SCIENCE

VOL. LXI JANUARY 16, 1925 No. 1568

CONTENTS

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.
New York City: Grand Central Terminal.

Annual Subscription, $6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 3, 1879.

SOME EFFECTS OF THE ATMOSPHERE UPON PHYSICAL MEASUREMENTS[1]

IT has, I believe, been the custom for the retiring vice-president to address the section either upon the subject of his own research interests or upon recent progress or problems connected with some special field of his science. With your permission, I will to-day depart from this custom by adopting the rôle of a revivalist and delivering an exhortation. In one respect at least I feel that I possess the necessary qualifications for the part, since it is well recognized that the most effective exhorters are those repentant sinners who know, from personal experience, whereof they speak.

I take, as my text, the evil influences of a vagrant atmosphere upon physical measurements. This requires some explanation since the term atmosphere has several different connotations.

In the first place, we have that somewhat vague and impalpable atmosphere which is determined by the intellectual conditions surrounding an investigator and is ordinarily referred to as the research atmosphere of the institution.

Secondly, we have the insidious influences of meteorological conditions, temperature, barometric pressure and humidity, upon the physical and mental well-being of an observer and hence upon his ability to make accurate and trustworthy observations.

Thirdly, these same insidious influences frequently affect the properties of materials to an extent sufficient to cause the measuring instruments of the investigator to behave in a way no self-respecting piece of apparatus should and he is consequently put to all kinds of trouble in his efforts to combat them.

Each of these various types of atmospheric influences is important enough to be worthy of an essay, but none of them forms the topic of to-day's sermon. Instead, I shall direct your attention to certain effects of the physical atmosphere which sometimes result in causing an investigator to be under the delusion that he is measuring or utilizing one quantity when as a matter of fact he is dealing with something, not greatly perhaps but still appreciably different. I do not expect to tell you anything new. No revivalist in good standing would be expected to do that. In so far as any of us may have been guilty of backsliding it is because we have been immoral, not unmoral;

---

[1] Address of the vice-president and chairman of Section C—Chemistry, American Association for the Advancement of Science, Washington, D. C., December, 1924.

we knew better, but we "didn't think." Let me warn you in advance that I shall divide my subject into a firstly, a secondly, etc., up to a ninthly and lastly, so that as we progress you may have some idea of how long-drawn-out this sermon is going to be and can govern yourselves accordingly. At the end of the sermon, however, no collection will be taken up.

The presence of the atmosphere in contact with a substance or system which is being subjected to quantitative investigation affects the situation in two ways which we shall designate, respectively, as (1) the direct-pressure effect, and (2) the air-solubility effect. As a result of the first of these effects the system is studied under a condition of uncontrolled (but of course not necessarily unknown) external pressure which varies with time and with location on the earth's surface. In other words, different determinations of the same property of a given system under "atmospheric" pressure are not necessarily comparable. In the case of gaseous systems this effect is of course very pronounced and no trouble is experienced in such cases, since the precautions or corrections necessary to obtain comparable results are always taken care of. With liquids and solids, on the other hand, the effect is so much smaller that it is usually neglected, although not always negligible.

The second effect, that due to the presence of dissolved air in the system, in contrast to the first effect, changes the nature of the system rather than merely its condition. This effect is too often entirely neglected by investigators without taking the trouble to ascertain its magnitude or even to insure its constancy.

(1) CHEMICAL ANALYSIS

The direct-pressure effect.—In computing the results of a chemical analysis, the analyst makes use of certain factors which are stoichiometrically calculated from atomic weights. Since atomic weights are based upon experiments in which the buoyant effect of the atmosphere has in all cases been corrected for, it is evident that analytical factors are likewise all upon the *"in-vacuo"* basis. In ordinary chemical analysis, however, the vacuum correction is seldom made; that is, all the weighings made during the course of the analysis represent weights-in-air. Consequently, when these weighings are combined with the analytical factors in computing the result of the analysis in the form desired, the result obtained is a hybrid quantity, since it is based neither upon *weights-in-vacuo* (true mass) nor upon weights-in-air. Moreover, two analysts working under different meteorological conditions will not only both obtain incorrect results, but their results will not agree, owing to the variability in the buoyant effect of the atmosphere with meteorological conditions.

At this point let me hasten to say, however, that this source of error in analytical chemistry, while theoretically existent, is of no practical importance except in analytical work of very high precision, and usually then only in the case of analysis which involves the weighing of one material or substance of low density (1 or less) and another of high density (5 or more). The magnitude of the errors which can arise under these extreme conditions through failure to reduce all weighings *ad-vacuum* is illustrated by the following tables, which show for three analytical examples (1) the correct result of the analysis, (2) a result which might be obtained by an analyst in Boston and (3) a result which might be obtained by an analyst at Santa Fé (Mexico City; Boulder, Colo.; or Mt. Wilson, Calif.), using the same procedure, if both analysts neglected to reduce their weighings *ad vacuum.*

I. Determination of chlorine in an organic liquid ($d = 0.7$) by weighing as AgCl.

True per cent.	Boston	Santa Fé
10.0000	10.0157	10.0109
Per cent. error	0.16	0.11

II. Solubility of I_2 in a light organic liquid determined by titrating a weighed sample of the saturated solution with a solution standardized against solid I_2.

True per cent.	Boston	Santa Fé
10.0000	10.0155	10.0108
Per cent. error	0.16	0.11

III. Solubility of $PbCl_2$ in H_2O at 0°. Weighed sample evaporated to dryness.

True per cent.	Boston	Santa Fé
0.6700	0.6693	0.6695
Per cent. error	0.10	0.07

From these illustrations, the following conclusions may be drawn:

(1) If the accuracy of the method justifies the use of more than four significant figures in reporting the result, the analyst should compute the magnitude of the correction for the buoyant effect of the air, and should reduce all his weighings *ad vacuum,* if this effect is significant.

(2) If the accuracy of the method justifies the use of five significant figures in reporting the result, the vacuum correction should always be made; but if the laboratory is located at a high altitude, this correction should not be taken directly from the tables given in handbooks for this purpose, since these tables have been computed for average meteorological conditions at sea-level.

Whenever an investigator takes the trouble to make a weighing to a precision of 0.05 per cent. or better, the additional trouble of recording the barometric pressure and the temperature of his balance case is worth while, and, unless the balance case contains a drying agent, a psychrometer record may also be useful in some cases of high precision work. The habit of recording these observations in the note-book is a good one to acquire, even though they may not be needed in the majority of cases.

The air-solubility effect.—The effect of dissolved air upon the weight of a substance is usually very small in the cases of liquids and will be discussed in section 9 below. In the case of solids, however, it is sometimes of great importance, especially when the solid is in a finely powdered or colloidal condition so that it exposes a large surface to the atmosphere. Such solids after drying and cooling in an atmosphere of dry air are customarily weighed in closed tubes to prevent the adsorption of moisture from the atmosphere. The avidity for moisture displayed by some materials ordinarily not considered as especially hygroscopic is sometimes astonishingly great when they expose a large surface to the atmosphere. Thus a perfectly dry clay brick will gain in weight if placed in a desiccator over calcium chloride or 1.84 sp. gr. sulphuric acid. A similar behavior has been reported by Hillebrand[2] in the case of a powdered mineral which, after dehydrating at 280°, gained 1½ per cent. on standing over sulphuric acid.

The adsorption of dry air by such materials is usually not sufficient to be significant, but in certain extreme cases and where a high degree of accuracy is sought, the possibility of such adsorption should be investigated. One extreme case of this kind has been reported by Friedel,[3] who states that certain zeolites and chabozites will adsorb up to 1.8 per cent. of their own weight of "dry" air.

(2) THE THERMOMETRIC ICE POINT AND OTHER FREEZING POINTS

The thermometric ice point is defined[4] as the "temperature of melting ice." Although not so stated in the official wording of the definition of the fundamental interval, it is usually understood that the melting ice shall be under a pressure of one "normal atmosphere." Even with this additional specification, however, the definition fails to define a definite temperature, the uncertainty being something less than 0.0024° C., depending upon whether the water is free from or saturated with air. The definition might be made perfectly definite by wording it in any of the following ways:

(1) The thermometric ice point is the temperature at which pure ice is in equilibrium with pure air-free water when both phases are under a pressure of one normal atmosphere and the surface of contact is a plane;

(2) The thermometric ice point is the temperature at which pure ice is in equilibrium with pure water saturated with pure air at the same temperature, and at the pressure p_A where $p_A + p_W$ equals one normal atmosphere, p_W being the vapor pressure of ice under these conditions, and both the ice and the solution being consequently under a pressure of one normal atmosphere) and the surface of contact is a plane; or

(3) The thermometric ice point is the temperature of the triple-point, Ice I-liquid-vapor, for the system H_2O.

The conditions corresponding to any one of these definitions might be realized experimentally, but those corresponding to the second definition are perhaps the most convenient for everyday use. They can probably be most conveniently realized,[5] for all present-day purposes, by immersing the thermometer in a stirred mixture of pure water and finely divided ice in a vacuum-jacketed or ice-jacketed vessel, the water being saturated with air by bubbling through it, previous to taking the final reading, a current of pure air, precooled by passing it through a column of ice. The temperature thus obtained requires only to be corrected to the standard barometric pressure whenever this correction is significant. This correction may be computed as follows:

An increase in barometric pressure lowers the temperature of equilibrium between ice and air-saturated water from two causes, (1) the direct effect of external pressure upon the two-phase equilibrium and (2) the indirect effect of an increased amount of dissolved air in the solution. The lowering, $-\Delta t_P$, due to the first effect, is

$$-\Delta t_P = 0.0075^\circ \text{ per atm.} = 0.000099^\circ \text{ per cm of Hg.} \qquad (1)$$

The lowering, $-\Delta t_S$, due to the second effect, is

$$-\Delta t_S = 1.86 \times \frac{pv}{RT} = \frac{1 \times 0.0292}{0.08206 \times 273.1} = 0.0024^\circ \text{ per atm.} = 0.0000316^\circ \qquad (2)$$

---

[2] Hillebrand, Geol. Survey Bull. *422*, 69 (1916).

[3] Friedel, *Compt. rend.*, *122*, 1006 (1895).

[4] Resolution of the International Committee on Weights and Measures, October 15, 1887. Bureau of Standards Bulletin *3*, No. 4, p. 664.

[5] Julius Meyer (*Z. physik. chem. 90*, 722 (1915)) suggests the first definition and proposes to attain the required condition by determining the melting point starting with carefully purified ice and presumably packing the thermometer with this ice and allowing drainage. Constancy of temperature, however, requires equilibrium between the two phases, and the thin film of water covering the surface of this melting ice would probably contain an indefinite amount of dissolved air if in contact with the atmosphere, even though this liquid film were renewed continuously by melting and drainage. The uncertainty arising from this factor, however, could only be determined by experimental investigation.

per cm of Hg where v ($= 0.0292$) is the number of cc (measured at 0°, 760 mm) of dissolved $O_2 + N_2$ in water saturated with CO_2—free air at 0° and 1 atm.[6]

The total correction to take care of barometric influences is therefore given by the equation

$$\Delta t = 0.00013(76 - B) \qquad (3)$$

Thus, if a mixture of ice and air-saturated water at 76 cm has the temperature 0° by definition, the same mixture at a barometric pressure of 58 cm (*e.g.*, at Mexico City; Boulder, Colo.; Mt. Wilson, Calif.; Santa Fé, N. M., etc.) will have the temperature 0.0023°.

It is also obvious that in determining the freezing point lowering of dilute aqueous solutions, where a precision of 0.0001° or better is now attainable, similar precautions to insure either saturation with, or better freedom from, air are necessary since the freezing-point lowering produced by the dissolved air is sometimes a large fraction of the lowering produced by the solute under investigation.

In all determinations of the normal freezing points of pure substances, the uncertainties arising from the presence of the atmosphere must likewise be either eliminated or corrected for as in the case of water. With substances other than water there is, however, also the added complication arising from the presence of aqueous vapor in the atmosphere in variable amounts, thus making it necessary, in many cases, to scrupulously exclude all direct contact with the atmosphere during the measurement. This is necessary even with substances, such as benzene, for example, which are ordinarily considered as non-hygroscopic.

On the other hand, while in the case of the ice point the "direct pressure effect" and the "air solubility effect" act in the same direction and are therefore additive, in the case of most substances the two effects act in opposite directions and therefore tend to neutralize each other. Thus, in the case of benzene, Richards, Carver and Schumb[7] found that the direct pressure effect amounted to + 0.028° between the triple point and one atmosphere, while the corresponding air-solubility effect (for dry air) amounted to — 0.031°.

Hence, although the two separate effects are each very much larger than in the case of water, the net correction, if moisture is carefully excluded, amounts to only 0.003° as against 0.009° in the case of water for the same pressure difference. In other words, a change ¼ atmosphere in barometric pressure would be required in order to change the normal freezing point of benzene by as much as 0.001°.

The same authors studied also the effect of moisture upon the freezing point of benzene and found that an amount of water corresponding to 1 per cent. of saturation was sufficient to lower the freezing point by 0.001°, thus making it necessary to carefully dry the benzene and to exclude all contact with moisture during the temperature measurement. The precautions necessary to realize this condition, while attainable, are, to say the least, bothersome and for this reason the benzene-point is not likely to find great favor as a thermometric fixed point, in spite of its convenient location on the temperature scale and its great constancy with respect to barometric changes.

It seems possible, however, that the 4-phase invariant point, H_2O liq. — C_6H_6 liq. — C_6H_6 crys., under one atmosphere, with complete air saturation, might prove to be an acceptable substitute. At all events, the system seems worthy of investigation in this connection. The temperature of the point should be, according to the data given by Richards and Schumb, about 0.095° below the benzene freezing point.

(3) THE VAPOR PRESSURE OF A SOLID OR LIQUID

The two methods which have been most frequently employed for measuring vapor pressure are (a) the "static" method and (b) the "dynamic" or "aspiration" method. In comparing the results obtained by the two methods it is not always realized that they do not measure identical quantities. In the static method the quantity measured is the vapor pressure of the liquid or solid phase when under its own vapor pressure. In the dynamic method the liquid or solid phase is usually under atmospheric pressure, and in the case of a liquid, the phase under investigation is not the pure substance but a solution saturated with the gas employed in the experiment, and it is the partial pressure of the substance from this solution which is indirectly measured. The method is indirect because the quantity directly measured is not the vapor pressure but the concentration of the saturated vapor. From this concentration, however, the vapor pressure *under these conditions* is calculable if the equation of state of the vapor is known. Either of these two vapor pressures may be calculated if the other is known, and the difference between them, while small, is by no means insignificant.

The detailed vapor pressure tables for water as given in the various handbooks of physical data, although not always so labelled, represent presumably the vapor pressure of pure water when under its own vapor pressure. If one desires to find from these

---

[6] The effect produced by the normal CO_2 content of the atmosphere (*i.e.*, 0.004 per cent. by vol.) is only 0.0004° and therefore negligible for all practical purposes. Laboratory fumes are, however, a possible source of error and should be avoided in determinations of the ice point.

[7] Richards, Carver and Schumb, *Jour. Amer. Chem. Soc. 41*, 2019 (1919).

tables the aqueous tension above water in equilibrium with the atmosphere, it is necessary to add a small correction to the value taken from the table. This correction for any solid or liquid is computed as follows:

(a) The variation of the vapor pressure, *p*, of a liquid or solid with the external pressure, *P*, at constant temperature is given by the thermodynamic equation

$$\frac{dp}{dP}=\frac{V_0}{v_0} \qquad (4)$$

where V_0 is the volume of one mole of the liquid, and v_0 the volume of one mole of the vapor. Introducing the gas law, $pv_0=RT$, and integrating gives

$$\log\frac{p}{p_0}=V_0(P-p_0) \qquad (5)$$

or with sufficient approximation

$$100\,\frac{p-p_0}{p_0}=100\,\frac{\Delta p_r}{p_0}=100\,\frac{V_0}{RT}(P-p_0) \qquad (6)$$

where p_0 is the vapor pressure when $P=p_0$.

For a solid, equation (6) gives the total correction factor in per cent. Thus, for example, substituting the numerical data for ice we obtain with sufficient approximation

$$100\,\frac{\Delta p_r}{p_0}=\frac{20}{T} \qquad (7)$$

For ice at —5°, $p_0=3.013$ mm,

$$\frac{100\,\Delta p_r}{p_0}=\frac{20}{268}=0.075 \text{ per cent.,}$$

and hence the vapor pressure of ice in contact with the atmosphere at —5° is 3.015 mm.

(b) In the case of a liquid it is necessary to include in the correction equation a term to take care of the lowering of the vapor pressure due to the solubility, *S*, of the gas in the liquid. Thus we have

$$S=\frac{C'}{C} \qquad (8)$$

where C' is the concentration of the gas in the gas phase, and C its concentration in the liquid. We may write with sufficient approximation

$$C=\frac{C'}{S}=\frac{P-p_0}{SRT} \qquad (9)$$

and from Raoult's law

$$\frac{\Delta p_g}{p_0}=x=(\text{approx.})\frac{C}{\frac{1000D}{M}}$$

$$=V_0C=\frac{V_0(P-p_0)}{SRT} \qquad (10)$$

where *M* is the molecular weight and *D* the density of the liquid.

Combining this equation with equation (6), we obtain for the net correction, in per cent.

$$100\,\frac{\Delta p}{p_0}=\frac{100V_0(P-p_0)}{RT}\left(1-\frac{1}{S}\right) \qquad (11)$$

which may also be written

$$\frac{100\,\Delta p}{p_0}=\frac{100V_0(P-p_0)}{RT}\left(1-\frac{\alpha T}{T_0}\right) \qquad (12)$$

where α is the Bunsen absorption coefficient.

This equation is applicable to any liquid in contact with a not-too-soluble gas under a not-too-large total pressure *P*.

It can be put in a convenient form for use by constructing a graph of $\frac{\Delta p}{p_0}$ against *t* or p_0. If, for example, this is done in the case of water in contact with the atmosphere under a barometric pressure of 760 mm, the graphs obtained can be represented with sufficient approximation by the following empirical equations:

$$100\,\frac{\Delta p}{p_0}=0.0775-0.000313t, \text{ valid up to } 40° \qquad (13)$$

and

$$\frac{100\,\Delta p}{p_0}=0.0652-0.0000875p, \text{ valid above } 50° \qquad (14)$$

Between 40° and 50° the average from the two equations may be used, $t=$ °C, $p=$ mm Hg.

Table IV below shows the values of p_0 for water at various temperatures, together with the corrections which must be added to these values in order to obtain the vapor pressure above water in equilibrium with the atmosphere. These corrections also represent the difference between the vapor pressures of water, as measured by the static and by the dynamic methods, respectively.

(4) CORRECTION OF BOILING POINTS TO NORMAL ATMOSPHERIC PRESSURE

This correction is usually made with the aid of Craft's Rule, and this method is entirely satisfactory for moderate barometric variations. For boiling points determined at high altitudes or under artificially reduced pressures, however, some more accurate means of computing the normal boiling point is re-

TABLE IV

t° C.	0	10	20	30	40	50	60	70	80	90
p_0, mm Hg	4.579	9.209	17.535	31.824	55.324	92.51	149.38	233.7	355.1	525.76
Δp, " "	0.0036	0.0069	0.0124	0.0217	0.036	0.053	0.078	0.104	0.121	0.102

quired. Mr. C. S. Cragoe, of the U. S. Bureau of Standards, has suggested[8] for this purpose an equation which may be written most conveniently in the following form:

$$\Delta t = \frac{273.1 + t}{A} (2.8808 - \log_{10} B) \qquad (15)$$

where Δt is the correction in degrees which must be added to the boiling point, t, determined under the barometric pressure, B mm of mercury, in order to obtain the normal boiling point. A, like the Craft's constant, is a constant characteristic of the class of substances to which the liquid under examination belongs, and may be taken from a table of values of A for a variety of different types of substances. It may also be calculated from Trouton's constant, with which it is in fact identical, except for a constant factor independent of the nature of substance, as shown by the following relation:

$$A = 0.2186 \frac{L}{T_B} \qquad (16)$$

In fact, equation (15) is nothing more than our old friend the integral of the Clausius-Clapeyron equation, somewhat rearranged and with the ratio $\frac{L}{T_B}$ taken as a constant, in accordance with Trouton's rule. For small pressure differences, equation (15) reduces directly to the familiar form known as Craft's equation. It assumes further that log p is a linear function of $\frac{1}{T}$.

The constant c in Craft's equation

$$\Delta t = c T_B (760 - P) \qquad (17)$$

is related to the constant A, by the equation

$$c = \frac{5.72 . 10^{-4}}{A} \qquad (18)$$

The following table illustrates the difference in the correction, Δt, as calculated by equation (15) and by Craft's equation, respectively, for two barometric pressures.

TABLE V

$\frac{L}{T_B}$ assumed = 22	Boston	Santa Fé
T_B, assumed = 500°	$B = 770$	$B = 580$
Δ_t, from equation 15	–0.590	12.20
Δ_t from Craft's equation	–0.594	10.7

The value of B at which the difference between the equations amounts to a given fraction of a degree depends upon the value of T_B. Thus for $T_B = 500°$, or $t_B = 227°$, this difference reaches 0.1° at $B =$ about 710 mm.

The "air-solubility" effect of the atmosphere upon the boiling point of a liquid has apparently never been investigated. The normal boiling point of a *pure* liquid should in general be higher than the normal boiling point of the same liquid saturated with dry air. The difference, while small, should be capable of experimental determination with our present accurate methods of measuring boiling points. The effect, if appreciable, would cause the boiling point determined in the usual manner to fall off of the vapor pressure curve of the liquid as determined by the static method.

(5) Boiling Point Raisings

In the determination of the boiling-point elevation produced by non-volatile solutes it is essential for accurate work either to use a manostat or to make the method a differential one; that is, duplicate sets of apparatus, one containing the boiling solvent and the other the boiling solution, should be operated side-by-side and simultaneously. If this is not done the boiling point of the solvent will not be known for the conditions prevailing at the time the measurements are made with the solutions, due to local fluctuations in barometric pressure frequently too small to be registered by a mercury barometer but still large enough to produce errors in the boiling point measurements, which with the differential method can be made with a precision of 0.001° C.

The molal boiling-point raising for a given solvent is itself likewise a function of the barometric pressure and in recording in the literature measured values of this constant the barometric pressure should always be stated or, better, the measured value should be corrected to standard barometric pressure. The correction varies somewhat with the nature of the solvent, but it is approximately 0.3 per cent. per cm of mercury for all solvents.[9] Thus two determinations of the molal boiling point raising by identical methods of measurement, one made at Harvard and one at the University of Colorado, might differ by as much as 5 or 6 per cent. owing to differences in barometric pressure. Some of the apparent discrepancies in the "ebbullioscopic constants" reported in the literature may perhaps be traced to this cause.

(6) Specific Heats

Corresponding to the conditions under which the calorimetric measurements are carried out, we may distinguish the following types of specific heats:

---

[8] Personal communication.

[9] The exact expression for this correction is given on page 737, Volume 41, *Jour. Amer. Chem. Soc.*, (1919).

(1) C_v, the specific heat at constant volume. This quantity is seldom if ever directly measured in the case of liquids. When required, it is computed from one of the other types.

(2) C_P, the specific heat under constant external pressure. This quantity is also, strictly speaking, seldom if ever directly measured in the case of liquids. It is ordinarily identical, within the experimental error, with the quantities C_p or C_S and in any case can be obtained from them by applying the proper corrections.

(3) C_p, the quantity $\frac{dH}{dt}$ for unit mass of the liquid (or solid) in contact with a negligible (or allowed-for) mass of its saturated vapor and under its own vapor pressure at all temperatures. In the case of solids this quantity is also the so-called specific-heat-in-vacuo which is directly measured in calorimeters of the Nernst aneroid type. This quantity as directly measured is not, strictly speaking, a true specific heat, since it includes also a certain amount of latent heat, namely, the amount required to vaporize that amount of substance which is required to produce saturated vapor at the higher temperature. The amount of this latent heat is thus a function of the size of the container. The quantity C_p also includes the (usually negligible) change in internal energy corresponding to the change in pressure. When correction is made for these two effects the corrected C_p becomes C_P for $P = p$.

(4) C_S, the quantity $\frac{dH}{dt}$ when the liquid is heated in equilibrium with the atmosphere under constant barometric pressure but in a confined space. To obtain C_P from C_S it is necessary to correct for evaporation as in case (3) and also to correct for the heat absorbed in volatilizing the amount of dissolved $O_2 + N_2$ corresponding to the different solubilities of these gases at the initial and final temperatures respectively unless, as is usually the case under the conditions of the experiment, this volatilization is made negligible.

It is also necessary to subtract the partial specific heats, $\bar{C}_S$, of the dissolved $O_2 + N_2$ from the measured $\bar{C}_S$ of the saturated solution. Needless to say when working with liquids other than water contact with atmospheric moisture should be avoided in accurate work.

With the exception of the latent heat correction (which is significant under certain conditions), all the above corrections are in most if not all cases probably within the experimental errors of modern calorimetry, and therefore have only an academic interest at the present time.

(7) LATENT HEAT OF VAPORIZATION OF A LIQUID

The following discussion of the latent heat of vaporization will exemplify the effect of atmospheric conditions upon the measurement of latent heats of phase changes in general. We may distinguish the following three kinds of latent heats of vaporization, L:

(1) L_p, the latent heat under the vapor pressure p. This is the quantity ordinarily measured calorimetrically either by boiling the liquid in the calorimeter or by condensing into the calorimeter the saturated vapor of the boiling liquid.

(2) L_P, the latent heat of the pure liquid under constant external pressure P, the same at all temperatures. This quantity is never measured calorimetrically, although it appears in thermodynamic equations and is calculable therefrom.

(3) L_S, the latent heat of vaporization of the liquid plus its dissolved air under constant atmospheric pressure. This is the quantity measured calorimetrically by the method of A. W. Smith, in which the liquid contained in the calorimeter is vaporized by means of a current of dry air.

With the aid of the First Law of Thermodynamics we can readily deduce the following relations:

$$L_p - L_P = (P - p)V - \Delta E \qquad (19)$$

where ΔE is the decrease in internal energy which accompanies the isothermal compression of the liquid from p to P.

$$L_S - L_P = \bar{L}_O S_O + \bar{L}_N S_N \qquad (20)$$

where $\bar{L}_O$ and L_N are the partial latent heats of vaporization of the dissolved O_2 and N_2 (neglecting Ar), and S_O and S_N the corresponding solubilities of these gases.

Calculation for Water at 30°.—To illustrate the order of magnitude of the corrections in the case of water, we will apply the equations to the vaporization of water at 30°.

(a) The direct pressure effect.—By interpolation on the graph given by Bridgman,[10] we find

$$\Delta E = 0.00297P \text{ cal. mole}^{-1} \qquad (21)$$

and hence

$$\Delta E \text{ from } p \text{ to 1 atm.} = \frac{0.0297(760 - 31.8)}{760} = 0.028 \text{ cal. mole}^{-1} \qquad (22)$$

$$(P - p)V = \frac{760 - 31.8}{760} \times 0.001004 \times 18 = 0.0181 \text{ l. atm.} = 0.044 \text{ cal. mole}^{-1} \qquad (23)$$

and hence

$$L_p - L_P = 0.044 - 0.028 = 0.016 \text{ cal. mole}^{-1} \qquad (24)$$

---

[10] Bridgman, Proc. Amer. Acad., *48*, 348 (1912).

This difference is well within the accuracy with which L_p has been measured.

(b) The air-solubility effect.—From the solubilities of O_2 and N_2 in water at 16° and 30°, the Second Law enables us to compute $\bar{L}_0$ and $\bar{L}_N$, giving

$$L_o = 3360 \text{ cal. mole}^{-1} \quad (25)$$

$$L_N = 3040 \text{ cal. mole}^{-1} \quad (26)$$

and from the determinations of Winther at 30° we obtain

$$S_o = 4.23 \times 10^{-6} \text{ moles per mole} \quad (27)$$

$$S_N = 8.34 \times 10^{-6} \text{ moles per mole} \quad (28)$$

and hence

$$L_oS_o + L_NS_N = 0.040 \text{ cal.} \quad (29)$$

$$L_S - L_P = 0.040 \text{ cal. mole}^{-1} \quad (30)$$

and

$$L_s - L_p = 0.024 \text{ cal. mole}^{-1} \quad (31)$$

The difference between L_S and L_p is thus also well within the experimental accuracy with which either of these quantities has been measured up to the present.

(8) DENSITY OF LIQUIDS

Owing to the slight compressibility of liquids it is customary to ignore barometric influences in making density determinations, and this is indeed justifiable except in determinations where the fifth or sixth decimal is significant. The following table illustrates the order of magnitude of the direct pressure effect for two liquids.

TABLE VI

Density at Room Temperatures

	at Boston $B = 770$	at Santa Fé $B = 580$	Per cent. Difference
Water	0.998230	0.998217	0.0013
Ether	0.713500	0.713464	0.005

The effect of dissolved air upon the density of a liquid can not be computed. It has, however, been determined in the case of water, and its maximum total effect is only 3 units in the sixth decimal place.

It may seem superfluous to point out that all density determinations reported by investigators should be based upon weights *in-vacuo* but it is unfortunately true that many such data recorded in the literature have apparently not been reduced to the *in-vacuo* basis, since information on this point is frequently entirely lacking in the paper.

(9) OTHER PHYSICAL PROPERTIES

Information is lacking concerning the magnitude of the effect of the atmosphere upon the measurement of most physical properties of solids and liquids, since it can usually be discovered only by direct investigation. The inference is that it is probably negligible in most instances. The following additional illustrations of the "direct pressure effect" may, however, be deduced from available information.

VISCOSITY OF ETHYL ETHER

at Boston $B = 770$	at Santa Fé $B = 580$	Per Cent. Difference
0.0023400	0.0023381	0.08

SOLUBILITY

m — Dinitrobenzene in ethyl acetate.		
34.432	34.435	0.01
$Ba(OH)_2.8H_2O$ in H_2O.		
8.3000	8.2984	0.02

EDWARD W. WASHBURN
NATIONAL RESEARCH COUNCIL
WASHINGTON, D. C.

THE TOLL OF THE AUTOMOBILE

WE hear and read a good deal of the enormous annual toll of human life due to the mania for speed so generally prevalent among automobile drivers. On this account our city streets and country highways are dangerous places for pedestrians as well as for other and more discreet motorists. Even the widely heralded "dirt roads" of Iowa are tainted with human blood. "As a killer of men, the automobile is more deadly than typhoid fever and runs a close second to influenza. . . . Up to August of this year (1924) 9,500 lives were sacrificed, chiefly in preventable accidents." Thus reads a recent account in one of our popular magazines.

Not only is the mortality among human beings high, but the death-dealing qualities of the motor car are making serious inroads on our native mammals, birds and other forms of animal life.

This matter was most forcefully brought to my attention during June and July, 1924, when my wife and I made the journey overland from Iowa City, Iowa, to the Iowa Lakeside Laboratory, on West Lake Okoboji, Iowa, a distance of 316 miles. Parts of two days were occupied in the going journey on June 13 and 14, while approximately the same time was required for the return trip on July 15 and 16.

Within a few minutes after we had started from Iowa City and a considerable number of dead animals, apparently casualties from passing motor cars, had been encountered in the road, it occurred to us