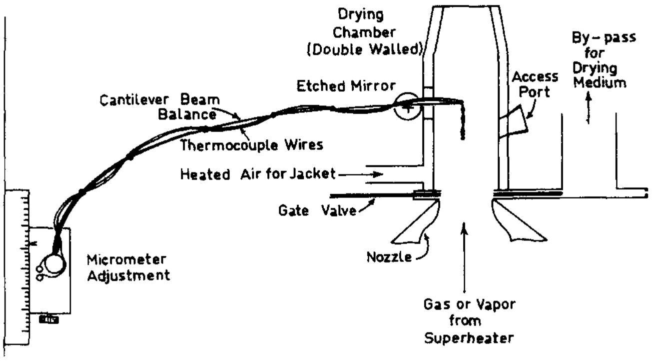

Fig. 1. Details of drying chamber and balance.

$$\frac{\overset{\bullet}{h}}{h} = \frac{(w_A \hat{C}_{pA})/(Ah)}{\exp[(w_A \hat{C}_{pA})/(Ah)] - 1} \qquad (4)$$

and h is evaluated with the aid of Equation (1). Application of Equation (1) assumed that the temperature at the surface of the drop was the same as the temperature measured by the thermocouple. The area available for heat transfer was taken as the total surface of the drop based on the drop's volume. The two 0.076-mm. thermocouple leads reduce the area available for heat and mass transfer for a 1-μ liter drop by less than 0.2 %. The effect of the rate of evaporation or drying on the rate of heat transfer, given by Equation (4), is based on the film theory and was applied uniformly over the entire surface of the drop.

The rate at which heat was transferred to the drop by radiation was taken as

$$Q_r = \sigma A F_A F_\epsilon (T_g^4 - T_d^4) \qquad (5)$$

The geometry factor was assumed equal to unity because the drop was, for all practical purposes, entirely surrounded by the drying chamber. The emissivity factor was considered equal to the emissivity of the drop because the drop was so much smaller than the drying chamber. The temperature of the inner wall of the drying chamber was maintained nearly equal to the temperature of the drying medium, and the temperature of the drop's surface was again assumed to be equal to that measured by the thermocouple.

The rate at which heat was transferred to the drop along each of the two thermocouple leads was estimated from

$$Q_t = 2\pi \left\{ R^3 k_t \left[\sigma\epsilon T_g^4 (T_d - T_g) - \frac{\sigma\epsilon (T_g^5 - T_d^5)}{5} + \frac{h_t (T_g - T_d)^2}{2} \right] \right\}^{1/2} \qquad (6)$$

whose derivation is reviewed in the Appendix. The evaluation of h_t from available correlations for gases flowing axially to thin wires (*17*) did not seem justifiable because the flow pattern was well disturbed by the presence of the drop. It seemed reasonable for lack of other information to assume that the heat transfer coefficient, along that portion of the thermocouple wire which was significant for transmission of heat to the drop, was not much different from the heat transfer coefficient obtained from Equation (1). This approach was then used in evaluating h_t.

MATERIALS AND CONDITIONS STUDIED

The loss in weight and variation in temperature as a function of time were determined for droplets of a number of aqueous solutions and suspensions in both air and steam. Similar sets of measurements were made in both drying media for the following systems with initial concentrations as indicated: a commercial clay (6 wt. %), sodium sulfate (25 wt. %), potassium nitrate (20 wt. %), stoichiometric mixture of nickel hydroxide and sodium sulfate (20 wt. %), a commercial detergent (20 wt. %), sucrose (50 wt. %), tomato juice (about 4 wt. %), coffee concentrate (25 wt. %) and skimmed milk (40 wt. %). Similar measurements were also made for evaporating drops of pure water in air and steam.

Because of the exploratory nature of this work, only a limited set of conditions were studied. For the majority of the systems these conditions were

Temperature of drying medium	150° and 250°C.
Velocity of drying medium	1.5 to 2.1 m./sec.
Volume of drop	2×10^{-3} ml.
Diameter of drop	1.560 mm.

On occasion, only one level of temperature was studied, and in a few instances the nominal volume of the drops was about 1.5×10^{-3} ml. Although the sizes of the drops were nearly one order of magnitude larger than those met under actual conditions of spray drying, extension of the results obtained to smaller drops is deemed qualitatively feasible.

EXPERIMENTAL RESULTS AND OBSERVATIONS

Presentation of Data

For purposes of comparison, the histories of evaporation and drying were plotted as unaccomplished evaporation or drying. The unaccomplished drying was defined as the ratio of the moisture content at any time to the initial moisture content. This procedure made comparison somewhat simpler as variations in the initial weights of the drops, and, for a few materials, variations in the final weights of the particles because of rupturing accompanied by spattering were smoothed out. The initial weights of the drops were based on the measured weights for no evaporation of the water drops and on the measured weights for no drying and complete dryness for the aqueous solutions. All reported rates of drying and evaporation were obtained di-

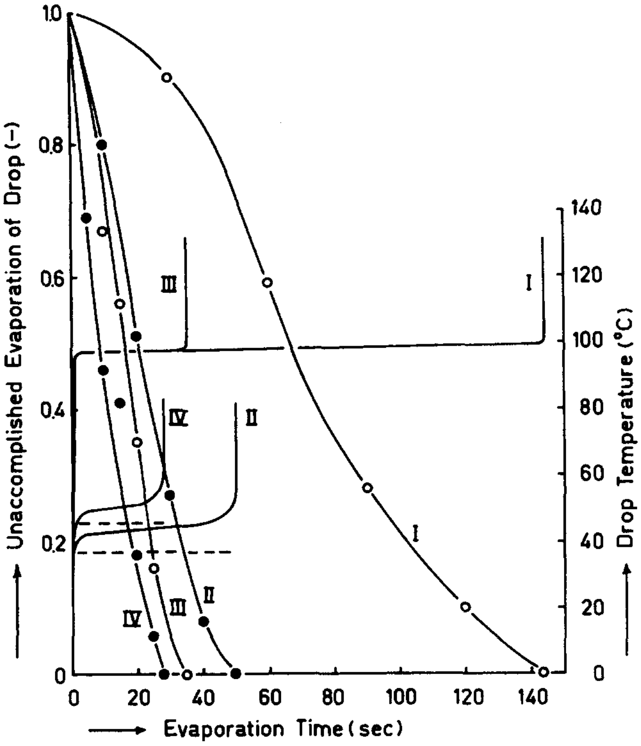

Fig. 2. Effect of temperature and drying medium on the evaporation of water drops.

(--- wet bulb temp.; ○ superheated steam; ● dry air.)

I. $m_0 = 1.38$ mg., $T_g = 130$°C., $v = 1.6$ m./sec.
II. $m_0 = 1.22$ mg., $T_g = 135$°C., $v = 1.6$ m./sec.
III. $m_0 = 1.38$ mg., $T_g = 200$°C., $v = 1.9$ m./sec.
IV. $m_0 = 1.22$ mg., $T_g = 202$°C., $v = 1.8$ m./sec.

rectly from plots of weight vs. time.

The temperatures of the drops were obtained from the millivolt output of the recording potentiometer. The reported temperatures are time smoothed values and do not indicate the slight fluctuations induced by the local variation of the temperature of the drying medium.

Evaporation of Water Drops

Drops of distilled water were evaporated in both air and superheated steam. The drops had a nominal volume of 1.5 μliters when formed and a temperature, ranging from 25° to 30°C., which approximated that in the laboratory. A portion of the recorded histories of the weights and temperatures of the evaporating drops are shown in Figure 2 for both air and steam.

For both drying media the evaporation took place in distinct periods: an induction period and a constant temperature period. During the induction period the temperatures of the drops rose from the initial temperature to a dynamic equilibrium temperature for the system, and the rates of evaporation increased from the initial rate to a maximum value at the beginning of the constant temperature period. Throughout the constant temperature period the rates of evaporation continually decreased as is characteristic for evaporating drops. As a result of the experimental technique used in this work, the dynamic equilibrium temperature was slightly above the wet bulb temperature and increased slightly throughout the constant temperature period when drops evaporated into air. The increased rate of heat transfer to the drop, beyond that due to convection, which resulted from both conduction along the supporting thermocouple and direct radiation, caused the drop's temperature to rise above the wet bulb temperature. As evaporation proceeded, the drop's diameter became smaller, and that proportion of the total heat transferred to the drop by direct radiation became less, whereas the relative amount of heat transferred through the thermocouple became greater. Consequently, the temperature of the drop increased somewhat during its lifetime. When evaporation took place in superheated steam, a certain amount of condensation usually occurred on the drops during the induction period which resulted in an increase in weight. The amount of condensation depends upon the degree of superheat and the rate at which heat is transferred to the drop by other means. A nonsupported drop of water initially at 30°C. will experience a maximum increase in weight of about 12.5% when exposed to steam with a superheat of 50°C. at atmospheric pressure. During this period, the temperatures of the drops rose to the boiling point of water. The recorded temperatures are slightly below 100°C. as the measurements were carried out at an elevation of 905 ft. above sea level. During the constant temperature period, the temperature of the drops did not change as there was no resistance to mass transfer and only the total pressure of the system then controlled this temperature. The formation of minute bubbles inside the drops was observed during this phase of the evaporation. The bubbles appeared to form on the junction of the thermocouple where nucleation sites were undoubtedly available. If the thermocouple was at a temperature of only a fraction of a degree Centigrade above the boiling point, which probably was the case, boiling could readily occur.

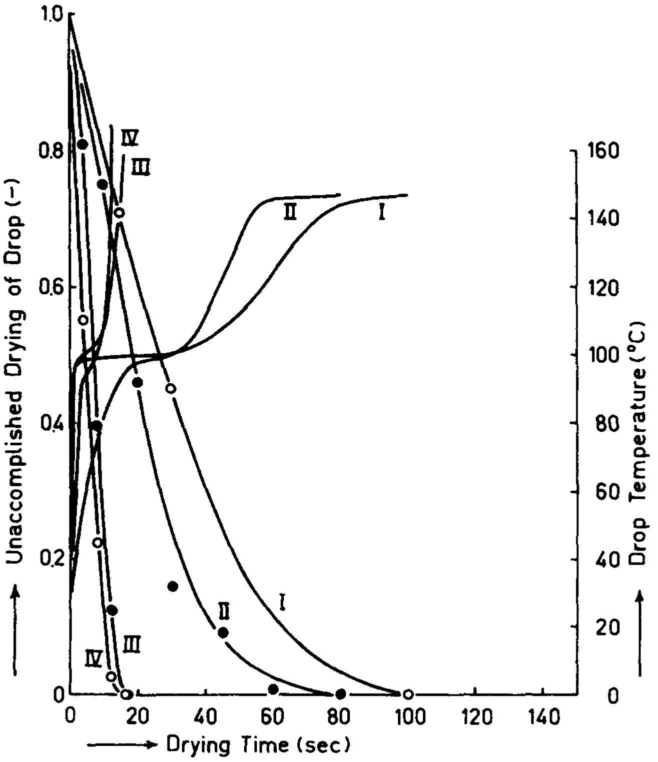

Fig. 3. Effect of temperature and drying medium on the drying of sucrose drops.
(○ superheated steam; ● dry air.)
I. $m_0 = 2.56$ mg., $T_g = 150$°C., $v = 1.6$ m./sec.
II. $m_0 = 2.40$ mg., $T_g = 150$°C., $v = 1.7$ m./sec.
III. $m_0 = 2.29$ mg., $T_g = 250$°C., $v = 1.9$ m./sec.
IV. $m_0 = 2.33$ mg., $T_g = 250$°C., $v = 2.1$ m./sec.

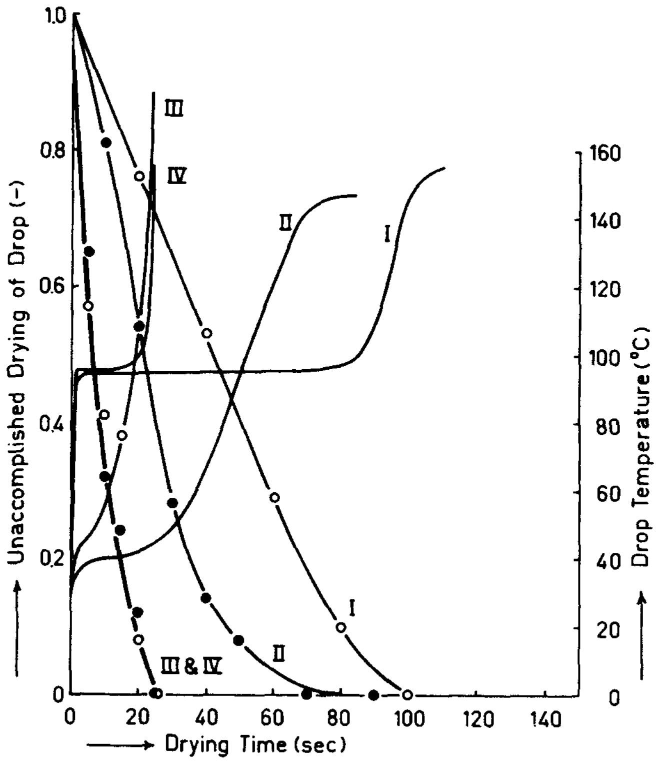

Fig. 4. Effect of temperature and drying medium on the drying of tomato juice drops.
(○ superheated steam; ● dry air.)
I. $m_0 = 1.80$ mg., $T_g = 155$°C., $v = 1.7$ m./sec.
II. $m_0 = 1.78$ mg., $T_g = 147$°C., $v = 1.6$ m./sec.
III. $m_0 = 1.55$ mg., $T_g = 250$°C., $v = 2.1$ m./sec.
IV. $m_0 = 1.78$ mg., $T_g = 250$°C., $v = 1.9$ m./sec.

In all instances, evaporation increased with the velocity and temperature of the drying medium. At equal temperatures and velocities the rate was greater for air than for superheated steam. However, as the drying temperature increased, this difference between the rates of evaporation in the two media decreased.

The adequacy of the experimental procedure, and hence the significance of the results, was checked by comparing the measured rates of evaporation with those predicted by Equations (3) to (6). In those calculations the emissivity of water was taken as 0.95, the emissivity of the thermocouple wires was assumed to be 1.0, and the thermal conductivities of the wires were based on reported values of 0.064 and 0.045 cal./(sec.)(cm.)(°C.) for constantan and chromel, respectively, at 100°C. Experimental and calculated rates of evaporation for run Nos. III and IV, when the weights of the drops were 1 mg., are presented in Table 1. The predicted rate for air was about 2% greater than the measured rate, and the predicted rate for steam was about 2% less than the measured rate. This agreement was well within the estimated accuracy of the experimental measurements.

Drying of Drops Containing Food Products

Generally, this class of materials did not exhibit any constant temperature period, for which the temperature of the drop was near the wet bulb temperature, when drying took place in air. The temperature of the drop rose continuously from its initial temperature to that of the air throughout the course of drying. This rise was interrupted only near the boiling point for those materials whose drops were prone to undergo one or more cycles of inflation, rupture, and collapse. When drying took place in superheated steam, a constant temperature period for drying occurred near the saturation temperature of the steam. This period covered a major portion of the total drying cycle. There was no indication that complete dryness could not be obtained with superheated steam.

TABLE 1. COMPARISON OF EXPERIMENTAL AND CALCULATED* RATES OF EVAPORATION FOR 1-MG. WATER DROPS

	Drying medium	
	Dry air	Superheated steam
Drying temperature, °C.	202	200
Drop temperature, °C.	48	98
Relative velocity, m./sec.	1.8	1.9
Fraction of initial weight equal to 1 mg.	0.820	0.725
Drop diameter at 1 mg., mm.	1.25	1.26
Experimental rate of evaporation, mg./sec.	0.0694	0.0494
Heat transfer coefficient [Equation (1)], cal./(sec.)(sq.cm.)(°K.)	0.00432	0.00403
Heat transfer rate by convection [Equation (3)], cal./sec.	0.0327	0.0206
Heat transfer rate by radiation [Equation (5)], cal./sec.	0.00255	0.00198
Heat transfer rate by both thermocouples [Equation (6)], cal./sec.	0.00483	0.00350
Total rate of heat transfer to drop, cal./sec.	0.0401	0.0261
Predicted rate of evaporation, mg./sec.	0.0704	0.0484

* Properties of air and steam from reference 8.

In Figure 3 are shown the histories of moisture content and temperature for the drying of 2-μ drops of the sucrose solution. At 150°C. drying took place more rapidly in air than in superheated steam, and the final product was a clear, but somewhat sticky, particle. The stickiness may have been due to the prescence of a small amount of invert sugar. When drying with steam, the drop began a sequence of inflations and ruptures after some 15 sec. of drying at this temperature. At 250°C. the rate of drying was slightly greater in steam than in air. Inflation and

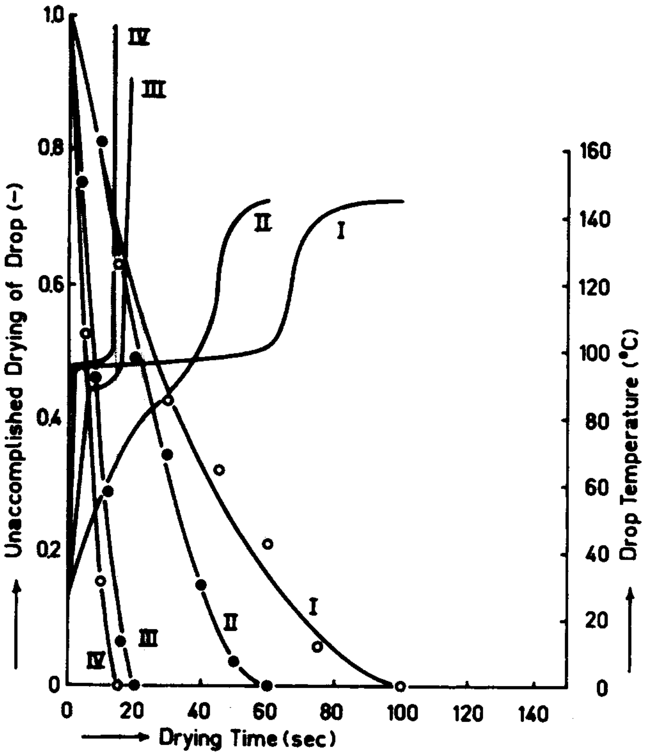

Fig. 5. Effect of temperature and drying medium on the drying of coffee extract drops.
(○ superheated steam; ● dry air.)
I. $m_0 = 2.08$ mg., $T_g = 145$°C., $v = 1.7$ m./sec.
II. $m_0 = 1.93$ mg., $T_g = 145$°C., $v = 1.6$ m./sec.
III. $m_0 = 2.04$ mg., $T_g = 255$°C., $v = 1.9$ m./sec.
IV. $m_0 = 2.10$ mg., $T_g = 250$°C., $v = 2.1$ m./sec.

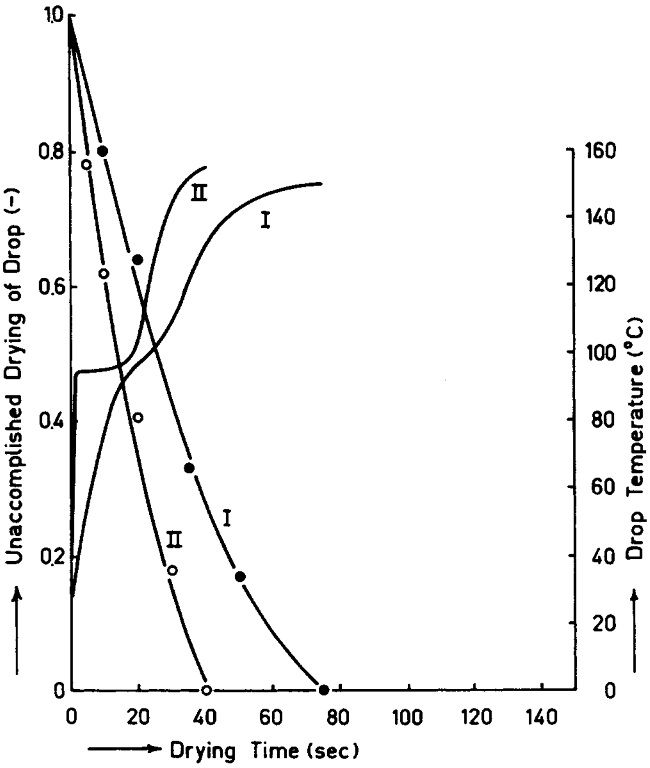

Fig. 6. Effect of drying medium on the drying of milk drops.
(○ superheated steam; ● dry air.)
I. $m_0 = 1.96$ mg., $T_g = 150$°C., $v = 1.6$ m./sec.
II. $m_0 = 2.04$ mg., $T_g = 155$°C., $v = 1.7$ m./sec.

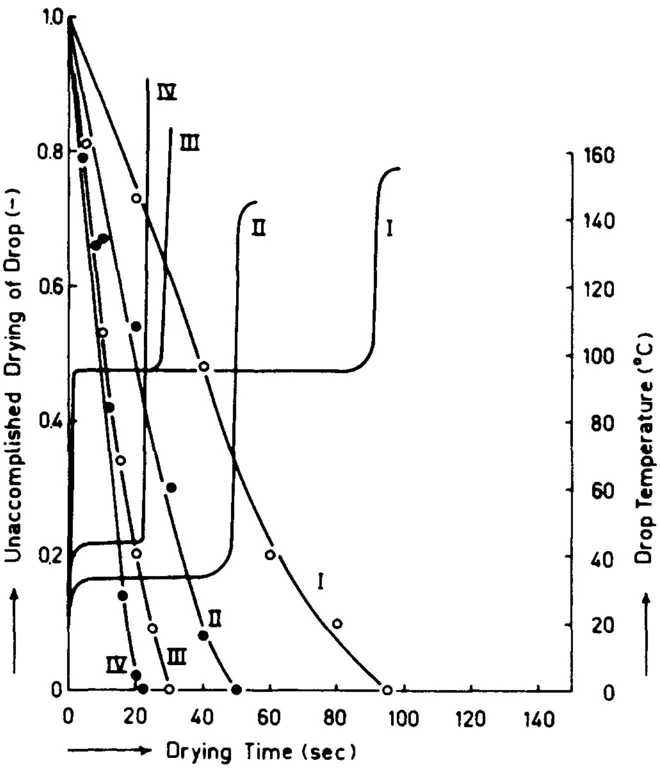

Fig. 7. Effect of temperature and drying medium on the drying of clay slurry drops.

(○ superheated steam; ● dry air.)

I. m_0 = 1.93 mg., T_g = 155°C., v = 1.7 m./sec.
II. m_0 = 1.98 mg., T_g = 145°C., v = 1.6 m./sec.
III. m_0 = 1.98 mg., T_g = 250°C., v = 2.1 m./sec.
IV. m_0 = 2.08 mg., T_g = 255°C., v = 1.9 m./sec.

rupture of the drying drop took place in both air and steam at this temperature. Carmalization also took place in both drying media after the temperature of the drop reached the necessary 215° to 220°C.

The drying characteristics of nominally 2-μliter drops of tomato juice are summarized in Figure 4. Drying proceeded much more rapidly in air than in superheated steam when the temperature was 150°C. In this case, a constant temperature period of drying was obtained with air and probably occurred because of the initially low concentration of solids. At 250°C. there was no appreciable difference in the drying rates for the two media. For all conditions the resulting particles turned brown in color because of a breakdown of the pigments by thermally catalyzed chemical reactions.

Temperatures and moisture contents are given in Figure 5 for drying 2-μliter drops of coffee concentrate in air and steam. The drying rate was considerably higher in air than in steam at 145°C. A certain amount of inflation and rupture took place during the second half of the drying period in steam at this temperature. As with the sucrose solution, drying in steam gave somewhat higher drying rates than did air at 250°C. Inflation and rupture occurred during most of the drying process in steam at this temperature as opposed to practically none for in the case of air. It was also noted that drying in air produced somewhat larger dried particles as compared with drying in steam.

As shown in Figure 6, 2-μliter drops of skimmed milk dried considerably faster in steam than in air at about 150°C. Inflation and rupture occurred continuously in both drying media, but the magnitude of the inflation was much greater in the case of steam. In both instances the dried particle was relatively large and hollow. The degree of discoloration, for which the color was light brown, was the same in both drying media.

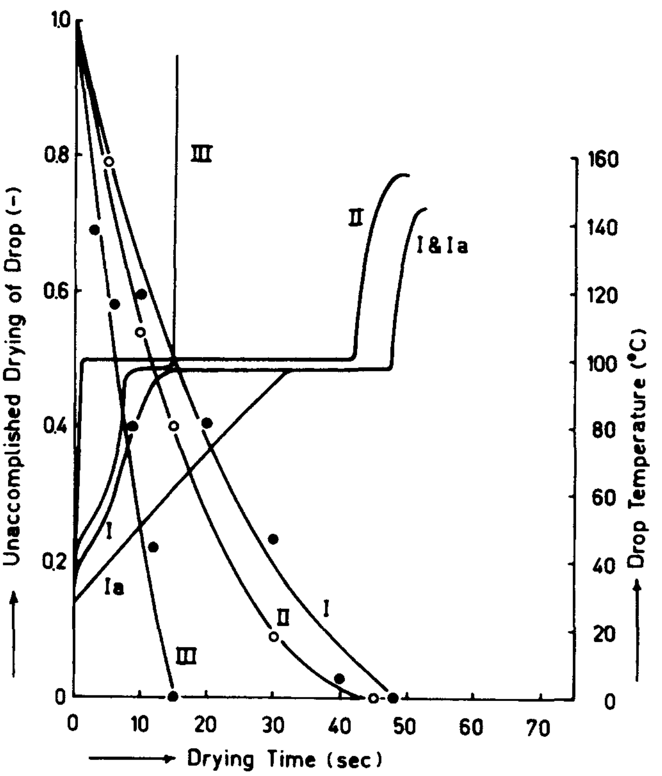

Fig. 8. Effect of temperature and drying medium on the drying of sodium sulfate drops.

(○ superheated steam; ● dry air.)

I. m_0 = 1.46 mg., T_g = 145°C., v = 1.6 m./sec.
II. m_0 = 1.38 mg., T_g = 155°C., v = 1.7 m./sec.
III. m_0 = 1.52 mg., T_g = 250°C., v = 1.9 m./sec.

Comparison of the drying histories for these four food products suggested that air generally gives equivalent or more rapid drying than steam at temperatures near 150°C., whereas superheated steam gives equivalent or slightly faster drying than air at around 250°C. However, there was some indication that the relative rates of drying and the differences in properties of the dried particles for these drying media are product specific. The effects of thermal degradation were equally as severe in air as in steam.

Drying of Drops Containing Miscellaneous Materials

In Figures 7 to 10 are recorded the histories of temperature and moisture content for drops of materials with certain mutually different chemical and/or physical properties. The pattern of drying for these drops was quite similar to the evaporation of water drops when superheated steam was used as the drying medium. Without exception, a rather long constant temperature period existed for steam during which time the temperature of the drop was near the boiling point of water. The drop attained this temperature very rapidly, usually in less than 2 to 3% of the total drying time. When drying took place in air, the course of drying varied considerably from one material to another.

In Figure 7 is shown the manner in which 2-μliter drops of a clay suspension dried in both air and steam. The variation of a drop's moisture content and temperature followed very closely that of evaporating water drops in both drying media. For all practical purposes, the constant temperature period extended throughout the entire drying cycle for both drying media. This may, in part, have been due to the initially low concentration of the suspension, but the nature of the material was probably more responsible for such behavior. (Compare these results with those of tomato juice in Figure 4). At 150°C. the drying took place much faster in air than in superheated steam, where-

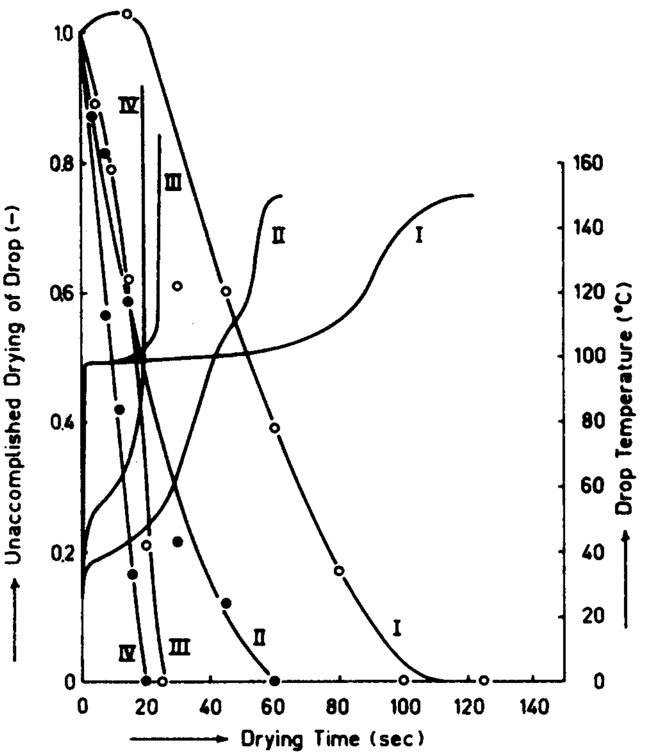

Fig. 9. Effect of temperature and drying medium on the drying of potassium nitrate drops.

(○ superheated steam; ● dry air.)

I. $m_0 = 2.30$ mg., $T_g = 150$°C., $v = 1.7$ m./sec.
II. $m_0 = 2.04$ mg., $T_g = 150$°C., $v = 1.6$ m./sec.
III. $m_0 = 2.11$ mg., $T_g = 250$°C., $v = 2.1$ m./sec.
IV. $m_0 = 2.16$ mg., $T_g = 250$°C., $v = 1.9$ m./sec.

as there was little difference between the drying times for these two media at 250°C. For all conditions of drying, the final product was a small, solid, beadlike particle. The drops showed no tendency to inflate in either air or steam during drying.

The manner in which nominally 1.5-μliter drops of sodium-sulfate solution dried is shown in Figure 8. The drops dried much more rapidly in steam than in air at temperatures near 150°C. For drying in air, there was no depressed dynamic equilibrium temperature similar to a wet bulb temperature. Instead, the temperature of the drop rose from its initial temperature to near the boiling point of water where it remained until near the very end of the drying cycle. At 145°C. the manner in which the drops dried varied somewhat from one drop to another. This variation was also noted by Charlesworth and Marshall (3) when drying at temperatures below 100°C. The time required for drying was dependent upon whether the crust of the partially crystallized drop ruptured or not, as well as on the degree of rupture. The experimental procedure used in this study necessitated that any recorded history of drying be an average history. The moisture contents reported here were the average of two separate determinations. However, the complete thermal history for a single drying drop was readily obtained. The temperatures of similar drops also varied from drop to drop as shown for two cases. When the temperature of the air was increased to 250°C., drops were observed to dry much more uniformly. Under these conditions there was no rupturing of the shell, and like drops gave like drying times. When drops were dried in steam, their temperatures were very near the boiling point of water throughout practically the entire drying cycle. No visual differences were detectable between the final particles obtained from drying in air and steam except for occasional ruptures in the shell when drying took place in air at the lower temperature.

Potassium nitrate dried quite differently from sodium sulfate as can be seen in Figure 9 for 2-μliter drops. There was no constant temperature period for drying in air, and this period occupied only 50% of the drying cycle for drying in steam. At 150°C. the drying proceeded much more rapidly in air than in steam. At 250°C. the drying rates in air and steam were nearly equal. A certain amount of inflation and rupture of the drops took place in steam, whereas the drops inflated only and did not rupture in air. A dried particle of considerably higher density was produced with steam as compared with air. The pronounced initial increase in weight of the drop as compared with pure water (see Figure 2), which resulted from condensation while drying with superheated steam at the lower temperature, was promoted by the rather large positive heat of solution for this material.

In Figure 10 are given the drying histories of 2-μliter drops of a commercial laundry detergent. Drying occurred considerably more rapidly in air than in superheated steam at 150°C., whereas there was no noticeable difference between the rates of drying in the two media at 250°C. The histories of the temperatures of the drops were almost identical to those for potassium nitrate. A certain amount of inflation and rupture took place when the drops dried in steam, but essentially none occurred when drying took place in air. Particles of higher density were produced by an atmosphere of superheated steam relative to air, as illustrated in Figure 11.

The drying histories of 2-μliter drops of a suspension/solution of nickel hydroxide and sodium sulfate indicated that there was little difference between the total drying

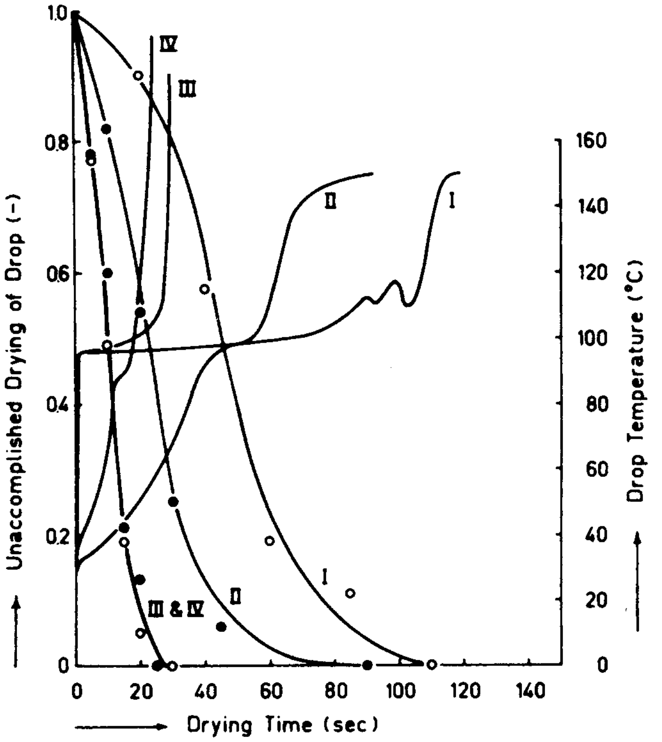

Fig. 10. Effect of temperature and drying medium on the drying of detergent drops.

(○ superheated steam; ● dry air.)

I. $m_0 = 2.15$ mg., $T_g = 150$°C., $v = 1.7$ m./sec.
II. $m_0 = 2.06$ mg., $T_g = 150$°C., $v = 1.6$ m./sec.
III. $m_0 = 2.16$ mg., $T_g = 250$°C., $v = 2.1$ m./sec.
IV. $m_0 = 2.09$ mg., $T_g = 250$°C., $v = 1.9$ m./sec.

times in steam and air. The temperatures of the drops, when being dried in both media, fell rather quickly after reaching about 130°C. and shortly thereafter continued to rise toward the temperature of the drying medium. This temporary decrease in temperature suggested that some of the nickel hydroxide decomposed to nickel oxide. Although no visible change in the drops was observed at 150°C., there was a definite change in color from green to black spots in a green background when drops were dried at 250°C. in both air and steam.

A comparison of the drying histories for these five materials suggested that no general trends as to drying rates vs. drying conditions exist. The relative rates of drying and properties of the dried particles for the two drying media were quite product specific. Dehydration occurred just as readily in steam as in air.

DISCUSSION

Exclusive of the induction period, the drying process ideally takes place in three stages depending upon whether the resistances to heat and mass transfer exist only in the drying medium, in both the drying medium and the material being dried, or only in the material being dried. For those drying operations where the interfacial area available to heat and mass transfer is constant, for example, tray drying, the first stage composes the constant rate period, and the second and third stages compose the first and second portions of the falling rate period. In spray drying, the interfacial area is not constant during the first stage of drying, and therefore no constant rate period per se exists. However, in both geometries the temperature at the interface is constant during the first stage. This condition is exactly so for the evaporation of liquids and the drying of slurries, and it is approximately so for the drying of soluble solids in solution. In spray drying the first stage of drying is generally designated as the first period of drying and the two final stages of drying as the second period of drying. Charlesworth and Marshall (3) have discussed in detail these two drying periods for the drying of drops in air at moderate temperatures.

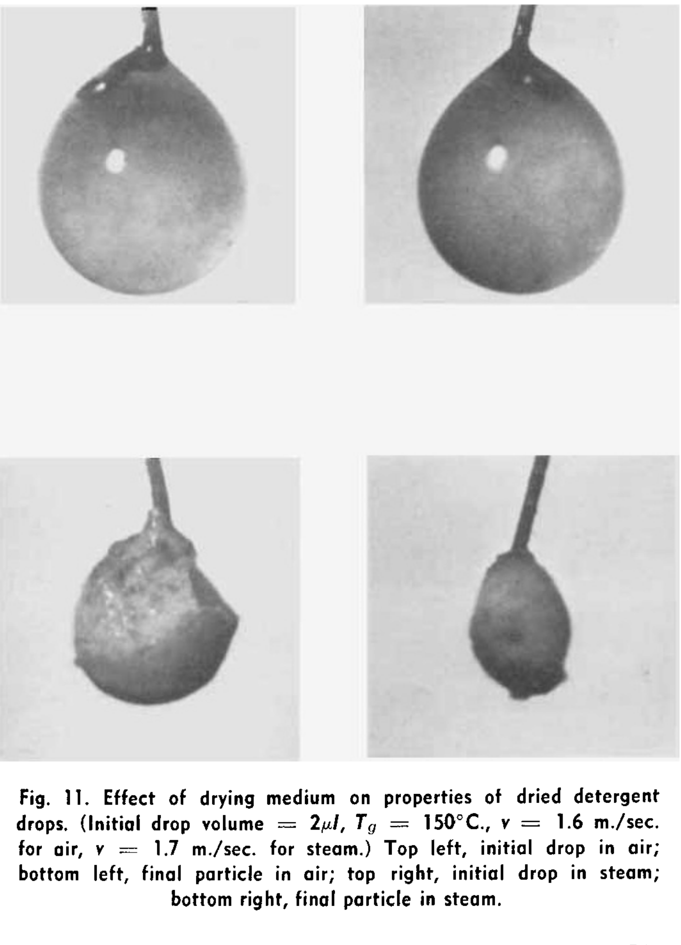

Fig. 11. Effect of drying medium on properties of dried detergent drops. (Initial drop volume = $2\mu l$, T_g = 150°C., v = 1.6 m./sec. for air, v = 1.7 m./sec. for steam.) Top left, initial drop in air; bottom left, final particle in air; top right, initial drop in steam; bottom right, final particle in steam.

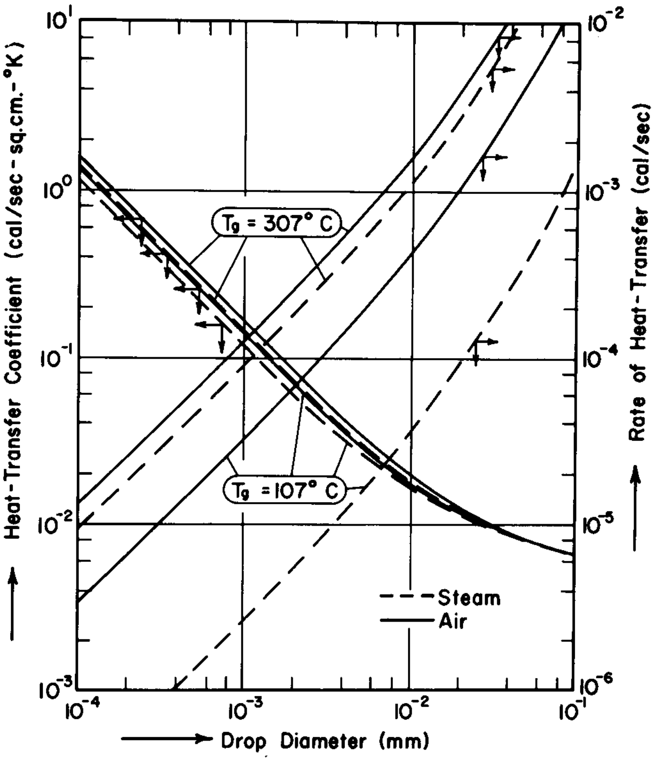

Fig. 12. Predicted rates of heat transfer to freely falling water drops in dry air and steam. (For T_g = 107°C., T_d = 32.2°C. in air and T_d = 100°C. in steam; for T_g = 307°C., T_d = 52.8°C. in air and T_d = 100°C. in steam.) (Properties of air and steam from reference *8*.)

Period of Constant Temperature (First Period of Drying)

When this period of drying prevails, the rate of heat transfer to the drop is given by Equation (3) and is a function of the heat transfer coefficient, the difference between the temperature of the drop, and that of the drying medium and the size of the drop. The heat transfer coefficient depends basically upon the physical properties of the drying medium, the relative velocity between the drying medium and the drop, and the size of the drop. For pure liquids, the temperature of the drop will be, for all practical purposes, the boiling point for evaporation into superheated vapors and will be near the wet bulb temperature for evaporation into air. When solids are present, the temperature of the drops in these two drying media will be equal to or greater than that for pure liquids.

Sjenitzer (*20*) considered the relative rates of evaporation of water drops in superheated steam vs. dry air and concluded that such a comparison should be based on equal thermal driving forces. This requires that the steam must be maintained at considerably subatmospheric pressures. Spray dryers normally operate at atmospheric pressures, and consequently a comparison based on equal dry bulb temperatures is perhaps more desirable. Calculated rates of convective heat transfer to water drops falling at their terminal velocities in dry air and steam are summarized in Figure 12. Water drops of less than 1 mm. in diameter exhibit negligible circulation and distortion in these drying media, and any oscillations resulting from the formation of the drops damp out very rapidly (*9*). These calculations, contrary to previously reported comparisons which were based on experimental data from different pieces of equipment for flow parallel to flat surfaces (*4, 14*), indicate that the rate of heat transfer and hence the rate of evaporation is greater in air than in superheated steam. This difference in the rates is primarily due to the difference in thermal driving forces rather than heat transfer coefficients. At a pressure of 1 atm. and a drying temperature of 100°C., the rate of heat transfer will be zero for steam and finite for air, while at a drying temperature of about 400°C. both rates will be finite and nearly equal. The experimental results obtained in this study quantitatively confirm these calculations.

The presence of solids altered the evaporation process markedly, especially when air was the drying medium. For the drying temperatures used in this study, the only material to exhibit a constant temperature period of any duration in air was the clay suspension. At about 150°C. there was a tendency on the part of potassium nitrate, nickel hydroxide/sodium sulfate mixture, and the very dilute tomato juice to develop a constant temperature period in air. Such was not the case at near 250°C. The suspension/solution of nickel hydroxide and sodium sulfate dried as a solution rather than as a suspension. Those materials, whose drops experienced inflation, rupture, and collapse in air, were prone to sustain a temperature near the boiling point of the solvent during a portion of the drying cycle. This occurred well after the onset of drying and generally was not too prolonged.

When superheated steam was used as a drying medium, a period of constant temperature always occurred. The relative length of this period decreased as the drying temperature increased for all materials except the clay suspension. In this particular instance, the constant temperature period prevailed throughout the entire drying cycle. As was the case for drying in air, the fact that the clay is insoluble and forms a porous particle probably explains this result.

The disadvantage of using superheated steam as a drying medium for thermally sensitive materials was evident from the experimental results. During the first period of drying, the minimum temperature experienced by the drop was the boiling point of the solvent. No matter what the flow pattern within the dryer, the temperature of the drop would never fall below this value. The only way to lower the drop's temperature would be to lower the operating pressure in the dryer. Dilution of superheated steam with, for example, air as suggested by Chu et al. (*4*) would give the same result coupled with a major sacrifice in the thermodynamic efficiency of the dryer. To reduce the temperature of the drop from 100 to 86°C. would require operating either at 0.6 atm. or with 40% air present.

Second Period of Drying

Drops of solutions and colloidal suspensions generally exhibited internal resistance to heat and mass transfer, and the majority of drying occurred during the second period of drying. When the drying medium was air whose temperature was reasonably high and the concentration of the solids in the drop was not low, the first period of drying did not develop. The manner in which the drops dried during this second period was very much dependent on the material being dried. Drops of sodium sulfate, when dried in air, maintained a temperature near the boiling point throughout nearly the entire drying cycle, whereas drops of potassium nitrate continually increased in temperature during drying. Even when no period of constant temperature existed in air, the temperature of the drop was lower in air than in steam during the first portion of the drying cycle. However, during the latter portion of the drying cycle the reverse was generally true. In the case of film forming materials, which in this study were the food products and the detergent, it was not possible to distinguish by temperature between the first period of drying and the initial portion of the second period of drying when steam was the drying medium. Only the visible detection of inflation, rupture, and collapse indicated that the second period of drying had obtained. The skin which formed around drying drops of these materials was much more pliable when the drying occurred in steam. This produced less resistance to inflation and rupture, and consequently the drop's temperature remained at the boiling point for a longer period in steam than in air.

Total Drying Cycle

The drying medium for which the time averaged value of the thermal driving force was greater usually yielded the shorter drying cycle. Even though the drying rate during the first period of drying was both predicted and measured to be lower in superheated steam than in air, complete drying was sometimes found to occur more rapidly in steam than in air. This resulted when the first period of drying was effectively longer because the inflation of the drop was markedly greater and/or because the skin which formed around the drop had relatively less resistance to mass transfer for drying in steam as opposed to air.

The results given in Figure 6 indicate that at about 150°C. milk dried more rapidly in steam than in air. The more elastic and pliable nature of the skin developed in steam did not extend the effective length of the first period of drying so as to produce a lower time averaged temperature for the drop. However, the degree of inflation was greater in steam, and consequently more surface area was available for heat transfer.

As indicated by Figure 8, sodium sulfate dried faster in superheated steam than in air, even though the time averaged temperature of the drop was lower in air. The similarity in the size of the final particles, the nondependency of sodium sulfate's solubility on temperature, and the constancy of the drop's temperature during the latter phase of drying suggests that the resistance to mass transfer in the crust was somewhat less for steam.

Conceivably, a strong dependence of solubility on temperature might affect the total time of drying. If solubility increases markedly with temperature, formation of a solid phase would be retarded by drying in steam because of the higher temperature of the drop. This, in turn, would extend the length of the first period of drying in which the rate of drying is greatest, and the total drying time might then be reduced. The solubility of potassium nitrate increases greatly with increasing temperature, but the results given in Figure 9 show that drops of this material dried more rapidly in air than steam for the drying temperatures studied. Apparently other effects overwhelmed the difference in solubility, such as the early formation of a crust and subsequent inflation of the drop with no rupture which then produced a greater surface area for heat and mass transfer when air was the drying medium.

CONCLUSIONS

The results of this study support the findings of Toei et al. (*21*) and indicate that the accepted correlation of heat transfer coefficients which is applicable for evaporation of small drops of pure liquid in air is also valid for evaporation in a superheated vapor. Under comparable conditions, the heat transfer coefficients to drops in steam are no more than about 15% less than those in air. At equal dry bulb temperatures, the rate of evaporation is greater in air than in steam. Near 100°C., the rate in air is many times greater than that in steam, and at much higher temperatures, say 400°C., the rates are nearly equal.

Drops containing only suspended inert solids dry in the same manner as drops of water evaporate. Drops containing solutions or colloidal suspensions of some materials follow the same trend as evaporating water drops in that drying takes place more slowly in steam than air at low drying temperatures. However, there are a number of materials for which drying occurs more rapidly in superheated steam than in air because of differences in the drying rates during the second period of drying. Radical differences in the internal mechanism of drying are caused by extension of the first period of drying because of increased solubility, by alteration of resistance to heat and mass transfer because of a greater proneness of the skin to inflate and rupture, or because of a more pervious crust, and by generation of more surface area because of inflation without rupture.

No radically different properties of the dried particles result from drying in steam as compared with air. However, drops dried in steam sometimes yield denser particles. Dehydration and thermal degradation occur just as readily in both drying media.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial assistance extended to A.M.T. by Unilever N.V. during the course of this work and to thank the Union Carbide Corporation for initiating interest in this study and supplying the photographic equipment.

NOTATION

A = surface area of drop, sq.cm.
c_f = average total molar concentration of drying medium in transfer path adjacent to drop, g.-mole/cc.
$\hat{C}_{pA}$ = heat capacity of water vapor, cal./(g.)(°K.)
$\hat{C}_{pf}$ = average heat capacity of drying medium in transfer path adjacent to drop, cal./(g.)(°K.)
D = diameter of drop, cm.
D_{AB} = binary diffusivity for water vapor in air, sq.cm./sec.
F_A = geometry factor, dimensionless
F_ϵ = emissivity factor, dimensionless
h = average heat transfer coefficient between drop and drying medium at low rates of evaporation, cal./(sec.)(sq.cm.)(°K.)
h = average heat transfer coefficient between drop and drying medium at high rates of evaporation, cal./(sec.)(sq.cm.)(°K.)
h_t = average heat transfer coefficient between thermocouple wire and drying medium, cal./(sec.)(sq.cm.)(°K.)
k_f = average thermal conductivity of drying medium in transfer path adjacent to drop, cal./(sec.)(cm.)(°K.)
k_t = thermal conductivity of thermocouple wire, cal./(sec.)(cm.)(°K.)
k_y = average mass-transfer coefficient between drop and drying medium at low rates of evaporation, g.-mole/(sec.)(sq.cm.)
N_{Nu} = Nusselt number, hD/k_f, dimensionless
N_{Pr} = Prandtl number, $\hat{C}_{pf}\mu_f/k_f$, dimensionless
N_{Re} = Reynolds number for heat and mass transfer calculations, $\rho_f Dv/\mu_f$, dimensionless
N_{Sc} = Schmidt number, $\mu_f/\rho_f D_{AB}$, dimensionless
N_{Sh} = Sherwood number, $k_y D/c_f D_{AB}$, dimensionless
P = total pressure of system, atm.
p_{Bm} = average partial pressure of air in transfer path adjacent to drop, atm.
Q_c = rate of heat transfer to drop by convection, cal./sec.
Q_r = rate of heat transfer to drop by radiation, cal./sec.
Q_t = rate of heat transfer to drop through supporting thermocouples, cal./sec.
R = radius of thermocouple wire, cm.
T = temperature of thermocouple wire at axial position z, °K.
T_d = temperature of drop, °K.
T_g = temperature of drying medium, °K. (°C. in figures)
v = relative velocity between drop and drying medium, cm./sec.
w_A = rate at which water evaporates, g./sec.
z = coordinate along axis of thermocouple wire, cm.
ϵ = emissivity, dimensionless
μ_f = average viscosity of drying medium in transfer path adjacent to drop, g./(cm.)(sec.)
ρ_f = average density of drying medium in transfer path adjacent to drop, g./cc.
σ = Stefan-Boltzman constant, 1.355×10^{-12} cal./(sec.)(sq.cm.)(°K.$^{-4}$)

LITERATURE CITED

1. Anonymous, *Chem. Eng. News*, **46**, No. 1, 50 (Jan. 8, 1968).
2. Bainbridge, J. R., and K. Satchwell, *Fuel*, **26**, 28 (1947).
3. Charlesworth, D. H., and W. R. Marshall, Jr., *AIChE J.*, **6**, 9 (1960).
4. Chu, J. C., A. M. Lane, and D. Conklin, *Ind. Eng. Chem.*, **45**, 1586 (1953).
5. Chu, J. C., S. Finelt, W. Hoerrner, and M. S. Lin, *ibid.*, **51**, 275 (1959).
6. Downing, C. G., *AIChE J.*, **12**, 760 (1966).
7. Hausbrand, E., "Das Trocknen mit Luft und Dampf," Julius Springer Verlag, Berlin, Germany (1908).
8. Hilsenrath, J., "Tables of Thermal Properties of Gases," Circular of Nat. Bur. Stds. C564, U.S. Dept. of Commerce, Washington, D. C. (1955).
9. Hughes, R. R., and E. R. Gilliland, *Chem. Eng. Progr.*, 48, 497 (1952).
10. Hughmark, G. A., *AIChE J.*, **13**, 1219 (1967).
11. Karrer, J., Schweizerische Bauzeitung, Nov. 6 and 13 (1920), as reported in *Engineering*, **110**, 821 (1920).
12. Keey, R. B., and J. B. Glen, *Can. J. Chem. Eng.*, **42**, 227 (1964).
13. Lee, K., and D. J. Ryley, *J. Heat Transfer, Trans. Am. Soc. Mech. Engrs.*, **90**, 445 (1968).
14. Lane, A. M., and S. Stern, *Mech. Eng.*, **78**, 423 (1956).
15. Ranz, W. E., and W. R. Marshall, Jr., *Chem. Eng. Progr.*, **48**, 173 (1952).
16. Rowe, P. N., K. T. Claxton, and J. B. Lewis, *Trans. Inst. Chem. Engrs.*, **43**, T14 (1965).
17. Sano, U., and S. Nishikawa, *Chem. Eng. (Japan)*, **28**, 275 (1964).
18. *Ibid.*, **29**, 294 (1965).
19. Shepherd, C. B., C. Hadlock, and R. C. Brewer, *Ind. Eng. Chem.*, **30**, 388 (1938).
20. Sjenitzer, F., *Chem. Eng. Sci.*, **1**, 101 (1952).
21. Toei, R., M. Okazaki, K. Kubota, K. Ohaski, and K. Mizata, *Chem. Eng. (Japan)*, **30**, 43 (1966).
22. Ungewitter, C., "Science and Salvage," Crosley Lockwood and Son, London, England (1944).
23. Walker, W. H., W. K. Lewis, W. H. McAdams, and E. R. Gilliland, "Principles of Chemical Engineering," p. 635,

McGraw-Hill, New York (1937).
24. Wenzel, L., and R. R. White, *Ind. Eng. Chem.*, 43, 1829 (1951).

Manuscript received October 11, 1968; revision received February 26, 1969; paper accepted February 28, 1969.

APPENDIX

The thermocouple wires were likened unto two long rods whose terminal temperature was that of the drop and which exchanged heat with their surroundings by both radiation and convection. The wires were considered not to interfere with each other regarding this heat exchange. The usual assumptions of constant physical properties, a constant temperature environment, a constant heat transfer coefficient along the rod, no radial temperature profile in the rod, and a mathematically infinitely long rod, plus the additional assumptions of a geometry factor for radiation of unity and an emissivity factor equal to the emissivity of the wire, gave

$$\frac{d^2T}{dz^2} + \frac{2}{Rk_t}\left[\sigma\epsilon(T_g^4 - T^4) + h_t(T_g - T)\right] = 0 \qquad \text{(A1)}$$

for which the boundary conditions are at $z = 0$, $T = T_d$, and at $z = \infty$, $T = T_g$ or at $z = \infty$, $dT/dz = 0$. Integration gave

$$\frac{dT}{dz} = \pm \left\{ \frac{2}{Rk_t}\left[\frac{2\sigma\epsilon}{5}(T^5 - T_g^5) - 2\sigma\epsilon T_g^4(T - T_g) + h_t(T - T_g)^2\right]\right\}^{1/2} \qquad \text{(A2)}$$

The rate at which heat was transferred to the drop by each wire followed from

$$Q_t = -\pi R^2 k_t \left.\frac{dT}{dz}\right|_{z=0} \qquad \text{(A3)}$$

Evaluation of Equation (A3) with the aid of Equation (A2) yielded Equation (6).

Experimental Determinations of Several Thermal Properties of a Mixture Containing 51 Mole Percent Propane in Methane

V. F. YESAVAGE, D. L. KATZ, and J. E. POWERS
The University of Michigan, Ann Arbor, Michigan

Results of calorimetric determinations are reported for a mixture containing approximately 51 mole % propane in methane. Measurements were made with both isobaric and throttling flow calorimeters in the liquid, critical, gaseous, and two-phase regions in the temperature range from —250° to +300°F. at pressures of between 100 and 2,000 lb./sq. in. abs. Tables of experimental values of heat capacity, Joule-Thomson coefficient, and isothermal throttling coefficient are presented, and the values of C_p and ϕ are summarized on parametric plots.

Experimental values of enthalpy differences within the two-phase region determined under both isobaric and isothermal conditions are also reported together with the experimentally determined phase boundary data. A skeleton enthalpy table is presented which is based almost entirely on experimental data obtained in this investigation. Comparisons are made with other published calorimetric data and with calculations based on PVT data.

This article summarizes additional results in the continuing effort to obtain accurate experimental data on the thermal properties of light hydrocarbons, fixed gases, and their mixtures. It is anticipated that such data will serve to improve engineering design calculation not only by presenting accurate data but also by providing a firm basis for testing and extending methods of predicting the enthalpy of such materials.

All available literature data on methane, propane, and their mixtures have been summarized in previous publications (*17, 19 21, 25, 26, 36*). No additional calorimetric data have been noted since the last of the above reports (*36*) was presented.

THERMODYNAMIC RELATIONS

The basic equations for the interpretation of flow calorimetry data have been presented previously in a number of references (*21, 35, 38*). In brief, the first law of thermodynamics is applied to relate the change in specific enthalpy between inlet and outlet conditions to the measured rate of transfer of electrical energy $\dot{W}$ and the mass flow rate F. For the calorimeters used in the course of this investigation, kinetic and potential energy effects are insignificant, and the rate of heat leak $\dot{Q}$ is negligible.

$$(\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1})_x = -\frac{\dot{W}}{F} \qquad (1)$$

In applying this equation to interpret results obtained in the isobaric flow calorimeter, the slight pressure drop through the calorimeter is taken into account. Similarly, the isothermal flow calorimeter is usually operated with a temperature difference of less than 0.05°F., and this measured difference is accounted for in interpreting the results. Such corrections rarely amount to as much as 1%.

V. F. Yesavage is at Shell Oil Company, Houston Research Laboratory, Deer Park, Texas.