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The Joule Effect in Air

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Previous methods used in determining the magnitude of the Joule effect are reviewed and their significance discussed. Essential requirements on apparatus and the technique necessary for measuring reliably this effect to within 0.1 percent are analyzed. The construction of and operational technique for a set of apparatus built to these requirements are described. Sample data on air are given and compared with other values in the literature. It is concluded that with indicated improvements in detail, the method developed here will achieve precision and reliability to within 0.1 percent.

I. INTRODUCTION

THE Joule effect may be visualized in terms of an "armchair" experiment. Imagine a vessel with thermally non-conducting and mechanically rigid walls, divided into two compartments by a partition. Suppose that a gas is admitted into one compartment, and the other is evacuated. If the partition is removed, the gas will undergo what is known as a "free expansion" in which no external work is done and no heat transfer with the environment takes place. Then in the statement of the first law,

$$\Delta U = Q - W, \tag{1}$$

$Q = W = 0$; and hence ΔU, the change in the internal energy, is also zero.

If, during this expansion, internal energy shifts take place between the various degrees of freedom or energy levels in the gas, one may expect a corresponding change in temperature to result. An example of such an internal energy shift would be that corresponding to work done against the intermolecular forces. This temperature change is measured by what is known as the "free expansion" or "Joule" coefficient. Thus:

$$\eta = \left(\frac{\partial T}{\partial v}\right)_u, \tag{2}$$

and

$$\eta' = \left(\frac{\partial T}{\partial p}\right)_u. \tag{3}$$

Other measures of the "Joule effect" are,

$$\lambda = \left(\frac{\partial u}{\partial v}\right)_T = -\left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_u = -C_v\eta, \tag{4}$$

$$\lambda' = \left(\frac{\partial u}{\partial p}\right)_T = -\left(\frac{\partial u}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_u = -(C_p - pv\alpha)\eta', \tag{5}$$

where α is the coefficient of volume expansion.

There are several reasons why it is desirable to know the values of η, η', λ and λ' with the greatest possible precision. First, since these quantities are zero for ideal gases, the finite values for real gases serve to measure the departure of real gases from the ideal condition.[1] Second, these quantities are connected with the virial coefficients which, in turn, are associated with the law of molecular attraction.[2] Third, these quantities enable one to measure the value of the Kelvin ice point.[3]

II. EXPERIMENTAL METHODS

Attempts to measure $(\partial T/dv)_u$ have followed two general methods. Joule (1843)[4] and later Regnault, permitted the gases after expansion to come to thermal equilibrium with the walls of the containing vessel. Their hope was to infer the change in temperature of the gas on expansion from the subsequent change in temperature of the entire system including the vessel and a surrounding water bath. Actually the heat capacity of the system, roughly 1000 times that of the gas alone, so reduced this final temperature

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[1] A. L. Clark, Trans. Roy. Soc. Can. [3] 28, 293–311 (1924).

[2] J. O. Hirschfelder, R. B. Ewell, and J. R. Roebuck, J. Chem. Phys. 6, 205 (1938).

[3] J. R. Roebuck and T. A. Murrell, in *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1941), p. 65.

[4] J. S. Ames, *The Free Expansion of Gases* (Harper & Bros., New York, 1898).

change as to make it undetectable with the instruments at their disposal.

Hirn,[5] Cazin,[6] and Keyes and Sears[7] attempted to measure the change in temperature of the gas before it came to equilibrium with the containing vessel. Hirn and Cazin attempted to make the gas serve as its own thermometer. Keyes and Sears used a special platinum resistance thermometer. Results by the second method vary, but are usually high by a large factor. These may be explained by assuming energy interchange with the vessel during expansion. When the expansion occurs through a valve, apparently the predominating effect is the dissipation of kinetic energy of streaming into heat which is conducted through the valve. When the gas is released by the shattering of a glass partition, the kinetic energy conferred upon the fragments affects the result in the same way. The experiment thus fails to satisfy the adiabatic condition. Seventy-five years of work have not brought a solution to this difficulty.

Measurements of $(\partial u/dp)_T$ have followed two methods, both of which involve letting the gas come to equilibrium with the containing vessel. In Washburn's method[8] carried out by Rossini and Frandsen[9] the system includes a water bath as Joule's did. The wall of the second chamber is, however, omitted; the expansion occurs into the atmosphere through a long tube immersed in the bath. These modifications reduce the heat capacity of the system by about one-half, and approximately double the pressure drop, i.e., for the same mass of gas and the same initial pressure. By means of measured electrical energy injected into the bath during expansion the experiment is made nearly isothermal. The constancy of temperature is indicated by a highly sensitive platinum resistance thermometer. It is essentially the 250-fold greater sensitivity of this thermometer over that used by Joule which makes this method capable of yielding quantitative results, whereas that of Joule did not.

For the case of this experiment the first law may be written,

$$u(P_2, T)-u(P_1, T)=\frac{Q-W}{n}-\frac{\Delta U}{n}\,\text{(metal)} \qquad (6)$$

where Q is the electrical energy input, W is the mechanical work done against the atmosphere, n is the number of moles of gas, ΔU (metal) is the increase in internal energy experienced by the vessel during the expansion, and $u(P, T)$ is the molar intrinsic energy of the gas.

By holding P_2 and T constant one obtains $u(P_2, T)-u(P_1, T)$ for a series of values of P_1, and this is plotted against P_1. The slopes of such curves then are the values obtained for $(\partial u/\partial p)_T$.

Rossini and Frandsen estimate their results to be accurate to within $\pm 2\frac{1}{2}$ percent. Since this accuracy depended on the determination of bath temperatures to within 0.0001°C, the method does not appear susceptible of any appreciably greater degree of accuracy.

In the present method the system consists merely of the gas itself and two thin metal shells, as shown in Fig. 1. The shells are constructed for minimum heat capacity. The system at maximum working pressure has thus a heat capacity only about fifteen times greater than that of the contained gas, instead of 1000 times as in the case of Joule. With this heat capacity ratio the change in temperature which would

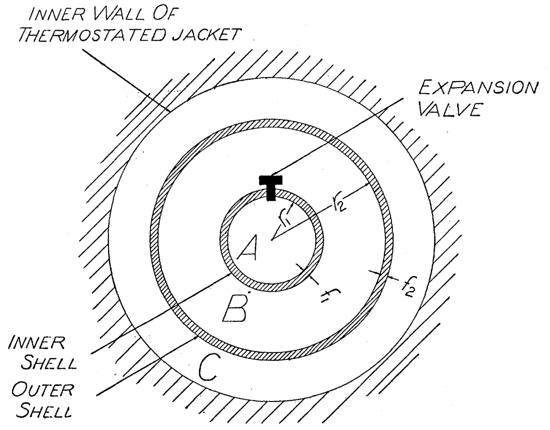

FIG. 1. Diagram of system. A is inner chamber containing n_1 moles of air at pressure P_1 before expansion; B is outer chamber containing n_2 moles of air at pressure P_2 before expansion; C is insulating layer of air at pressure P_0. Pressure in A and B after expansion is P_3.

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[5] G. A. Hirn, *Exp. Anal. et Exp. de la Th. Mec. de la Chaleur* (Paris, 1875), third edition.

[6] A. Cazin, Phil. Mag. **40**, 81 (1870).

[7] F. B. Keyes and F. W. Sears, Proc. Nat. Acad. Sci. **11**, 38 (1925).

[8] E. W. Washburn, Bur. Stand. J. Research **9**, 521 (1932).

[9] F. D. Rossini and M. Frandsen, Bur. Stand. J. Research **9**, 733 (1932).

result if an expansion could occur under adiabatic conditions would be about $1\frac{1}{2}$°C.

III. THEORY OF PRESENT APPARATUS

The design of the present apparatus was governed by three general objectives.

First, it was necessary that the heat capacity of the shells relative to that of the contained gas be a minimum.

Second, it was necessary that transfer of heat between the system and its surroundings during the equilibrating period be a minimum, and that means be devised to measure and correct for such flow as could not be prevented.

Third, it was necessary that heat absorbed or liberated by the shells upon alteration of their stress be minimized, and that means be devised to correct for such heat exchange as could not be prevented.

In regard to the first condition, a vessel of small relative mass was attained, primarily through use of a material of high tensile strength, combined with a design devoid of massive fittings, such as flanges, etc. Since the heat capacities per unit volume of most suitable materials do not differ greatly, this property did not feature particularly in the reasoning. The spherical form was found to be optimum, and was adopted; there were two concentric shells. See Fig. 1 and Fig. 2. It was noted that nothing was to be gained in regard to the first objective by going either to very large or to very small shells. Because of a combination of desirable properties Invar was chosen as a material and was used at stresses up to an elastic limit of about 45,000 lb./in.^{2}.

Since gas densities at any given pressure increase with decreasing temperature the ratio of gas mass to vessel mass (and hence of thermal capacities) will tend to be higher. The apparatus will hence tend to be more sensitive when one is working at low than when working at relatively high temperatures. Also when the pressure drops are relatively large, $u(P_2, T) - u(P_1, T)$ in the gas is, in general, larger without the mass of the shells being greater. Thus, when one is working at relatively large pressure drops, the apparatus tends also to be more sensitive.

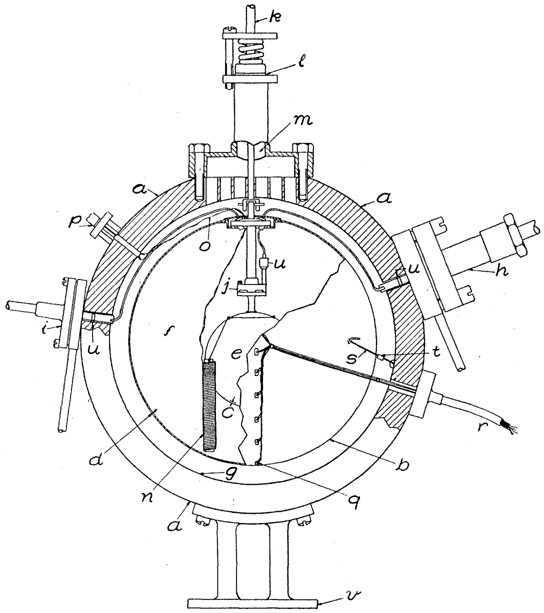

FIG. 2. Vessel and central mounting plate assembly. *a*—central mounting plate; *b*—vessel; *c*—inner shell; *d*—outer shell; *e*—inner chamber; *f*—outer chamber; *g*—jacket surface; *h*—inlet valve; *i*—outlet valve; *j*—expansion valve; *k*—forked valve stem; *l*—ground metal seal; *m*—passage to vacuum system; *n*—heater coil; *o*—heater leads; *p*—battery and potentiometer connection; *q*—thermopile junctions; *r*—thermopile leads; *s*—guy wires; *t*—turnbuckle; *u*—union; *v*—insulating support.

To achieve the second objective various measures were found suitable. Thus to minimize the heat transfer to the surroundings during the equilibrating period, it was necessary to minimize both the rate of transfer and the duration of this period.

In regard to the latter it was inferred from various calculations that this period would be shorter for a smaller vessel than for a large one. Since, however, the quantity of working substance decreases with the size of the vessel, other things being equal, and small spurious quantities of heat, such as that generated in opening the valves, tend to become magnified in importance, it was not deemed advisable to reduce the size below a certain minimum. For this the equilibrating period was about ninety minutes.

To minimize the rate of transfer, conduction, convection, and radiation were dealt with separately. Since all three depend on the temperature difference, the outer shell was surrounded by a jacket maintained at a temperature near that of the shell.

Conduction was minimized by as nearly as possible eliminating all heat paths through solids from the vessel to the surroundings. Thus, the shells were supported by six fine piano wires (0.005″ diam.). Electrical connections were made through long, fine wires of low conductivity material (manganin). Tubes for conveying the working substance, i.e., the gas to and from the vessel, were long, fine, and of low conductivity material (1/64″ and 1/32″ diam. stainless steel).

Convection and gaseous conduction were to have been eliminated by maintaining a high vacuum in the space between the outer shell and the jacket. Actually this was not achieved in the present work; however convection was greatly reduced by the absence of any appreciable temperature gradients in the space. Making the shells spherical with one shell inside the other minimized the surface exposed to radiation and convection transfer.

Radiation transfer was further reduced by making the jacket spherical, concentric, and near to the outer shell, and by providing a high reflection coefficient on the opposing surfaces.[10] (The jacket surface was of polished silver; the outer shell of polished Invar.)

To measure the heat actually transferred, it was assumed that the transfer would take place according to the equation,

$$\Delta q = e\int_{t_1}^{t_2} \Delta T dt \qquad (7)$$

where, t = time; ΔT = average temperature difference between the jacket and the outer shell; e = emission constant. Since ΔT was never more than 1°C this assumption was probably not seriously in error.

In order to measure ΔT as a function of t during the equilibrating period, twenty-four thermoelectric junctions were distributed over the exterior surface of the outer shell. These were in series, while the corresponding junctions were in the jacket flow. The jacket was assumed to be of uniform temperature.

To determine the emission constant, e, an electric heater symmetrically disposed was provided within the shells. At a constant wattage ΔT would become constant, resulting in a constant galvanometer deflection. It was not necessary to convert the latter to degrees centigrade. The constant e was simply taken as a ratio of the steady power input to the magnitude of the resulting galvanometer deflection.

There is a tendency for ΔT to be very large during the period immediately following expansion. The gas expands from the space within the inner shell to the space between the two shells. Hence the temperature in the outer chamber rises and that in the inner chamber drops. Such gas as remains within the inner shell has then undergone a semi-adiabatic expansion doing work on the gas packed into the outer chamber.

For air at 20°C and a doubling of volume on adiabatic expansion this rise in temperature in the outer space might be as much as 85°C. For larger expansion ratios this peak temperature decreases. If the substance is one for which $(\partial T/\partial v)_u$ is negative, it may be possible to find an expansion ratio for which the decrease in temperature due to the Joule effect just offsets this tendency to adiabatic rise in temperature. For air this is feasible; however, it works for but one initial pressure. In the present work, where other initial pressures were used, this transient rise was still appreciable.

In regard to the third objective there are three modes by which heat exchange might occur between the gas and the shell materials. These are heat of plastic deformation, heat of adsorption, and heat due to the thermoelastic effect.

Heat of plastic deformation[11] is eliminated by keeping all stresses in the shells below the elastic limit of the material. The spherical form, resulting in nearly homogeneous stress, facilitates this.

A change, during an experiment, of the quantity of gas adsorbed upon the inner surface of the shells would involve heat transfer. This effect is probably small at nearly constant temperature and moderate pressures.[12] Experiments with varied adsorbing areas would yield corrections for this error.

Thermoelastic energy shifts between potential and heat energy, when materials are strained, are known to be appreciable,[13] and such shifts will

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[10] M. Fishenden and O. A. Saunders, *The Calculation of Heat Transmission* (H. M. Stationery Office, London, 1932), pp. 28–29.

[11] W. S. Farren and G. L. Taylor, Proc. Roy. Soc. London, **A107**, 423 (1925).

[12] K. Fischbeck, H. Mass, and H. Meissenheimer, Zeits. f. physik. Chemie **A171**, 385 (1934).

[13] K. T. Compton and D. B. Webster, Phys. Rev. **5**, 159 (1915).

unavoidably take place in the inner and outer shells. As far as the writer can determine, previous data and computation formulae on this effect have been limited to the one-dimensional case.[13] These formulae involve certain dubious approximations, and experimental determinations differ from one another by several percent.[13] The magnitude of this error is thus left in doubt.

To remove this doubt an exhaustive theoretical analysis has been made.[14] The three-dimensional case was treated. Quantitative estimate was made of possible discrepancies due to all assumptions made.

Kelvin's formula,[15]

$$\Delta q = -\frac{T}{J}\left[\frac{\partial(\Delta w)}{\partial T}\right]_T, \qquad (8)$$

was used as the basis for this analysis. Here Δq is the heat absorbed by, and Δw the work done upon, a body when strained isothermally at temperature T. Kelvin made no approximations and limited application only by stipulating reversability.

The quantity $[\partial(\Delta w)/\partial T]_T$ was expressed in the form of a Taylor's expansion in three dimensions. It was found that successive orders of terms after the second in this expansion decrease by a factor which for most metals is of order 10^2 to 10^3. Hence those beyond the quadratic were neglected. The formula arrived at was

$$\frac{\Delta q}{\Delta v} = \frac{T}{J}\left\{ s[X_x + Y_y + Z_z] + \frac{\sigma}{E}\left[\frac{1}{E}\frac{\partial E}{\partial T} - \frac{1}{\sigma}\frac{\partial \sigma}{\partial T} + \frac{(1-3\sigma+5\sigma^2)s}{\sigma(1-2\sigma)}\right] \times (X_xY_y + X_xZ_z + Y_yZ_z) + \frac{1}{2E}\left[-\frac{1}{E}\frac{\partial E}{\partial T} + \frac{(1-6\sigma+2\sigma^2)s}{1-2\sigma}\right] \times (X_x^2 + Y_y^2 + Z_z^2)\right\}, \qquad (9)$$

where $J = 4.185 \times 10^7$ ergs/cal. mechanical equivalent of heat, s = the linear coefficient of thermal expansion, X_x = direct stress in the x direction, Y_y = direct stress in the y direction, Z_z = direct stress in the z direction, σ = Poisson's ratio, E = Young's modulus, and T = Kelvin temperature.

Trial calculations were made with the following assumed values: $\sigma = 0.3$ for steel and annealed Invar, $E = 2.01 \times 10^{12}$ dynes/cm^2 for steel, $E = 1.44 \times 10^{12}$ dynes/cm^2 for annealed Invar,[16] $s = 13.22 \times 10^{-6}$ (deg. C)$^{-1}$ for steel, and $s = 1.7 \times 10^{-6}$ (deg. C)$^{-1}$ for annealed Invar.[17] $(1/E)(\partial E/\partial T) = -24 \times 10^{-5}$ (deg. C)$^{-1}$ for steel,[18] $(1/E)(\partial E/\partial T) = 48.2 \times 10^{-5}$ (deg. C)$^{-1}$ for annealed Invar,[16,18] $(1/\sigma)(\partial\sigma/\partial T) = 1.3 \times 10^{-5}$ (deg. C)$^{-1}$ for steel,[18] $(1/\sigma)(\partial\sigma/\partial T) = 35.1 \times 10^{-5}$ (deg. C)$^{-1}$ for annealed Invar,[19] $X_x = Y_y = 27.6 \times 10^{-8}$ in dynes/cm^2 (40,000 lb./in.^{2}), $Z_z = 0$, and $T = 273$°K.

For a thin, spherical, annealed Invar shell, Eq. (9), with the above values, reduces to

$$\Delta q = \pm 5.1 \times 10^{-13} pr^3 T - 2.3 \times 10^{-23} \times (p^2 r^4 T/f), \qquad (10)$$

where p is the increase in internal pressure, f the wall thickness, and r the mean radius, c.g.s. units.

It is found that the linear term is much larger than the sum of the quadratic terms in Eq. (9), i.e., 120 times for steel, four times for Invar. At higher stresses this ratio decreases. The calculation assumes that Hooke's law holds. Investigation shows that the change in Eq. (9), made by assuming the elastic constants to be linear functions of the strain is, for most metals, of the order of magnitude of the quadratic terms in s. The terms in s are greatly reduced for Invar.

The discrepancies due to elastic hysteresis effects are not calculated. These were studied experimentally on the actual shells used.

Where the vessel consists of two concentric shells, the expansion taking place from the inner shell to the annular space between, each shell in turn confines the gas. As the gas leaves the inner shell the stress change there is one of decrease; whereas it is an increase for the outer shell. It is

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[14] H. D. Baker, Doctor's Thesis, Library of the University of Wisconsin, Madison, Wisconsin, 1938.

[15] W. T. Thomson (Lord Kelvin), Math. Phys. Pap. **1**, 297 (1882).

[16] G. K. Burgess, Circ. Bur. Stand. No. 58, "Invar and related Nickel steels" (June 22, 1923), p. 90.

[17] See reference 17, p. 59.

[18] G. H. Keulegan and M. R. Houseman, Bur. Stand. J. Research **10**, 289 (1933).

[19] P. Chevenard, Traveaux et Memoires de Bur. Int. des Poid et Mes. **17**, 51 (1927), Fig. 21.

easily shown that for shells whose walls are "thin" the total linear effect in Eq. (9) is equal in magnitude for both shells. The two effects should then almost exactly cancel one another provided the shells are made from the same sample of material and similarly annealed.

It is found that the ratio of the magnitude of this first-order term to the energy magnitude of the quantity dealt with in the Joule effect is independent of the actual size of vessel. It is smaller, however, at lower working temperatures and larger expansion ratios. Large pressure drops are to be achieved by using the highest practical pressure in the inner chamber and the largest feasible expansion ratio. For Invar the magnitude of this linear term is minimized. It is advisable to take advantage of these means of reducing the relative and absolute magnitude of the linear term. This tends to lessen the error due to deviation from exact cancellation which may result from imperfect similarity of the two shells.

The magnitude of the quadratic terms is small. It may be computed as a correction with sufficient accuracy by using the second term of Eq. (10).

IV. THE APPARATUS

The preceding principles were applied in the apparatus shown in Figs. 1 and 2. The shells, $2\frac{1}{2}''$ diam., 0.021″ wall, and $6\frac{3}{4}''$ diam., 0.009″ wall, respectively, were made from the same sample of sheet Invar spun into hemispheres. This material possessed, besides a very small coefficient of thermal expansion S, the other required properties. It did not, however, possess the desired high thermal conductivity. To avoid oxidation the annealing, intermediate between spinning operations, was done in an atmosphere of hydrogen. The walls were reduced to uniform thickness with carborundum cloth.

A lapped seam, only slightly greater than the wall thickness and evidently of at least equal strength, was made by grinding male and female tapers to a glove fit and silver soldering. During soldering the spherical shells were filled with hydrogen; the exterior was protected by molten *fluxine*. The exterior surface of the outer shell was polished.

Before assembly of the outer shell about it, the inner shell was stretched 100 times at its yield point (100 atmos.). Volume-pressure plots measured the hysteresis effect as 0.17 joule per cycle. For air, the resulting error would not exceed 0.04 percent. Both shells were seasoned three years at 75°F.

The expansion valve between the inner and outer chambers consisted of a brass disk lapped smooth and flat carried on an airtight flexible diaphragm. A No. 3–48 screw pressed this disk against an equally flat Invar valve seat. On repeated closings the surfaces shaped themselves to mate. It has not proved possible to detect leakage past such a valve.

The inner shell had a heat capacity about three times that of the air it confined at its elastic limit; while the total heat capacity of both shells, including the valve mechanism, was only about fifteen times that of the air used in an experiment.

Six 0.005″ diam. steel piano wires with turnbuckles trussed the shells in place. The inner chamber was supplied through a 0.009″ inside diam., 0.003″ wall tube, while the outer chamber emptied through a 0.025″ inside diam., 0.005″ wall tube, both of stainless steel.

Valves in the inlet and outlet lines, necessarily without cavities, which would be parts of the two chambers, were of the same style as the expansion valve. Because these are outside the vessel their construction could be more rugged. The high pressure valve had a perforated diaphragm and packed stem, not entirely satisfactory. The diaphragm should have been airtight and adequately strong.

It was arranged for air from a storage cylinder to be filtered through a wad of oily cotton and then passed to the inner chamber through a tube cooled by liquid air. This was assumed to remove dust and condensable material. A two-liter ballast tank immersed in the main bath served to stabilize pressure as initial equilibrium was approached in the inner chamber. Pressure was measured by a Bourdon gauge with 1 mm dial graduations representing lb./in.^{2}. The usual gear drive had been replaced by a continuous metal belt, eliminating the periodic errors common in such gauges. This gauge was calibrated on an American Gauge Tester Type 1300, and on a Crosby Steam and Valve Company tester.

The central mounting plate, Fig. 2, carried all

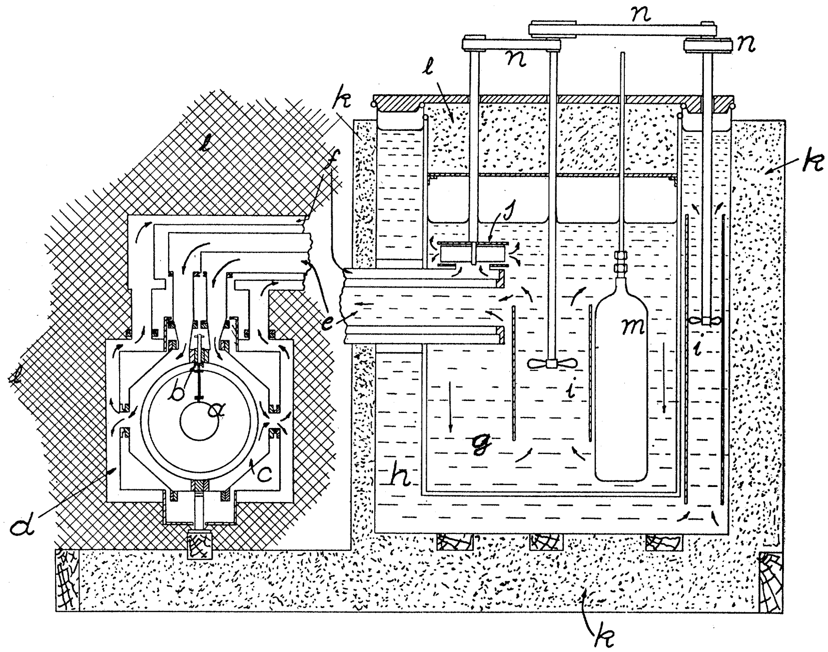

FIG. 3. Jacket and bath assembly. *a*—vessel; *b*—forked valve stem; *c*—vacuum jacket; *d*—outer jacket; *e*—flow to jacket; *f*—return flow; *g*—main bath; *h*—outer bath; *i*—propeller tubes; *j*—centrifugal circulating pump; *k*—ground cork; *l*—loose cotton; *m*—gas ballast tank; *n*—drive belts.

elements, mechanical, pneumatic, and electrical, running to the shells. The shells could thus be completely installed before the jacket was assembled about them. A stem running through this plate carried a fork to operate the expansion valve. A flat ground monel shoulder on this stem pressed against a flat ground base on the brass mounting plate. Ordinary stopcock grease proved to be an adequate vacuum seal.

The jacket was spherical, double-layered, and fed by circulation maintained from a ten-gallon, constant temperature bath. Complexity of function prevented its immersion within the bath, Fig. 3. Its inner surface was silver plated and polished. To prevent an uncontrolled change in temperature along the pipe line, this duct, $2\frac{1}{2}''$ diam., was surrounded by, but insulated from, the return flow. To avoid temperature disturbance due to turbulence, the pump, of special centrifugal design, was located at the end of the return flow.

The bath was arranged for electrical heat input along the outer surface through which heat was also removed, across the air gap to an outer ice bath. The heater was equipped with a toluene bulb and Gowy regulator.[20] In the present work ice was used in the inner bath also. An ordinary propeller tube stirred each bath.

The space between the outer shell and jacket was arranged to be evacuated to about 10^{-6} mm mercury. The present preliminary work was, however, done at atmospheric pressure.

A thermopile measured the mean difference between the jacket and the outer shell temperatures. This contained 24 series connected junctions of manganin and constantan wire, No. 38 B & S gauge, distributed along two vertical great circles. These were in thermal contact with, but electrically insulated from, the outer shell. The other set of junctions was immersed in the jacket flow. The actual temperature of the jacket fluid was measured relatively to an ice point by a 12 junction thermopile of the same materials.

The metals, manganin and constantan, were chosen for their high mechanical strength, their low thermal conductivity, their high thermoelectric power, and their low temperature coefficient of resistance. A galvanometer was chosen

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[20] Gowy, J. de Phys. **6**, 479 (1897).

of such sensitivity as to keep deflections on a 90 cm scale.

Unavoidably cramped conditions made insulation, adequate to resist dampness, difficult to achieve. The high humidity prevailing during the present set of readings gave rise to small, steadily drifting e.m.f.'s, probably electrolytic, and resulted in the largest error to which this work was subject.

A 6500-ohm manganin wire heater was symmetrically mounted within the vessel. The wiring was such that it was possible (see Fig. 4) to measure the resistance of this heater and the potential across its terminals without dismounting anything. The heater leads, while of negligible thermal path, have resistance small in comparison to heater resistance. The heater was used to measure the emission constant *e*.

All resistances (Fig. 4) and the standard cell were carefully compared with certified units. The volume of the chambers was measured by weighing against certified weights when filled with distilled water at controlled temperature. The elastic constant of the inner shell was measured. The heat capacity of both shells was found to be 0.125 cal./g deg. C.[21]

V. PROCEDURE IN A MEASUREMENT

The thermostat was set into operation and the bath circulation established. Careful tests for leaks were made. The resistance of the heater was measured. When the reading of the galvanometer in the jacket-vessel thermopile circuit became steady, it was noted, and a current of a few milliamperes started in the heater. When the galvanometer reading again became steady, it was noted again along with the current through, and the potential difference across, the heater. Then the heater current was stopped. The indicated shift in the galvanometer reading measured the rise in outer shell temperature above the jacket necessary to dissipate the steady electrical energy input. The ratio of heat input to the galvanometer deflection gives the emission constant *e*.

The heater was then shut off, the ballast tank filled to the chosen pressure and put in communication with the inner chamber. After a sufficient quantity of purified air had been passed through both chambers, the expansion valve was closed, the outer chamber remaining open to the atmosphere. When thermal and pressure equilibrium had been reached, the barometer and the Bourdon gauge were both read. The temperature of the jacket was also read. Both valves leading to the vessel were closed, the expansion valve was opened, and readings begun simultaneously on the galvanometer and on a clock. When (usually after about 90 minutes) the galvanometer reading showed the outer shell to be at jacket temperature, readings were stopped. It was assumed that thermal equilibrium within the outer shell had also been reached at this time. The jacket temperature was then read once more, and another determination of the emission constant made. The whole procedure required about 10 hours.

VI. REDUCTION OF DATA

The galvanometer readings were plotted against time. The area under the curve was measured with a planimeter and multiplied by the emission constant *e*. This product gave the

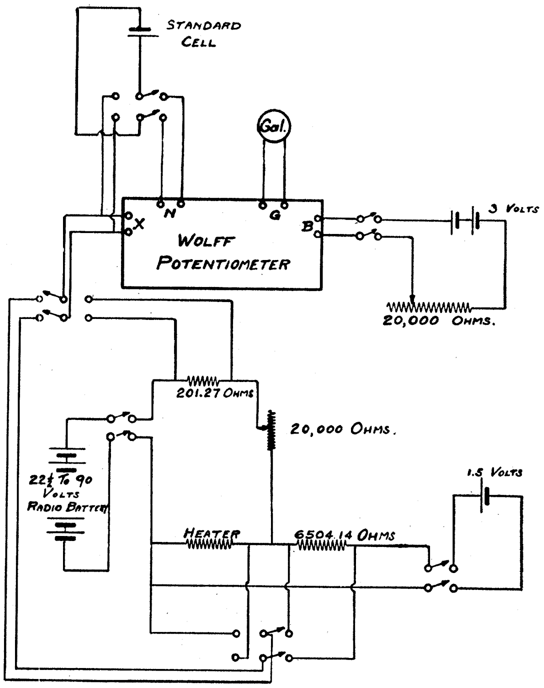

FIG. 4. Diagram of heater circuit.

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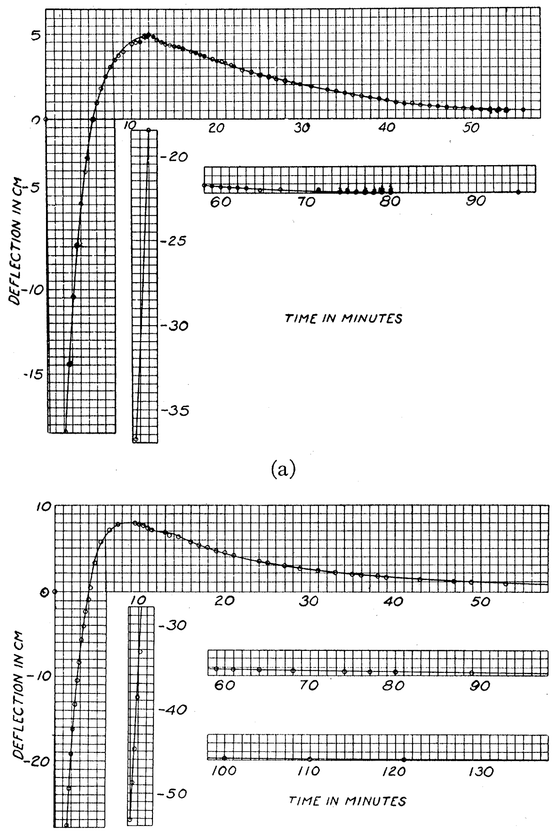
[21] International Nickel Company.



(a)

(b)

FIG. 5. Readings taken during first and fourth runs. Times in minutes from instant expansion valve is opened are plotted horizontally. Deflections in centimeters on galvanometer in thermocouple circuit are plotted vertically. Positive deflections correspond to vessel temperatures below jacket temperature; negative, above. (a) Data for the first run. (b) Data for the fourth run.

total heat transferred from the jacket to the system composed of gas and two shells.

The jacket temperature readings at the two equilibrium situations were taken to be the vessel temperatures, respectively. The heat necessary to restore the system to its initial temperature was computed by multiplying this temperature shift by the heat capacity of the shells and contained air.

Estimate of thermoelastic heat absorbed by the shells was based on Eq. (10). It was found that the magnitude of the linear term was only about 1.0 to 2.0 percent of the magnitude of energy involved in the Joule effects. The inner and outer shells were thin, made from the same sample of material, heat treated and aged in just the same way, and designed to achieve very nearly homogeneous stress in each case. Hence it was regarded a legitimate conclusion that this linear effect would cancel in the two vessels to within a very small fraction of its own magnitude. The resulting error is regarded as negligible in the present experiment.

The quadratic effect, which does not cancel, was computed as a small correction.

The amount of work done by the inner shell on the air was taken to be one-half the pressure drop times the dilatation, and similarly with the outer shell. The work done by the outer shell on the atmosphere was taken to be the pressure times the dilatation of the outer shell. The measured values of the dilatations of the inner shell were used. The dilatations of the outer shell were computed from those of the inner shell by the formula,

$$\Delta V_2=(r_2^4/r_1^4)\cdot(f_1/f_2)\cdot(P_3-P_0)/(P_1-P_2)\Delta V_1, \quad (11)$$

where

ΔV_1 = dilatation of the inner shell under pressure (P_1-P_2), Fig. 1.

ΔV_2 = dilatation of the outer shell under pressure (P_3-P_0).

Upon opening the expansion valve, n_1 moles originally in the inner chamber experience a drop in pressure, P_1-P_3, while the n_2 moles of the gas originally in the outer chamber experience a rise in pressure, P_3-P_2. The average value of λ' over the pressure range was assumed to be given by

$$\lambda'=\left(\frac{\partial u}{\partial P}\right)_T=\frac{\Delta U}{n_1(P_3-P_1)+n_2(P_3-P_2)}. \quad (12)$$

ΔU is the corrected value of the energy required to maintain constant temperature on expansion. Thus,

$$\Delta U=e\int_{t_1}^{t_2}\Delta T dt+W(\text{elastic})+Q(\text{to restore initial temp.})+Q(\text{thermoelastic}). \quad (13)$$

The effective molecular weight of air was taken to be 29.

VII. RESULTS

In the present work this sequence was repeated four times. The second run was invalidated by evidence of leakage in the valve packing while closing just before expansion, the third by evidence of drifting spurious e.m.f.'s in the thermopile. During the first and fourth runs the behavior of the apparatus appeared good in all respects. The data taken are shown plotted in Figs. 5 (a) and (b). Results are detailed in Table I.

Comparison figures are given in Table II.

VIII. CONCLUSION

The values found for λ', while probably no more precise than those previously obtained by other means, checked sufficiently well with these to establish the soundness of the present method. The errors were indicated not as fundamentally inherent in the method, but rather as common types—i.e., electrical insulation and air leaks, readily eliminated by standard methods. Other refinements are obvious, such as: thermostating the bath above room temperature to prevent moisture condensation disturbing both the jacket temperature and the electrical insulation; evacuating the space around the vessel, evacuating the outer chamber before expansion; using the highest pressure the vessel is capable of; and using a piston gauge to measure this pressure.

TABLE I. Details of results.

Quantity	Run 1	Run 4	Units
Miscellaneous			
Area under curves Fig. 5(a) and 5(b)	41.4	138.6	cm min.
Emission constant e	0.131	0.174	cal. min.$^{-1}$ cm^{-1}
Initial pressure, inner chamber	28.26	55.40	atmos.
Ditto, outer chamber	0.97	0.97	atmos.
Final pressure	2.40	3.78	atmos.
Dilatation of inner shell	0.144	0.294	cm^3
Ditto, outer	0.932	1.884	cm^3
Initial temperature	0.057	0.056	deg. C
Ditto, final	0.059	0.063	deg. C
Thermal capacity of vessel	37.00	37.00	cal. (deg. C)$^{-1}$
Ditto, contained air	1.33	2.11	cal. (deg. C)$^{-1}$
Energy Quantities			
Heat absorbed from surroundings	5.423	24.116	cal.
Work performed by the inner shell on the air during expansion	0.048	0.194	cal.
Ditto, outer shell	−0.016	−0.064	cal.
Work performed on the vessel by the atmosphere	−0.022	−0.044	cal.
Net heat liberated by the thermoelastic effect [second term, Eq. (10)]	0.012	0.048	cal.
Heat to restore initial temperature of vessel	−0.074	−0.259	cal.
Ditto, contained air	−0.003	−0.015	cal.
Total	5.368	23.976	cal.
Results			
Energy attributed to the Joule effect, ΔU by Eq. (13)	5.368	23.976	cal.
Quantity of air initially in inner chamber, n_1	0.1676	0.3253	moles
Ditto, outer, n_2	0.1038	0.1042	moles
Total air	0.2714	0.4295	moles
Pressure drop, experienced by n_1	25.86	51.62	atmos.
Ditto, rise, n_2	1.43	2.81	atmos.
λ' computed by Eq. (12) with above data	−5.367	−6.082	joules mole^{-1} atmos.$^{-1}$

TABLE II. Comparisons with other investigations.

λ' for air in joules mole^{-1} atmos.$^{-1}$	Temperature deg. C	Pressure range atmos.	Kind of data	Reference
−6.495	0.0	1.0	Measurements of Joule-Thomson coeff.	[a]
−6.453	0.0	20.0	Measurements of Joule-Thomson coeff.	[a]
−6.345	0.0	60.0	Measurements of Joule-Thomson coeff.	[a]
−5.82	28.0	0 to 40	P.V.T. measurements	[b]
−6.08	28.0	0 to 40	Calorimetric measurements	[b]
−5.367	0.06	2.4 to 28.3	Calorimetric measurements	Present work
−6.082	0.06	3.8 to 55.4	Calorimetric measurements	Present work

[a] J. R. Roebuck, Proc. Am. Acad. **64**, 334 (1930).
[b] See reference 9 in text.

With these improvements perfected, there appears no obstacle to measuring λ' and λ reliably to within one-tenth of one percent. For helium and hydrogen the error would probably be greater, for carbon dioxide, less.

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[22] J. R. Roebuck, Proc. Am. Acad. **64**, 312 (1930).