NOTE ON THE VALUE OF JOULE-THOMSON OBSERVATIONS FOR COMPUTING STEAM TABLES.

By Harvey N. Davis.

THIS note is offered for two reasons. In the first place, it is often supposed that Joule-Thomson or throttling experiments are of value chiefly in evaluating the thermodynamic or Kelvin scale of temperature, and in discussions of molecular attraction. As a matter of fact, such observations afford by far the best available means of determining for the use of engineers many of the important thermal properties of such vapors as steam and ammonia. In the case of steam, a point has now been reached where such observations are especially appropriate, since all but one of the remaining gaps can best be filled by this method. In the case of ammonia, much work has still to be done to supply the constants of integration that are necessary in this line of attack, but even here, Joule-Thomson observations will soon be necessary, if the most accurate results are desired.

And in the second place, it is believed that a compact resume of the underlying theory will be useful. In the course of this presentation, the essential identity of certain procedures that have often been regarded as distinct will be pointed out, and a variation of one of them suggested. Furthermore the form of proof presented, although obvious, seems not to have been published.

The fundamental data from which a set of steam tables can be most easily computed are: For the one-phase region, data on (1) the specific heat of superheated steam, and (2) the specific volume of superheated steam. For the two-phase region, data on (3) either the specific volume of saturated steam, or the total heat of saturated steam, or the heat of vaporization, (4) the specific heat of orthobaric water, (5) the specific volume of orthobaric water, and (6) the vapor pressure of wet steam.

Satisfactory data of the fifth and sixth sorts are already at hand. Satisfactory data of the fourth sort are sadly needed, but can hardly be supplied by anything resembling a Joule-Thomson experiment. But everything that is still needed under either of the first three heads, and the outstanding needs are numerous and important, can be supplied better by suitable Joule-Thomson experiments than in any other way.

In the first place, such experiments, if carried out with a heating coil, as suggested by Buckingham in 1903, can yield a direct determination of the specific heat of superheated steam. The heating coil is embedded in the plug of the ordinary experiment, and enables one to put a measured quantity of heat into each gram of steam as it goes through the plug. By this means what would ordinarily be a cooling can be reduced to zero, or changed to a warming of the emerging steam as compared with the entering steam. When the change of temperature is exactly zero, the whole apparatus can be kept at one temperature, and the heat losses of the ordinary sort are zero. It was this advantage that led to the proposal of the plan in the first place. Unfortunately there are heat losses of another sort in the isothermal experiment which, although not as large as in the adiabatic experiment, are more difficult to handle. Nevertheless, let us suppose that the heat losses of both sorts can be controlled, measured and allowed for, and that a series of experiments can be made at different rates of heat input, the high side pressure and temperature and the pressure drop being the same for all. Then if the heat supplied per gram of steam is plotted against the corrected change of temperature (Fig. 1), the result will be a straight line (if c_p is constant within the small temperature range in question) and the slope of this line will be c_p itself for the *low-side* pressure and temperature. To prove this one has only to notice that the plotted curve is really a curve of total heat against actual temperature for various conditions of the low side steam all at the same pressure. Its slope is therefore

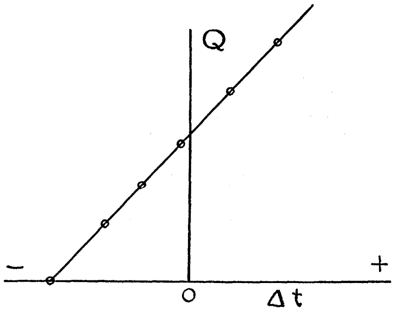

Fig. 1.

$$\left(\frac{\partial H}{\partial t}\right)_p = c_p.$$

Furthermore, since the t-intercept is obviously $\mu\Delta p$, the Q-intercept is $\mu c_p\Delta p$. Whether the inevitable heat losses of various kinds can be eliminated with sufficient accuracy to make this as good a method of measuring c_p as that of Knoblauch remains to be seen. At any rate, it will afford a useful check, either on c_p, or on the elimination of the heat losses, according to the relative accuracy of the previous knowledge of these two factors.

It should be noticed in passing that this is simply a combination in one experiment of the previously familiar principles of throttling experiments and of continuous flow calorimetry. The less the throttling provided for in designing the plug, the more does this method approach continuous flow calorimetry of the ordinary sort, like that of Knoblauch. But even in his case, where the throttling was made as small as possible, the correction for it is a troublesome one to apply unless it is handled from this point of view. And on the other hand, the introduction of as much throttling as is conveniently possible has the advantages both of helping to ensure that the steam is dry, and of providing twice as great a range of temperature for the specific heat measurements for the same maximum difference of temperature between the steam and its surroundings.

Besides this direct determination of c_p, Joule-Thomson experiments can give indirect but valuable information about c_p, in three substantially equivalent ways proposed originally by Dodge, by Davis and by Grindley. The value of each of these methods lies in the fact that it is easier, especially at high temperatures, to measure c_p at one atmosphere than at higher pressures; for each of these methods enables one to spread a c_p curve, determined at atmospheric pressure, into a family of curves covering as wide a range of pressures as are covered by the Joule-Thomson data. Dodge's and Davis's methods effect this by spreading c_p along lines of constant total heat or enthalpy; Grindley's spreads c_p along lines of constant temperature. The relative convenience of these three methods depends largely on how the Joule-Thomson experiments have been arranged and carried out.

Dodge's method requires that the experiments fall into groups, throughout each of which the high- and low-side pressures are held at fixed values: each group would contain experiments at different and well scattered temperatures. If such data are represented graphically by plotting high-side temperatures as abscissæ and low-side temperatures as ordinates, each group of experiments yields a curve which, at ordinary temperatures, lies below and close to the 45° line of symmetry of the figure, as in Fig. 2. Each point of this curve corresponds to a single experiment in which steam at a high-side temperature t, determined by the abscissa of the point, is throttled into steam at a low-side temperature t_0, determined by the ordinate of the point. Let the high- and low-side pressures corresponding to the whole curve be p and p_0. Then Dodge's theorem is that the slope of the curve at the given point is equal to the ratio of c_p at (p, t) to c_p at (p_0, t_0). If in each group of experiments, the low-side pressure is one atmosphere, the c_p curve at the high-side pressure is thus determined.

To prove this theorem, let Fig. 3 represent on the p, t plane two experiments corresponding to neighboring points of the curve. In one experiment steam is throttled from state (1) to state (2) with the total heat at the constant value H. In the second experiment steam is throttled from state (3) to state (4) with its total heat at the constant value $H + \Delta H$. At the constant pressure p (line 13), the average value of c_p would be

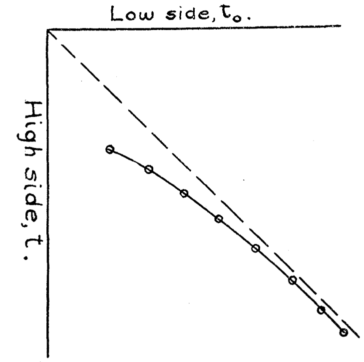

Fig. 2.

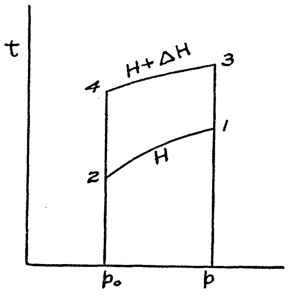

Fig. 3.

$$\bar{c}_p = \frac{\Delta H}{t_3 - t_1}.$$

At the constant pressure p_0 (line 24), the average value of c_p would be

$$\bar{c}_{p_0} = \frac{\Delta H}{t_4 - t_2}.$$

So

$$\frac{\bar{c}_p}{\bar{c}_{p_0}} = \frac{t_4 - t_2}{t_3 - t_1}.$$

But in Dodge's figure $(t_4 - t_2)$ would be the difference between the ordinates of neighboring points of the curve, and $(t_3 - t_1)$ would be the difference between their abscissæ. The ratio $\bar{c}_p/\bar{\ }_{p_0}$ is therefore equal to the slope of the secant. When ΔH approaches zero, this equation approaches the equation stated in words in Dodge's theorem.

This process is more accurate if modified by the use of the temperature difference $(t_0 - t)$ as ordinate instead of t_0 itself, as in Fig. 4. The curve then lies below and close to the t axis and can be plotted on a much larger scale. Its slope s for any value of t is now less by unity than before, and

$$\frac{c_p}{c_{p_0}} = 1 + s \quad \text{or} \quad s = \frac{c_p - c_{p_0}}{c_{p_0}} = \frac{\Delta c_p}{c_{p_0}}.$$

That is, the slope, which is now small, is the ratio of the increase in c_p between p_0 and p along a line of constant enthalpy to the value of c_p at the p_0 end of the interval. Since Δc_p is not more than a third of c_{p_0} for any pressure range occuring in ordinary practice, an accuracy of n per cent. in s would give an accuracy of $n/4$ per cent. in the computed c_p even under the most unfavorable circumstances, and a much higher accuracy over a large part of the plane. This offsets, at least in part, the disadvantage of having to use the derivative of an empirically determined function instead of the function itself.

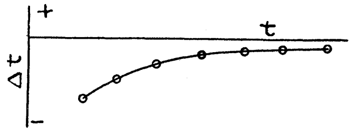

Fig. 4.

Davis's method is based on a differential equation that can be obtained directly from the modified form of Dodge's equation above. Let $p - p_0$ be called Δp_H. Then

$$\frac{1}{c_p}\left(\frac{\Delta c_p}{\Delta p}\right)_H = \frac{s}{\Delta p_H}.$$

s is the derivative with respect to t at constant p of the function $t_0 - t$, which is the drop of temperature through the plug and is negative. Let this function be called $-\Delta t_H$, so that a positive Δt may correspond to a rise of temperature as usual. Then

$$\frac{s}{\Delta p_H} = -\frac{1}{\Delta p_H}\frac{\partial}{\partial t_p}(\Delta t)_H = -\frac{\partial}{\partial t_p}\left(\frac{\Delta t}{\Delta p}\right)_H.$$

If now Δp_H approaches zero, this difference equation becomes

$$\frac{1}{c_p}\left(\frac{\partial c_p}{\partial p}\right)_H = -\left(\frac{\partial \mu}{\partial t}\right)_p,$$

where μ is the Joule-Thomson coefficient, and is the limit approached by $(\Delta t/\Delta p)_H$. This is Davis's differential equation.[1] Its integral is

$$c_p = c_{p_0} e^{-\int_{p_0}^{p}\left(\frac{\partial \mu}{\partial t}\right)_p dp},$$

the integration being at constant H. When μ is known as a function of

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[1] For other proofs of this equation see Davis, Proc. Am. Acad., 45, 1910, p. 291.

p and t, the integration can be effected by mechanical quadrature, and the ratio c_p/c_{p_0} determined. The chief advantage of Dodge's method over this is that, in Dodge's method, the integration is performed automatically by the steam itself for the pressure range covered by a set of experiments.

Grindley's method is based on a differential equation that can be deduced directly from this one. According to a familiar transformation formula,

$$\left(\frac{\partial c_p}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \left(\frac{\partial c_p}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \mu \left(\frac{\partial c_p}{\partial t}\right)_p .$$

Therefore the last equation becomes

$$\left(\frac{\partial c_p}{\partial p}\right)_t = -\mu \left(\frac{\partial c_p}{\partial t}\right)_p - c_p \left(\frac{\partial \mu}{\partial t}\right)_p = -\left[\frac{\partial(\mu c_p)}{\partial t}\right]_p .$$

This is Grindley's equation. Its integral is

$$c_p - c_{p_0} = \Delta_t c_p = -\int_{p_0}^{p} \left[\frac{\partial(\mu c_p)}{\partial t}\right]_p dp.$$

this integration being at constant temperature.

This equation has certain advantages over that proposed by Davis. Thus it spreads c_p along lines of constant temperature instead of along lines of constant enthalpy, which is more convenient. It also determines the increment in c_p instead of a ratio, which is conducive to accuracy. And finally it involves the product μc_p instead of μ alone. Whether this is an advantage or a disadvantage depends on whether the isothermal or the adiabatic plug experiment can be carried out with greater accuracy.

It is at very high superheats that all three of these methods are most useful, because, under these circumstances, other methods of getting c_p are facing their greatest difficulties. Thus, while the experiments of Knoblauch determine the spacing of the c_p curves at different pressures with much accuracy at moderate temperatures, they fail entirely to separate these curves at and above 500° C., the experimental points at the various pressures being inextricably mixed. Even the roughest sort of knowledge of μ in this region would space the curves more satisfactorily, after the experiments had determined the average height at which they should lie.

Whether Grindley's or Davis's equation will prove to be more useful at high superheats will depend on whether μ or the product μc_p comes nearer to following a law of corresponding states. It has frequently been assumed that μ follows such a law.[1] If so, Davis's equation is the

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[1] For instance, by Buckingham, by Berthelot, by Callendar, and by Davis.

useful one. But μ is essentially a calorimetric quantity, and if it does follow a law of corresponding states, it is the only calorimetric quantity known to do so. The product μc_p on the other hand is a specific volume, and it was for specific volumes that the law of corresponding states was originally proposed. One would therefore have predicted *a priori* that the product μc_p would be more amenable to such treatment than μ. If so, Grindley's equation is the useful one.

Turning now to the specific volume of superheated steam, we have the well known relation

$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^{T} \frac{\mu c_p}{T^2}\, dT,$$

where the integration is to be carried out at constant pressure. For a perfect gas, μ would be zero, the integral would vanish, and v would be proportional to T at constant pressure. For steam, the integral appears as a small correction term on the ratio v/T. v can therefore be computed as a function of T along an isopiestic, if its value is known at any one point of the isopiestic. Fortunately v is known close to the saturation line from computations with the Clapyron equation, and from the experiments of Knoblauch, Linde and Klebe. This gives a starting point for every isopiestic between 1 and 10 atmospheres. Within this pressure range, the best way to get specific volumes at any temperature however high is undoubtedly to make measurements, not on v itself, but on the product μc_p.

This procedure has certain great advantages. In particular, the object of the experiments is to determine, not the whole quantity sought, but a relatively small correction term. For example, in computing the specific volume of steam at 50 lbs. per sq. in. abs. and 600° F. superheat, the whole correction term is probably not more than 5 per cent. of the answer sought. If, therefore, the correction term is known within 2 per cent. of itself, the specific volume is known within 0.1 per cent. of itself, which is as good as the accuracy of the initial volume used as the constant of integration. Furthermore, the correction term is not an observed quantity but the integral of an observed quantity. The only chance for a 2 per cent. error in the integral is a *systematic* error in μc_p amounting to 2 per cent. throughout the whole range. The allowable *accidental* errors in μc_p might be considerably greater than 2 per cent. for an accuracy of 0.1 per cent. in v.

Let us now turn to saturated and wet steam. It is almost certain that suitable Joule-Thomson experiments with superheated steam can be made to yield a more accurate determination of the *shape* of the HT curve of saturated steam than can be obtained in any other way.[1]

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[1] See Davis, Proc. Am. Acad., *45*, 272, 1910.

Briefly, the fundamental principle is that if, by means of throttling experiments, we can plot the lines of constant H on the superheated steam plane, and if, by means of c_p values, for any one pressure, we can determine the differences ΔH from each curve to the next, we have a determination of the increase in H along the saturation line for each interval between points of intersection with our curves. If H is known by direct measurement at any one point of the saturation line, this process will give its value all along the line. Fortunately there are a number of good determinations of H between 0° C. and 160° C., particularly near 100° C. A good set of Joule-Thomson experiments is therefore all that is needed to determine a satisfactory HT curve over a considerable range.

This process, like that for computing the v of superheated steam, has the great advantage of concentrating the efforts of the experimenter, not on the whole quantity sought, but on a comparatively small increment term. Thus if H_{100} is assumed to be known, the term to be determined experimentally is never greater than 5 per cent. of H itself, and 1 per cent. on the correction term gives 0.05 per cent. on H, which is somewhat better than the accuracy of our present knowledge of H at the boiling point.

When the H curve is thus determined, it will be easy to compute the specific volume of saturated steam by means of the Clapyron equation, if only the specific heat of water and the vapor pressure curve are known. The latter is now well known over the whole range from 0° C. to the critical point, but our knowledge of the specific heat of water is very meager at high temperatures and very chaotic at ordinary temperatures.

Finally, when all these things have been computed, either from the satisfactory data already in hand or from a good set of Joule-Thomson data, an interesting check on the self-consistency of the whole steam table is afforded by Planck's equation

$$c_p = \frac{dH_{\text{sat}}}{dt} - \frac{L}{T} + T\left(\frac{dp}{dt}\right)\left[\left(\frac{\partial v}{\partial t}\right)_{p_{\text{steam}}} - \left(\frac{\partial v}{\partial t}\right)_{p_{\text{liquid}}}\right],$$

where L is the latent heat at the temperature in question. The derivatives in the last term refer to superheated steam and water close to, but not inside, the steam dome. The c_p thus computed is the limiting value on the saturation line approached by the c_p of superheated steam. The fundamental data from which the right hand side can be computed are (1) the value of $(dp/dt)_{\text{sat}}$, which is well known, (2) the value of L or H at 100° C., which is fairly well known, (3) a knowledge of the variations of L and H with temperature, which should depend chiefly on Joule-Thomson data, and (4) the value of $(\partial v/\partial t)_p$ for steam, which also should depend chiefly on Joule-Thomson data. The derivative for water is practically negligible. It is true that a knowledge of c_p itself, which is the quantity sought, is involved in the computation of the variation of L or H with temperature, but it happens that this indirect dependence of the right hand side on c_p is such as to make the computation insensitive to errors in the values of c_p originally assumed. The equation therefore affords a valuable method of successive approximations for computing c_p along the saturation line, where direct measurements are most difficult, as well as a useful check on the c_p curves in general.

It appears, then, that the only experiments that are now greatly needed to put our steam tables on a thoroughly satisfactory basis are a complete and accurate series of Joule-Thomson or throttling experiments, and a thoroughly satisfactory series of experiments on the specific heat of water, especially at high temperatures. Both sorts of experiments are now in progress in the Jefferson Physical Laboratory, and, I believe, elsewhere as well, and it is hoped that the results will be sufficient to serve the purposes which have been indicated.

Jefferson Physical Laboratory,
Cambridge, Mass., Jan., 1915.