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The Heat of Expansion of a Gas of Varying Mass

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In this paper equations are given for the direct treatment of experiments in which not only heat, but also masses, pass the boundary of the container of the system during the experiment. The theoretical development is correlated with the treatment of Gibbs, and certain difficulties, mentioned by others, in the physical interpretation of his equations, are incidentally removed. It was found possible, within a reasonable time, to cause a gas to expand slowly enough from a calorimeter to simulate a reversible expansion, and the special equation developed for the heat of expansion with the aid of the Beattie-Bridgeman equation of state was verified by the results for the slow expansion of carbon dioxide and ammonia. In the case of carbon dioxide the effect of the deviations from the ideal gas law was to make the heat effect in excess of that calculated for an ideal gas by a sufficient amount so that the excess itself

could be calculated within about 7 percent. A series of expansions of carbon dioxide was carried out at varying rates of flow, some as fast as permissible. The results, correlated by means of an empirical relation, serve to show that the results of the slow expansions correspond practically to an infinitely slow expansion. They also indicate that the heat effect for an infinitely rapid expansion is not zero for a real gas, but possibly vanishes with the pressure. In the absence of a perfectly sound method of calculating the heat effect for an infinitely fast expansion, a method is suggested which has at least the merit of agreement with the present experiments.

The bearing of the results on variable-pressure calorimetry, as practiced in experiments on the heat of adsorption, is briefly discussed.

I. Introduction

JOULE[1] measured the separate heat effects shown by a gas in expanding from one vessel into an originally empty vessel through a stopcock. He arranged his apparatus as shown in Fig. 1. R and E are two vessels connected by
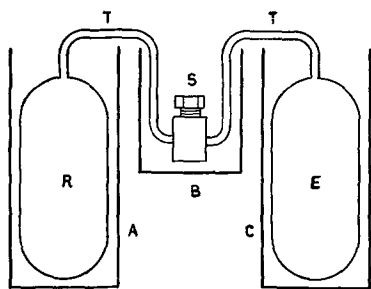

Fig. 1. Sketch of Joule's experiment.

small bore tubes $T-T$ and a stopcock S. The vessels and the stopcock are immersed in water calorimeters A, B, and C. To quote from his paper, "One of the receivers (whose volume was 136.5 cu. in.) had 2828 cubic inches of dry air compressed into it, while the other (volume 134 cu. in.) was vacuous. After equilibrium was re-

stored by opening the cocks, I found that 2.36° (Fahrenheit) of cold per pound of water had been produced in the receiver from which the air had expanded, while 2.38° of heat had been produced in the other receiver, and 0.31° of heat also in the can in which the connecting-piece was immersed."

We calculate by the use of the ideal gas law that 1.957 moles of air were initially present in the high-pressure vessel R, and 0.988 moles were left in it at the end of the experiment. The heat corresponding to 2.36° per pound of water is 595 g cal. The heat effect in the vessel R was therefore 614 g cal. per mole of gas escaping. For comparison, the value of RT may be taken as 574 cal. per mole at the temperature of the experiment, 288.7°C absolute.

Each of the vessels A, B, and C of Fig. 1 presents an example of a system open to exchange of mass with its surroundings. Such a system is called an *open system* by Defay,[2] in contrast to the *closed system*, across whose boundaries no mass is permitted to pass.

Problems involving the thermodynamics of open systems have been solved by special methods by chemists and physicists for special cases

* Contribution No. 294.
[1] J. P. Joule, Phil. Mag., series 3, May, 1845.

[2] Raymond Defay, Bull. Acad. Roy. de Belgique (Classe des Sciences) [5] 15, 678 (1929).

in which the mass exchange takes place at constant pressure. Thus, when a gas enters or leaves a calorimeter at constant pressure and temperature the observed heat effect is taken equal to a change in the so-called heat content $(U+pV,$ where U is the internal energy, p the pressure and V the volume). When a reaction takes place in a constant-volume calorimeter, the heat effect is equal to a change in the internal energy. When, however, the heat of adsorption of a vapor upon an adsorbent like charcoal is measured, we have to reckon with the fact that the equilibrium pressure of the system increases with the amount of vapor absorbed. The possibility that the heat effect is equal neither to the change of heat content nor to that of energy, but has a value lying between the two limits, was suggested by Williams.[3] Coolidge[4] showed, however, that "the observed heat will not differ from the true λ" when the gas is an ideal gas, provided that the temperature at which the gas enters the calorimeter is properly controlled, a condition which in practice would exclude a flow fast enough to make kinetic energy of importance, and which condition has in most cases not been imposed by the experimenter.

Gibbs used the idea of an open system solely for the purpose of defining the chemical potential. De Donder[5] and Defay[2] have written on the thermodynamics of open systems but have not interested themselves in the derivation of equations for the heat absorbed in actual experiments with open systems. The two laws of thermodynamics are announced for closed systems. Problems of opened systems can therefore be solved, if at all, by a comparison of the actual open system with an ideal closed system. The boundary of the open system is imagined shifted until it includes a constant amount of mass, and the ordinary thermodynamics of closed systems is applied, due account being taken of any significant difference between the original and the varied system. This is the method used in special applications.

It appears desirable, however, to summarize in equations the results of the shift of boundary, so that no shift of boundary is necessary in the application of the equations.

[3] Williams, Proc. Roy. Soc. (Edinburgh) **38**, 23 (1918).
[4] A. S. Coolidge, J. Am. Chem. Soc. **48**, 1795 (1926).
[5] Th. De Donder, Bull. Acad. Roy. de Belgique (Classe des Sciences) **15**, 615 and 900 (1929).

II. Equations for Open Systems

In order to retain a simple notation, sufficient for most cases, we shall suppose that when the volume of the system is varied, the external pressure against the boundary does not differ appreciably from the pressure of the system against it, and, similarly, when masses cross the boundary of the system at any point they have nearly the pressure at which they would be in hydrostatic equilibrium with the system at the given point. We shall also neglect the effects of gravity, electricity, distortion of the solid masses and capillary tensions.

The variation of energy, subject to the above general conditions, is

$$dU = dq - pdV, \qquad (1)$$

where dq is the heat received by the system in a small change of state, p the pressure and dV the increase of the volume of the enclosure, when no mass crosses the boundary. If dm_1 units of mass of kind 1 are brought up to the system without adding heat or changing the volume V, the increase of energy of the system brought about by *shifting the boundary* to include the dm_1 units is $u_1 dm_1$, where u_1 is the ordinary internal energy of the unit mass at its pressure p_1 (and volume v_1). Taking p_1 such as to allow smooth addition to the system, $p_1 v_1 dm_1$ is the increase of energy of the system of shifted boundary required to reduce the volume to the original volume V when no heat is transferred during the compression. Hence

$$(dU/dm_1)_{V, q} = u_1 + p_1 v_1, \qquad (2)$$

where the subscript q indicates an adiabatic variation. The complete variation, for simultaneous transfers of heat and mass and variation of volume is

$$dU = dq - pdV + \Sigma(u_1 + p_1 v_1)dm_1, \qquad (3)$$

where the summation is for all kinds of mass crossing the boundary and the dm's are taken algebraically.

If dq were a "perfect differential" like dU and dV, the substitution of partial derivatives in the expansion of dU in terms of the variations dq, dV and the dm's would call for no comment. Tunell[6] has emphasized that q is given by a line integral,

[6] George Tunell, J. Phys. Chem. **36**, 1744 (1932).

and that under certain circumstances dq is as true a differential of a function as any other. This is the case when a path for the line integral is fixed. In the present case we may suppose that all the heat is added or subtracted by means of a mechanism (used only for heat transfer) whose path of operation is arbitrarily fixed, thus making the heat added a function of a single variable. The relation $(dU/dq)_{V,m}=1$ is not affected by the nature or path of this mechanism and the choice of this path affects in no way the path which correlates the variations dq, dV, dm_1, etc., leaving these variations still arbitrary.

Eq. (3) is subject to the above stated restrictions relating to change of volume and exchange of masses with the surroundings, but applies to a system of any number of phases, either in internal equilibrium or not. This is because the energy of a system isolated by keeping dq, dV and the mass variations all zero cannot change. It applies to an enclosure in which a gas flame is burning. Gas enters, the products of combustion leave, and heat is lost from the surface of the enclosure by radiation and convection. If the volume is constant and we operate at a steady state, the variations of volume and energy with time are zero, and we have for the loss of heat

$$-dq = \Sigma(u_1+p_1v_1)dm_1 \qquad (4)$$

or the loss of heat equals the heat content of the entering gas minus the heat content of the products of combustion. (dm being negative for these.) Note that we do not have to speak of the loss of heat with the products if they escape at a high temperature, as the loss of energy is fully included in the heat content term, $(u+pv)$.

In constant pressure calorimetry it is convenient however to make the exchange of mass occur at constant temperature, so that we can measure directly the increase of heat content ΔH attending a reaction at constant temperature. In this case

$$\Delta H = -\int dq. \qquad (5)$$

ΔH is not always for the change of state in which we are most interested, and in writing the chemical equations we have to distinguish (except for mixtures of ideal gases) whether the products leave as a mixture, or separately as pure substances.

When some products leave at constant pressure, but other products remain as solids or liquids, or when the reactants are introduced into the enclosure at the beginning of the experiment, we do not have a steady state. Yet Eq. (5) holds in this case also. Suppose we measure the heat of vaporization of a liquid. Then the system is open to escape of vapor, but closed to entrance of liquid. The same heat would however be required to evaporate a given mass of liquid in the actual case as in an ideal case, in which water is slowly forced in as fast as it evaporates. For the ideal case differs only in that we should add the extra energy pv as work, where v is the volume of the added water, and should remove an equal extra quantity of energy, since the extra volume of vapor removed equals that of the water added. These considerations apply in the general case, provided only that the pressure is constant, including the case of a closed system whose pressure remains constant.

When no mass crosses the boundary, the variation of entropy is given by

$$dS = dq/T \qquad (6)$$

subject to the general condition that the variation must be produced reversibly in all respects.

If dm_1 units of mass of kind 1 are brought up to the system without adding heat, then the increase of entropy of the system brought about by merely *shifting the boundary* so as to include also the mass dm_1 is s_1dm_1, where s_1 is the entropy of unit mass. If this mass has the temperature T of the system and such a pressure p_1 (and molal volume v_1) as would make it in equilibrium with the system through a wall permeable only to matter of kind 1, we can mix it reversibly and adiabatically with the system, for instance by merely pressing it into the system through a semipermeable membrane without adding or subtracting heat, and without any change of entropy of the system of shifted boundary. Therefore

$$(dS/dm_1)_q = s_1, \qquad (7)$$

where s_1 is defined above. Hence the complete variation of the entropy, for simultaneous reversible transfers of heat and mass, is

$$dS = dq/T + \Sigma s_1 dm_1. \qquad (8)$$

Transfers of heat and mass together with adia-

batic changes of volume at constant mass are sufficient to produce every desired state of the system, and the change of entropy with volume at constant mass and adiabatically is zero.

If desired, the justification given above for ignoring the peculiarity of dq as a differential can be applied also to this case.

The consistency of Eqs. (3) and (8) with the Gibbs theory, in which dq does not appear, may be shown by eliminating dq from them. In this case we consider reversible variations only of a single phase. Thus all the quantities u_1, p_1, v_1, s_1 and T refer to the state of unit mass of kind 1 when it would be in equilibrium with the system through a membrane permeable only to this kind of mass, and similarly with regard to masses of other kinds. Elimination of dq from Eqs. (3) and (8) gives

$$dU = TdS - pdV + \Sigma(u_1 + p_1v_1 - Ts_1)dm_1, \quad (9)$$

where $u_1 + p_1v_1 - Ts_1$ is obviously the *zeta*-function of Gibbs per unit mass. This is shown by him to equal the chemical potential μ_1 in the case of a pure substance as above. Hence Eqs. (3) and (8) are consistent with his equation

$$dU = TdS - pdV + \Sigma\mu_1dm_1 \quad (10)$$

and therefore with his entire system, since none of his equations contain dq.

Inspection of Eqs. (3) and (8) shows that the right-hand sides contain terms (u_1 or s_1) which depend on the standard states used to define zero or unit values of energy or entropy, whereas the left-hand sides contain only differentials of energy and entropy. These differentials also depend upon the choice of standard states in the present case, in which the total energy and entropy are regarded as dependent in part upon the total mass.

In the application of Eqs. (3) or (8) to cases where the state is not steady, it will be necessary to evaluate the left-hand members. For this it is obviously not necessary, but certainly convenient to observe that the energy of zero mass is zero, and the entropy of zero mass at a temperature other than zero is zero. In all cases in which the production of heat and work is at the expense of material changes, this is obviously permissible to assume in the cases of the energy and the free energy (of Helmholtz), and since the latter equals

$U - TS$, the theorem for the entropy is established.[7]

One reason for here developing Eqs. (3) and (8) from fundamental thermodynamic principles rather than finding one of them from the other by comparison with Eq. (10) from Gibbs is that Gibbs' treatment has been held obscure by some authors. Thus, Milne[8] states: "Willard Gibbs simply introduced partial differential coefficients into a situation in which the ordinary 'physical' notion of a partial differential coefficient is physically not realizable. He considered the increase in energy of a system which occurs when its volume and entropy remain fixed but the mass of a chemical constituent is altered. How on earth (or in physics, which is the same thing) one can experimentally import matter into a system without importing or exporting entropy, or indeed knowing what entropy has been imported or exported, I have never been able to see, and the difficulty is largely responsible for the obscurity which is felt when reading Gibbs. The fact is that the idea is a purely mathematical one."

Also, Defay[2] states in part "W. Gibbs gave the principal equations which govern open systems. But his exposition is that of an intuition of genius which proceeds by leaps and which logic, advancing step by step, cannot follow. In order to build on a firmer foundation, De Donder, in his work *L'Affinité*, has voluntarily limited himself to the study of closed systems, a study which he has carried much further than Gibbs. With such systems, when one speaks of 'heat received by the system' or of 'work done by the system,' one knows exactly whereof one speaks.[9] It is not the same as respects open systems, as we shall see later."

Without maintaining that the treatment of Gibbs is in need of clarification, it may however be pointed out that Eq. (9) leads directly to

$$(dU/dm_1)_{S,V,m} = u_1 + p_1v_1 - Ts_1, \quad (11)$$

which suggests a direct physical interpretation of the chemical potential from its definition

$$\mu_1 = (dU/dm_1)_{S,V,m} \quad (12)$$

[7] These assumptions furnish a necessary justification for the omission of an integration constant in Gibbs' Eqs. (93) to (96).

[8] E. A. Milne, *The Aims of Mathematical Physics*, The Clarendon Press, Oxford, England (1929), quoted by Bancroft, J. Phys. Chem. **34**, 1614 (1930).

[9] " *de quoi il s'agit.*"

by the use of the sort of reasoning employed above in deriving Eqs. (3) and (8).

As a matter of fact Gibbs provides a physical interpretation, but postpones it to page 95 (of the reprinted paper) and, as usual, deals with entropy rather than heat.

III. Equations for the Heat of Expansion of a Gas of Varying Mass at Constant Temperature

We shall use Eq. (8) as a starting point, for convenience. Eq. (3) may also be used. In either case it is necessary to add a second-law equation (for closed systems). We shall consider only the case in which the gas does not change in composition during the expansion. Then the total entropy is given by

$$S = sm, \tag{13}$$

where s is the entropy of unit mass at the temperature and pressure of the gas, and m the number of units of mass.

Then we have in general

$$dS = sdm + mds. \tag{14}$$

Substituting in Eq. (8) we obtain

$$dq = Tmds. \tag{15}$$

The entropy of unit mass may be taken as a function of the temperature and pressure or of the temperature and the volume of unit mass. For the slow expansion at constant temperature we shall have for the integrated heat

$$\lambda = \int mT(ds/dp)_T dp = \int mT(ds/dv)_T dv, \tag{16}$$

which can be evaluated by the use of Maxwell's first and third relations as

$$\lambda = -\int mT(dv/dT)_p dp = \int mT(dp/dT)_v dv. \tag{17}$$

The last expression is convenient for the use of an equation of state implicit in the volume v of unit mass. This is equal to V/m, where V is the total constant volume of the container, so that

$$dv = -(V/m^2)dm. \tag{18}$$

Evaluation of the derivative dp/dT at constant molal volume by means of the Beattie-Bridgeman equation[10] gives a final expression for the heat

10 J. A. Beattie and O. C. Bridgeman, Proc. Amer. Acad. Arts and Sci. 63, 229 (1928).

$$\lambda = RT(n_i - n_f) + \frac{RT}{V}\left(\frac{B_0}{2} + \frac{c}{T^3}\right)(n_i^2 - n_f^2)$$
$$+ \frac{RTB_0}{V^2}\left(\frac{2c}{T^3} - b\right)(n_i^3 - n_f^3)$$
$$- \frac{RB_0bc}{2V^3T^2}(n_i^4 - n_f^4), \tag{19}$$

where n_i and n_f are the numbers of moles of gas initially and finally present in the volume V. The gas constant R may be taken throughout as 1.987 cal.$_{15}$ per mole per degree centigrade absolute. The volume V is in liters, and the constants B_0 c and b are in liters per mole, as given by Beattie and Bridgeman for many gases. The absence of the constants A_0 and a is perhaps noteworthy.

For an ideal gas, all the equation of state constants except R are zero, and the heat absorbed is RT per mole. The result of Joule mentioned above is in excess over the value of RT by about 7 percent.

For a real gas, the heat effect is not solely dependent upon the number of moles escaping from the volume, but depends upon the numbers n_i and n_f separately, and this is true even of the first correction term.

Eq. (19) can be applied also to calculate the heat evolved at constant temperature when a gas is caused to flow slowly *into* a calorimeter.

By thus applying Eq. (19) to the vessels A and C of Fig. 1 and finding the change of energy of the sum of the systems A, B, and C, the heat effect of the middle vessel containing the stopcock can be determined by difference. The general result is not simple algebraically, but the effect is zero for an ideal gas.

IV. Apparatus

The apparatus used in measuring the heats of expansion is shown in Fig. 2, in which the relative dimensions of the various parts have been retained.

The expansion vessel is shown at D. It is made of one-thirty-second inch cold-drawn steel tubing with welded steel ends. Its volume, determined by filling with air-free water at 0°C and weighing, was 110.473 cubic centimeters in the experiments on carbon dioxide. Before the experiments on ammonia, a one-inch hole was drilled in the bottom and fitted with a threaded plug sealed by a

copper washer. As a result of this change the volume of the bomb was 102.486 cubic centimeters for the runs on ammonia.

The bomb is connected by 0.0625 inch nickel-silver tubing to a steel cone and socket stopcock

FIG. 2. Apparatus used in the present experiments.

through which it can be opened to the atmosphere at A by a second stopcock—to vacuum pumps at B by a third stopcock—or to the gas reservoir at C by a fourth. The manometer J, shown connected to the bomb by a tee-joint below the stopcock, was used only during the rapid expansions of carbon dioxide and was completely absent during the slow expansion of carbon dioxide and ammonia. This manometer is made of heavy-walled glass capillary tubing connected to the bomb by steel capillary tubing.

The heat effect is measured by an ice calorimeter E which encloses the bomb and 0.5 inches of

the stem. The calorimeter is made of glass in the form of a Dewar tube filled with air-free water and mercury. When ice is frozen in the annular space E between the walls of the calorimeter, mercury is forced out of the capillary K into weighing bottles.

The calorimeter is enclosed in a water-tight, silver-plated copper can G to reduce heat exchange by radiation and is separated from it by an air space F. The metal can is in turn immersed in a freezing-mixture H. The freezing mixture used consists of an intimate mixture of finely-divided lead chloride and shaved ice. A relatively large proportion of lead chloride is used so that as the ice melts the liquid water will be practically immediately saturated with the salt. In this way a constant temperature a few tenths of a degree below zero is obtained which gives rise to a small and reasonably steady freezing of ice in the calorimeter.

The container of the freezing mixture is insulated by two inches of felt, I, and supported in a galvanized iron can. The calorimeter assembly is mounted on vertical rods (not shown) in such a way that it can be lowered away from the bomb to make way for a thermostat.
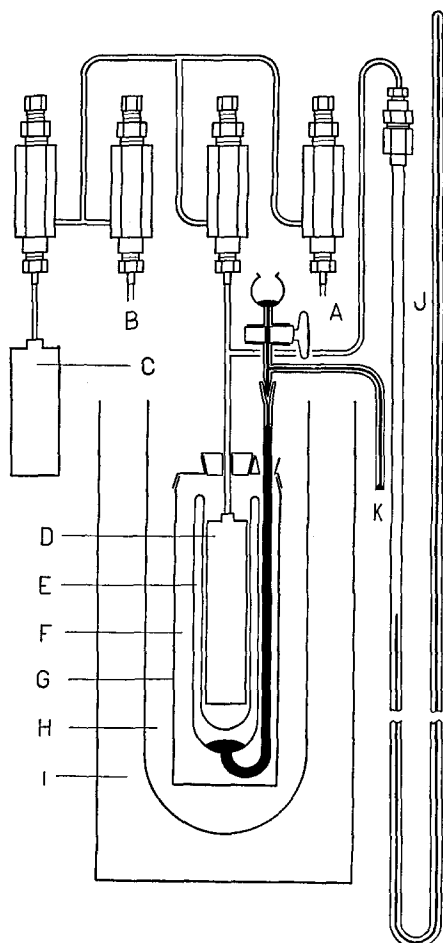
V. PREPARATION OF MATERIAL

The carbon dioxide used was obtained in cylinders as a liquid and was dried by passing through phosphorus pentoxide. It was purified by three fractional sublimations, the first and last quarters being discarded each time. The solid was pumped down after each sublimation to remove any permanent gases. It was finally frozen into the storage vessel C, and the latter temporarily disconnected and weighed to determine approximately the amount present.

Liquid ammonia which had been dried by standing in cylinders over sodium was further purified by three fractional distillations, the first and last portions again being discarded in each distillation. Between distillations the ammonia was pumped to remove permanent gases.

VI. EXPERIMENTAL PROCEDURE

The expansion bomb was first evacuated. It was then connected through the stopcocks to the reservoir which was kept immersed in an ice

bath. The bomb itself was immersed in a suitable thermostat so that the gas within it was at a known temperature and under the vapor pressure of the liquid at 0°C. When sufficient time had elapsed for equilibrium to be attained the stopcocks were closed. From these known values of the temperature and pressure the molal volume of the gas could be calculated by means of the Beattie-Bridgeman equation. By varying the temperature at which the bomb was thermostated, the molal volume of the gas in the bomb, and hence the amount of it, could be easily predetermined. The number of moles of gas loaded in was calculated from the molal volume and the volume of the container.

The bomb having been loaded, the thermostat was removed. The previously described freezing mixture was packed around the can containing the ice calorimeter, and after the latter had cooled to zero degrees, an ice mantle was frozen on its inner wall by means of a glass tube cooled in liquid air. The calorimeter was now raised into position around the bomb and the opening closed by means of a rubber stopper, more of the freezing mixture being added to cover the silvered can to a depth of two inches.

When sufficient time had elapsed for the system to reach a steady state, the creep of the calorimeter, that is, the slow freezing of ice due to heat being absorbed by the freezing mixture, was determined by weighing the amounts of mercury forced from K during three or four ten-minute intervals. The proper stopcocks were then opened and the gas allowed to escape very slowly into the atmosphere. When the expansion was completed the creep was again observed for three or four ten-minute intervals. The time required for the creep to return to a steady state was measured and the amount of mercury forced out in that time was corrected by subtracting the amount due to creep. The result was that amount due to the heat of expansion.

The magnitude of the creep was not the same for all experiments since it varied not only with the temperature gradient between the calorimeter and the freezing-mixture, but also with the atmospheric pressure and the room temperature. The effect of these last two variables was so small, however, that during any single experiment the mean deviation from the mean value of

the creep was rarely more than 2 or 3 percent of the latter. The creep itself during the course of all the expansions ranged in value from 0.00220 to 0.00300 grams of mercury per minute.

The value for the ice calorimeter constant used was 0.01546 grams of mercury per 15° calorie—a value given by Ostwald[11] and redetermined by Lamb and Coolidge.[12]

VII. THE SLOW EXPANSIONS OF CARBON DIOXIDE

The results of six slow expansions of carbon dioxide are given in Table I. In column 2 is given

TABLE I. *Expansion of carbon dioxide. Loaded at 20°C.*

1 Run No.	2 Atm. pressure mm	3 Δn	4 Calculated heat	5 Measured heat	6 Ratio Exp. heat: Calc. heat
1	752.5	0.1982	124.5	124.3±2.5	0.998±0.020
2	754.2	0.1982	124.5	121.4±6.9	0.975±0.055
3	753.0	0.1982	124.5	127.1±0.0	1.021±0.000
4	761.9	0.1981	124.5	123.6±0.3	0.993±0.002
5	749.1	0.1982	124.6	124.4±0.8	0.999±0.006
6	755.1	0.1982	124.5	124.8±0.6	1.002±0.005

the atmospheric pressure during each experiment. In column 3 is given the number of moles Δn of gas leaving the bomb. Preliminary experiments indicated that if the bomb be loaded at 20°C with the reservoir at 0°C, the gas in the expansion bomb will be sufficiently far from saturation when cooled to 0°C for the equation of state constants to be accurate. The values for the equation of state constants for carbon dioxide are:

A_0, 5.0065; a, 0.07132; b, 0.07235; B_0, 0.10476; c, 66×10^4; R, 0.08206.

The units are liters per mole, atmospheres, and °C absolute $(t+273.13)$.

In calculating the molal volume, Bridgeman's[13] value for the vapor pressure of carbon dioxide at 0°C was used; 34.4009±0.0013 atm. at 0°C. The molal volume of carbon dioxide at 20°C and 34.4009 atm. is calculated from the Beattie-Bridgeman equation to be 0.54427 liters per mole. From this and the volume of the bomb it was

[11] Ostwald-Luther, *Hand und Hilfsbuch*, 3d Ed., p. 334.
[12] A. B. Lamb and A. S. Coolidge, J. Am. Chem. Soc. 42, 1146 (1920).
[13] O. C. Bridgeman, J. Am. Chem. Soc. 49, 1174 (1927).

TABLE II. *Expansions of ammonia at 0°C.*

1 Run No.	2 Atm. pressure (mm)	3 Temp. of loading (°C)	4 Δn	5 Calculated heat (15° cal.)	6 Measured heat (15° cal.)	7 Ratio Exp. heat: Calc. heat
1	756.1	217.86	0.006322	3.589	3.467±0.275	0.966±0.077
2	755.3	217.69	0.006331	3.594	3.415±0.130	0.950±0.036
3	763.6	218.28	0.006266	3.558	3.486±0.086	0.980±0.024
4	760.2	99.99	0.009870	5.660	5.679±0.152	1.003±0.027
5	757.6	99.92	0.009887	5.670	5.647±0.518	0.996±0.091

found that 0.20312 moles of carbon dioxide were loaded into the bomb before all runs. In calculating the amount of gas remaining after the expansion, the value 22.2612 liters per mole[14] for the molal volume at 0°C and one atmosphere was used and was corrected for deviations of the pressure from one atmosphere.

In column 4 is given the calculated value for the heat effect, obtained from Eq. (19). The measured value for the heat effect is given in column 5, and it will be observed that it is in substantial agreement with the calculated value. The possible deviation indicated is due to the slight deviation of the creep from the mean value. In column 6 is given the ratio of the measured to the calculated heat.

The time during which mercury was collected varied in these experiments from 55 to 85 minutes. That such a time is long enough to correspond to slow smooth flow of gas is indicated first by the above agreement, and second by a series of measurements at different rates of flow, reported below.

The value of $RT(n_i - n_f)$ was very nearly 107.5 cal. in all cases. The agreement of the measured excess heat over this figure with that calculated is to about 7 percent of the calculated excess.

VIII. THE SLOW EXPANSION OF AMMONIA

Many unsatisfactory experiments, not reported in detail, were made in which ammonia, loaded at 20°C, at 30°C, at 100°C, and finally at 218°C, was allowed to expand slowly. The results obtained at the three lower temperatures were in all cases higher than was expected from Eq. (19), the differences amounting to 75 percent at 20°; to 50 percent at 30°; and to 25 percent at 100°.

[14] J. A. Beattie and O. C. Bridgeman, J. Am. Chem. Soc. 50, 3151 (1928).

The discrepancies at the two lower temperatures are attributed largely to inaccuracies in the equation of state constants at pressures so near the saturation value, while those observed at 100° are now believed to have been due to the presence of a water film on the walls of the expansion bomb.

Such a film would result in excessive adsorption of ammonia at the high initial pressure and this excess would be desorbed with an attendant heat absorption comparable to the heat of solution of ammonia in water, or perhaps higher, when the pressure falls during the expansion. A relatively small amount of adsorbed ammonia, therefore, would give a serious error in the observed heat effect. This hypothesis is borne out by the fact that when, before loading at 100°, the bomb was evacuated for four or five hours while being baked at 218°, the measured heat of expansion agreed with that calculated.

A small quantity of foreign material in the bomb might greatly change the absorptive properties. The bomb was opened, thoroughly cleaned, and the results shown in Table II were obtained.

In all these experiments the bomb was evacuated and baked at 218° before it was loaded. In column 2 is given the atmospheric pressure at the time of the expansion. In column 3 is given the temperature of loading. The thermostats employed were steam and naphthalene vapor baths; the true temperatures were obtained from vapor pressure data and the barometric pressure.

In column 4 is given the number of moles Δn of gas leaving the bomb during the expansion. In calculating the molal volume of the ammonia at the loading temperature the values for the equation of state constants used were:

A_0, 0.870175; a, 0.877102; B_0, 0.00766400;
b, 2.231074; c, 6.131196×10⁶; R, 0.08206.

The units are liters per mole, atmospheres, and °C absolute $(t+273.13)$.[15] The Bureau of Standards value for the vapor pressure of ammonia at 0°C was used: 4.2380 atm.[16] The molal volume of ammonia was found from the Beattie-Bridgeman equation to be 7.08698 liters per mole at 100°C; and 9.44294 liters per mole at 217.96°C; these values were corrected in each experiment for the small deviations of the thermostats from these temperatures. The value of Beattie and Lawrence—22.0753 liters per mole at 0°C and 1 atm.— was used in calculating the number of moles of gas remaining in the bomb after the expansion. This number and the number initially introduced were calculated from the molal volumes and the volume of the bomb.

In column 5 is given the heat effect calculated from Eq. (19). In column 6 is given the measured heat effect with a possible uncertainty in calories due to the possible deviation of the creep from its mean value. The numerical values given to these uncertainties are probably excessive. The experimental values are in good accord with the calculated values as is shown in column 7 where the ratio of measured to calculated effect is given.

The time during which mercury was collected varied from 32 to 50 minutes.

The value of $RT(n_i-n_f)$ is about 3.4 cal. for the first three runs, and about 5.36 for the last two. The measured (and computed) heat is in such slight excess over this, that the excess is only verified by the experiments with an average deviation of 50 percent of the calculated excess.

IX. Rapid Expansions of Carbon Dioxide

In addition to the slow expansions of carbon dioxide and ammonia, a series of seven expansions at increasingly greater rates was made with carbon dioxide. The results of these experiments, numbered from 4 to 10, together with those of the

TABLE III. *Rapid expansions of carbon dioxide.*

1 Run No.	2 Barometric pressure (mm of Hg)	3 Δn	4 Calculated heat (15° cal.)	5 Measured heat (15° cal.)	6 Ratio $\dfrac{5}{4}$	7 Time (minutes)
1	761.9	0.1981	124.5	123.6±0.3	0.9928±0.0025	57.633
2	749.1	0.1982	124.6	124.4±0.8	0.9986±0.0054	41.333
3	755.1	0.1982	124.5	124.8±0.6	1.0022±0.0051	32.583
4	765.3	0.1986	124.8	123.4±0.3	0.9885±0.0023	9.750
5	756.0	0.1986	124.9	119.7±0.2	0.9587±0.0014	2.583
6	759.9	0.1986	124.9	114.6±0.3	0.9175±0.0023	1.300
7	757.2	0.1986	124.9	110.1±0.2	0.8895±0.0018	0.767
8	769.3	0.1986	124.9	105.5±0.7	0.8446±0.0053	0.500
9	759.5	0.1986	124.9	91.9±0.3	0.7358±0.0025	0.267
10	763.3	0.1986	124.8	74.1±0.3	0.5936±0.0022	0.033

last three slow expansions are given in Table III.

In column 2 is given the barometric pressure at the time of each experiment; in column 3 the number of moles Δn of gas leaving the bomb; in column 4 the heat effect calculated from Eq. (19) for slow expansions; in column 5 the measured heat effect; and in column 6 the ratio of the measured to the calculated heats. Since the bomb was loaded before the rapid expansions in the same way as before the slow ones, it is only necessary at this point to mention, in connection with the above, a correction which had to be applied in calculating the amount of gas in the bomb before the expansion. This correction arose from the fact that the manometer, described above, which was now attached to the bomb, remained at room temperature when the bomb was cooled to 0°. As a result some of the gas originally in it was transferred to the bomb, an amount so small, however, that it could be determined closely enough by use of the ideal gas law.

In column 7 is given the time required for the pressure to fall to 10 cm above atmospheric pressure. This time was measured by means of the manometer and a stop-watch, and it gives a good measure of the rate of expansion. The time required for the pressure to fall exactly to atmospheric pressure cannot be measured.

It will be observed that the fraction of the cal-

[15] J. A. Beattie and C. K. Lawrence, J. Am. Chem. Soc. **52**, 12 (1930).

[16] Bur. Standard Sci. Paper No. 369 (1920).

culated heat obtained decreases with increasing rate of expansion.

X. Discussion of Rapid Expansions

It was found empirically that by plotting the cube root of the time t required for the pressure to fall to 10 cm above atmospheric pressure against the natural logarithm of the fraction $1-X$ of the calculated heat which was dissipated a straight line was obtained. The intercept of the straight line and its slope were determined by the method of least squares with the following relation:

$$A - B(100t)^{1/3} - \ln(1-X) = 0; \qquad (20)$$

where

$$A = -0.2389 \pm 0.0765$$

and

$$B = 0.4376 \pm 0.0141.$$

The experimental values of X, the fraction of the calculated heat obtained, were smoothed by means of this line, and the actual values and the smoothed ones are given in Table IV.

TABLE IV. *Comparison of experimental values of X with values smoothed by the method of least squares.*

1 Run No.	2 Time	3 X Calculated	4 X Experimental	5 $X_E - X_C$
–	Infinite	1.0000	——	——
1	57.633	0.9997	0.9928±0.0025	−0.0069
2	41.333	0.9993	0.9986±0.0054	−0.0007
3	32.583	0.9988	1.0022±0.0051	0.0034
4	9.750	0.9897	0.9885±0.0023	−0.0012
5	2.583	0.9515	0.9587±0.0014	0.0072
6	1.300	0.9142	0.9175±0.0023	0.0033
7	0.767	0.8773	0.8895±0.0018	0.0122
8	0.500	0.8429	0.8446±0.0053	0.0017
9	0.267	0.7869	0.7358±0.0025	−0.0511
10	0.033	0.5904	0.5936±0.0022	0.0032
—	0.000	0.2125	——	——

From the value of the intercept A it appears that the heat effect does not become zero for an infinitely rapid expansion, but that the fraction of the calculated heat effect becomes from 0.2705 to 0.1499. According to this, the heat effect for carbon dioxide is from 33.77 to 18.72 calories when the gas is allowed to expand infinitely rapidly under the given experimental conditions in our apparatus.

This extrapolated value agrees with a value 31.6 cal. calculated for the following ideal state of affairs. In the unresisted infinitely rapid expansion the work is here supposed not paid for at the expense of the energy of the gas in the container, but the energy change of separating the molecules against van der Waals forces of the gas in the container is supposed to be at the expense of the gas remaining in the container at any time. This energy loss is made up by a flow of heat after the expansion sufficient to restore the initial temperature. Under these assumptions the energy loss can be computed to a first approximation from an integration at constant temperature[17] of the equation:

$$dU = n(du/dv)_T dv = n[T(dp/dT)_v - p]dv \qquad (21)$$

with respect to the variable number of moles in the container. The resulting equation, based on the Beattie-Bridgeman equation, is

$$\Delta U = \left(A_0 + \frac{3Rc}{T^2}\right)\frac{\Delta(n^2)}{2V} + \left(\frac{3RcB_0}{T^2} - A_0a\right)\frac{\Delta(n^3)}{3V^2}$$
$$- \frac{3RcB_0b}{T^2}\frac{\Delta(n^4)}{4V^3}, \qquad (22)$$

where $\Delta(n^2)$ indicates $n_i^2 - n_f^2$, etc., and ΔU the decrease of energy.

We do not pretend to say how reasonable a representation of the actual conditions is given in this way, but it is the best way we can offer to explain the experimental value at an infinite rate of flow, and Eq. (22) is proposed in the absence of anything better. According to this equation the heat would drop to zero in the case of an ideal gas, or in the case of a real gas when the volume of the container is infinite.

XI. Application to Variable-Pressure Calorimetry

If charcoal is placed in the gas-free vessel C of Fig. 1 and a gas is admitted from vessel A, the heat evolved from vessel C at constant temperature is the measured heat of adsorption, and it remains to find the change of energy or of heat content for the adsorption process itself. In actual experiments the flow of gas has not always been throttled in a separate vessel B, nor even in any

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[17] To a first approximation, because the value of the line integral depends on the unknown variation of temperature during the expansion for the Beattie-Bridgeman equation, though it does not for the van der Waals or Keyes equations.

definitely known position. The change of energy in C is partly due to the heat effect studied in this paper and represented by Eq. (19).

For an ideal gas, the heat of throttling (even at variable pressures) is zero, and the part of the heat effect due to influx of gas is RT per mole of entering gas, provided that the flow is very slow, a result agreeing with that of Coolidge.[4]

If, however, the flow is rapid the effect is less than RT per mole, as shown by our experiments, and the limiting value for infinitely fast flow is certainly close to zero, if not equal to zero. This is in agreement with the result of Williams,[3] as in practice the condition of Coolidge, that the temperature of the entering gas be controlled, is necessarily violated in rapid flow.

The correction for deviations from the laws of ideal gases depend on the location of the throttling valve and upon more apparatus constants than are usually reported by experimenters, and we do not therefore develop the application of Eq. (19) in this direction.