A DETERMINATION OF THE RATIO OF THE SPECIFIC HEATS AND THE SPECIFIC HEAT AT CONSTANT PRESSURE OF AIR AND CARBON DIOXIDE.

By H. W. Moody.

I. Introduction.

As a result of some work done by Millikan, Chapman, and Moody (1) in investigating the temperature changes in a Wilson fog chamber and a later extension by Chapman (2) of the method to the observation of the temperatures produced, upon expansion, in chambers filled with saturated vapors, it became evident that the thermocouple was exceedingly well adapted to the measurement of instantaneous temperatures. The smallness of the wires now obtainable and, hence, the smallness of the heat capacities and heat conductivities of the leads give it decided advantages over other schemes for the direct measurement of the temperature changes produced by adiabatic expansions.

A marked advance in the accuracy of the determination of γ was made by Lummer and Pringsheim (3) when they first proposed to make this determination depend upon a direct temperature measurement. In their work, they made use of a platinum bolometer strip. Later, Makower (4) experimented according to the same method, save that he employed a platinum thermometer for the measurement of the temperature changes. In view of the fact that there is so little agreement in the values of γ found by earlier observers, it has seemed worth while to make a new determination, using the thermocouple for the detection of the changes in temperature.

II. Experimental Work.

Method of Experiment.—The method used rests directly upon the law of adiabatic expansion of the gas considered. If p and θ are taken as variables, we have, for the case of a perfect gas expanding adiabatically, from an initial pressure, p_1, to a final pressure, p_2,

$$(1) \qquad \left(\frac{\theta_1}{\theta_2}\right)^{\gamma} = \left(\frac{p_1}{p_2}\right)^{\gamma-1},$$

wherein θ_1 and θ_2 are the absolute temperatures before and after expansion and γ is the ratio of the specific heats by constant pressure and by constant volume. Upon the solution of equation (1) for γ, we obtain

$$\gamma = \frac{\log \frac{p_1}{p_2}}{\log \frac{p_1}{p_2} - \log \frac{\theta_1}{\theta_2}}. \tag{2}$$

Hence, to compute γ, we need to be able to measure p_1, p_2, θ_1, and θ_2. The first three of these quantities present little difficulty, since each can be measured with sufficient leisure to permit of careful measurement. To get θ_2, we need at our command such a device as will give us the instantaneous value of the temperature assumed by the gas in the adiabatic expansion, since this temperature changes rapidly from heat flowing in from the walls of the surrounding vessel.

Arrangement of Apparatus.—The arrangement of the apparatus and its operation are shown in Fig. 1. To hold the quantity of gas to be experimented upon, a large glass carboy, *C*, of about 60 liters capacity was employed. In this were three openings, one of which, O_1, communicated, by the way of the drying system, *D*, and the manometers, M_1, M_2, with the compression pump or other source of gas. For air, the drying system consisted of a number of bottles of sulphuric acid in series with several long tubes filled with granular calcium chloride. For carbon dioxide, the calcium chloride was replaced by tubes of phosphorus pentoxide, which was renewed whenever it showed any signs of moisture.

The second opening, O_2, was used for the introduction of the thermocouple into the carboy. The thermocouple, made of 1 mil copper and constantan wire, formed a part of one circuit in a potentiometer system. These wires, in order that the couple, c_1, might be placed approximately at the center of the body of gas, were led in through glass tubes. These latter were bent, just inside the walls of the vessel, so that they were spread, leaving a length of 20 or 25 cm. of bare wire with one junction in the middle. The inner end of these tubes were sealed with heavy wax in order to shut off communication with the outside. The second junction of the couple was enclosed in a small capsule, c_2, just outside the carboy, and so was always at the temperature of the bath, *B*, in which the carboy itself was placed. The lead wires continued from these capsules through glass tubes to the surface of the water bath, thence to the potentiometer system.

The other opening, O_3, was the avenue of outflow for the gas at expansion. It was closed by a large valve which, when opened, formed a vent of 8 sq. cm. and so made possible a very sudden expansion since this valve could be operated rapidly.

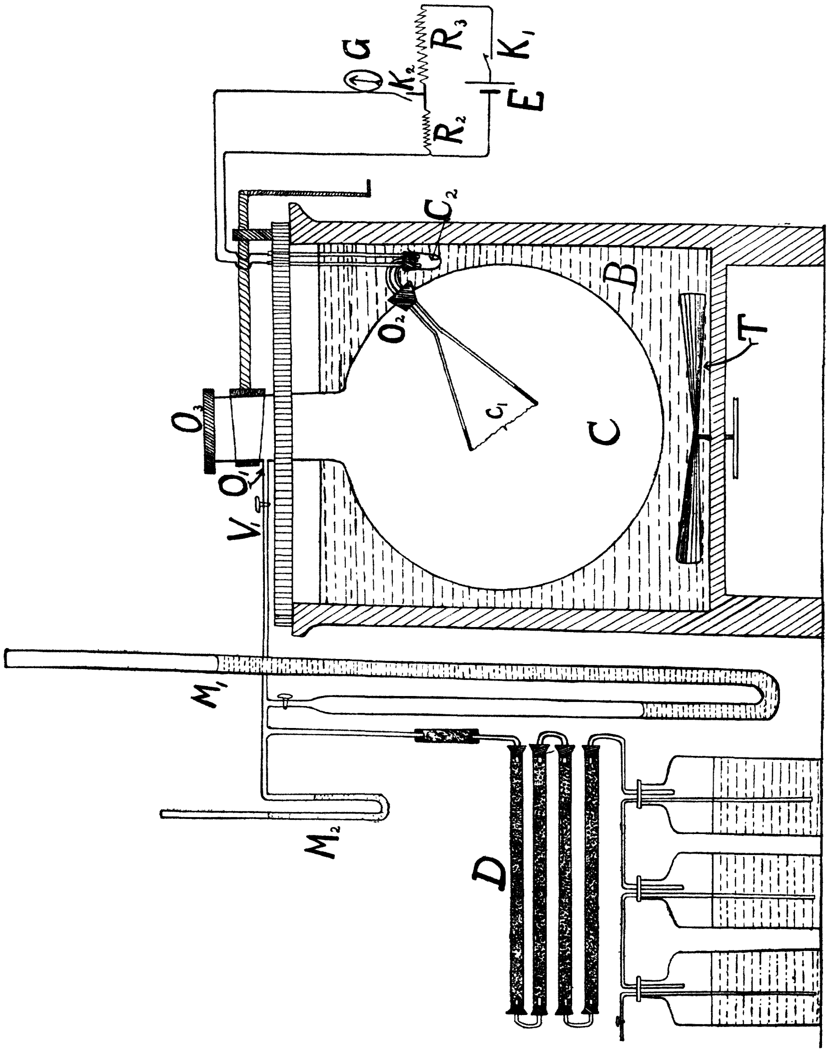

Fig. 1.

The carboy was supported in the center of a large water bath. The stirring device consisted in a large turbine fan, *T*, motor driven and placed in the center of the bottom of the tank. That the circulation of the water was excellent was evidenced by the movement of particles in the water. To test the uniformity of temperature throughout the tank, a sensitive thermometer was carried about, readings being taken at many points, and in no place was a variation noticed in excess of a few thousandths of a degree, an amount which could be accounted for by the effect of the variation of pressure on the thermometer bulb. That the temperature of the bath might be controlled, it was equipped with a mercury thermostat, not shown in the figure; the mercury tube being 2.5 cm. in diameter and 150 cm. in length and placed so that it extended from top to bottom and across the bottom of the tank. The thermostat system consisted in the mercury tube, in which the mercury, rising with the rise in temperature of the bath, bridged a circuit, I., through a battery, or other source of current, and an electromagnet. This latter, in turn, lifted an iron core to which was attached a key in circuit II., containing a set of incandescent lamps. Thus was comprised a system by means of which the temperature of the bath could be maintained constant to .01° for any length of time.

Measurement of Pressures.—In the measurement of pressure, the final pressure, p_2, was that of the atmosphere, registered upon a Schneider standard mercury barometer. This instrument had but recently been compared with the standard barometer of the U. S. Weather Bureau service, kept in the Federal Building at Chicago. During the experiments, it was kept in the room, near the manometers, and its reading taken immediately after each observation. Since this reading could be made with an accuracy of .1 mm. mercury, its influence could not introduce an error of more than .01 of 1 per cent. in the final result.

The initial pressure, p_1, was equal to that of the barometer reading plus an excess pressure which was registered upon a "transformer" oil manometer, M_1, and, as a check, upon a mercury manometer, M_2. The readings upon this oil manometer were made by means of a reading glass or microscope, held perpendicularly to the tube. Since the manometer had an internal diameter of 1 cm., a fair portion of the surface was horizontal so that by the above scheme the excess pressure could be measured to .1 mm. of oil. This made the possible error in p_1, expressed in mercury, not more than .06 of 1 per cent. at the lower pressures and .03 of 1 per cent. at the higher pressures.

For the conversion of the manometer readings in oil into terms of mercury, a temperature-density curve for the oil was plotted over a range of 10°, from 16° C. to 26° C. The mercury temperature-density curve was plotted from data taken from Castell-Evans Physico-Chemical Tables (5).

The valve, V_1, was closed immediately before an expansion and the reading taken immediately after, if the observation was satisfactory. Then the adjusting of pressures for a new trial was done, approximately, by the aid of a mercury manometer, M_2, so that the oil was not allowed to move up and down the tube for more than a few cms. This avoided errors in subsequent readings due to the gradual running down of oil that had adhered to the walls of the manometer tube.

Measurement of Temperature.—The temperature, θ_1, was that of the constant temperature bath in which the carboy was submerged. This was observed by the reading of a Baudin standard mercury thermometer. The readings upon the standard were made by the aid of a microscope, having a comparison scale in the eye piece. In this way, θ_1 was obtainable to .01° C., with interpolation to .001° possible. The error in γ introduced thus was not more than .01 to 1 per cent.

To obtain θ_2, the procedure is as follows: The thermal electromotive force developed in the couple circuit by a change in temperature incident to an expansion was evaluated in terms of the E.M.F. of a storage cell by means of a potentiometer made up from resistance boxes. The boxes had been standardized at the Bureau of Standards, Washington, D. C., and afforded a total of 120,000 ohms in the battery circuit and read by .5 ohm up, in the couple circuit, so that the thermal E.M.F. was known in microvolts. Immediately after each observation, the E.M.F. of the storage cell was evaluated by comparison with a Weston standard cell, which had a certificate from the Physikalische Technische Reichsanstalt.

Having, now, the value of the fall in temperature in terms of the thermal E.M.F., it remained to determine, by direct observation, the difference of temperature necessary to develop the same E.M.F. This was done by removing the couple from the carboy and placing the constant temperature junction in a bath at 25° C. and the second junction in another bath at a lower temperature. By this means, a temperature E.M.F. curve was plotted. For succeeding observations, it was only necessary to measure the thermal E.M.F. and, at once, θ_2 could be read from this calibration curve. This curve was plotted to such a scale that θ_2 could be read directly to .01° C. and, by interpolation, to .001° C. The error introduced in γ, thus, was not more than .01 of 1 per cent.

Systematic Errors.—Since some heat inflow will occur, the conditions of the experiment do not furnish a perfectly adiabatic expansion. The heat brought in by gaseous conduction is certainly negligible. That due to convection is small since the temperature is uniform on all sides and, so, there is little cause for circulation, save for that which is due to the surging and swirls arising at the sides of the outlet valve. Of these more will be said. Since we are dealing with wires of only .000009 sq. cm. cross section, it is seen that the heat capacity is very small and, likewise, the amount of heat which would actually be brought in by metallic conduction.

A greater source of error lies in the fact of internal radiation. The amount of this is a function of the emission coefficient of the glass and of the absorption coefficients of the copper and constantan wires. An experimental attempt at evaluating this was made. A determination of γ was made for a certain pressure with a bright couple and, then, again, after the couple had been blackened with a thin coat of "optical black." In the latter case, a smaller value of γ was obtained, owing to a higher coefficient of absorption and, hence, an apparently less fall in temperature registered. Then other couples were made, one bright and one blackened, and the two were placed in a vacuum tube. The ratio of the absorption coefficients was determined by comparing the times required for each, in turn, to acquire the same temperature when exposed to the same source of radiant energy. This ratio, as a mean of 12 observations, ranging from 9.2 to 10.3, was found to be 10. From this, it follows that we will make a close approximation to the correct value of γ, if we add to the value obtained with the bright couple one ninth of the difference between the values obtained with the bright and blackened couples. That this correction might not be a function of a particular couple, the difference was obtained on several couples, as shown in the following table:

TABLE I.

Pressure.	Bright Couple.	Blackened Couple.	Difference.
12.540	1.3980	1.3800	.0180
43.531	1.3932	1.3757	.0175
12.501	1.3962	1.3775	.0187
43.60	1.3926	1.3748	.0178
		Mean difference......	.0180

Hence the radiation correction is + .0020.

It was found advantageous, in order to avoid errors due to swirling eddies in the gas, following an expansion, to close the potentiometer circuit and to open the galvanometer damping key after an interval of two or three seconds. During this time, more or less heat had flowed in, according to the fall in temperature. To eliminate this, γ was measured at different levels of excess pressures and a pressure-γ curve plotted.


Air
Curve of Means
Curve of Points
T=2.
Pressure excess in mm. Hg.
γ
1.380
1.390
1.400
1.380
1.390
1.400
120
110
100
90
80
70
60
50
40
30
20
10
0

Fig. 3.

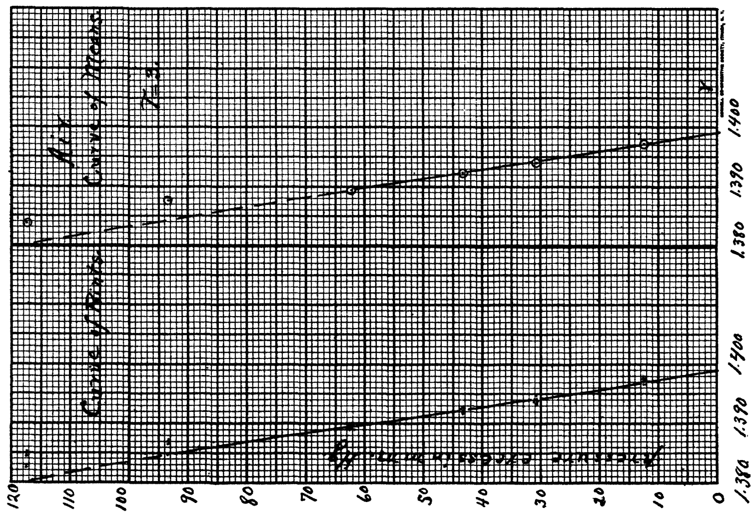
Air
Curve of Means
Curve of Points
T=3.
Pressure excess in mm. Hg.
γ
1.380
1.390
1.400
1.380
1.390
1.400
120
110
100
90
80
70
60
50
40
30
20
10
0

Fig. 2.

TABLE II.

Data on γ for Air, for $r = 3$.

p_2	dp	p_1	θ_1	θ_2	γ	D
751.228	12.470	763.698	298.006	296.614	1.3966	−.0006
748.113	12.375	760.448	298.007	296.620	1.3973	+.0001
742.005	12.323	754.328	298.007	296.617	1.3965	−.0007
748.365	12.489	760.834	298.007	296.607	1.3976	+.0004
753.121	12.560	765.681	298.006	296.608	1.3972	.0000
741.027	12.493	753.520	298.008	296.593	1.3980	+.0008
753.058	12.322	765.386	298.007	296.633	1.3972	.0000
746.795	30.868	777.663	298.007	294.617	1.3936	−.0003
750.293	31.032	781.325	298.007	294.612	1.3941	+.0002
749.113	30.893	780.006	298.007	294.617	1.3949	+.0010
753.121	30.996	784.117	298.006	294.626	1.3943	+.0004
754.227	30.942	785.219	298.006	294.646	1.3932	−.0007
740.648	31.002	771.650	298.008	294.575	1.3938	−.0001
754.503	30.836	785.339	298.007	294.652	1.3940	+.0001
744.515	43.520	788.035	298.037	293.307	1.3919	−.0005
751.230	43.436	794.666	298.006	293.316	1.3929	+.0005
745.475	43.372	788.847	298.017	293.317	1.3917	−.0007
750.070	43.500	793.570	298.007	293.305	1.3929	+.0005
734.291	43.501	777.792	298.009	296.214	1.3924	.0000
750.953	43.469	794.422	298.007	293.317	1.3925	+.0001
753.122	43.341	796.463	298.006	293.341	1.3927	+.0003
740.828	43.434	786.262	298.008	293.270	1.3916	−.0008
755.138	43.277	798.415	298.007	293.357	1.3931	+.0007
748.019	62.147	810.166	298.007	291.407	1.3900	+.0005
751.152	62.097	813.249	298.006	291.448	1.3891	−.0004
749.857	62.110	811.967	298.007	291.427	1.3899	+.0004
752.001	62.086	814.087	298.007	291.452	1.3897	+.0002
753.122	61.999	815.121	298.006	291.476	1.3890	−.0005
753.883	62.062	815.945	298.006	291.471	1.3894	−.0001
740.963	62.064	803.027	298.007	291.357	1.3894	−.0001
740.864	62.066	802.930	298.008	291.363	1.3894	−.0001
755.437	62.113	817.433	298.007	291.487	1.3897	+.0002
745.597	93.339	838.936	298.002	288.354	1.3870	+.0004
749.435	93.377	842.812	298.007	288.407	1.3866	.0000
752.001	93.361	845.362	298.007	288.467	1.3849	−.0017
753.221	93.246	846.467	298.006	288.461	1.3868	+.0002
755.763	93.240	849.003	298.007	288.477	1.3876	+.0010
748.679	117.494	866.173	298.017	286.197	1.3843	+.0006
748.350	117.597	865.947	298.007	286.217	1.3823	−.0014
750.307	117.539	867.846	298.007	286.267	1.3822	−.0015
740.704	117.496	858.200	298.008	286.058	1.3849	+.0012
755.813	117.359	873.172	298.007	286.287	1.3852	+.0015

TABLE III.

Data on γ for Air, for $\tau = 2$.

p_2	dp	p_1	θ_1	θ_2	γ	D
751.290	12.430	763.720	298.006	296.616	1.3980	+.0002
748.760	12.440	761.200	298.006	296.614	1.3971	−.0007
753.058	12.322	765.380	298.007	296.632	1.3984	+.0006
751.290	30.981	782.271	298.006	294.616	1.3949	−.0001
748.660	30.942	779.602	298.007	294.607	1.3952	+.0002
754.503	30.836	783.339	298.007	294.647	1.3949	−.0001
751.455	43.551	795.006	298.006	293.306	1.3930	.0000
747.464	43.298	790.762	298.007	293.312	1.3927	−.0003
755.138	43.264	798.402	298.007	293.357	1.3933	+.0003
751.790	62.157	813.947	298.006	291.446	1.3896	−.0001
747.164	61.887	808.051	298.007	291.437	1.3891	−.0006
755.437	61.871	817.308	298.007	291.487	1.3908	+.0009
752.387	93.222	845.609	298.006	288.476	1.3882	+.0007
747.153	93.269	840.422	298.007	288.367	1.3865	−.0010
755.813	93.187	849.000	298.007	288.477	1.3880	+.0005
752.622	117.470	870.092	298.006	286.256	1.3838	−.0013
747.129	117.375	864.504	298.007	286.137	1.3860	+.0009
755.813	117.359	873.172	298.007	286.272	1.3856	+.0004

Having measured γ for excess pressures varying from 12 cm. mercury down to 12 mm., a smooth curve, drawn through the plotted points and extended back to the γ axis, gave the value of γ for $dp = 0$, *i. e.*, when the effect on γ, due to the heat inflow was nil.

Results.—In Table II. is given the data on γ, for the case where the interval between the time of expansion and the time of closing the potentiometer circuit, τ, was 3 sec. These are the observations of several complete series, from high to low pressures, arranged in groups, according to the pressure levels. In these tables, D means the variation of that observation from the mean value for that pressure level.

In Fig. 2 are the graphs of these data, where dp is taken as the ordinate and γ plotted as abscissa. Since the variation in γ is far more than that due to the slight differences in pressure level, it was thought worth while, as a check, to plot a curve of means, *i. e.*, for each level, the mean pressure, for that level, was plotted against the mean γ for that level.

Table III. contains, similarly, the data on γ for air, for the trials in which $\tau = 2$. In Fig. 3 are the corresponding graphs.

In Table IV. will be found the data on γ for carbon dioxide, for $\tau = 3$.

Table IV.

Data on γ for Carbon Dioxide, for $\tau = 3$.

p_2	dp	p_1	θ_1	θ_2	γ	D
742.849	12.824	755.673	297.904	296.739	1.2968	+.0002
746.693	12.753	759.446	297.884	296.738	1.2961	−.0005
745.832	12.723	758.555	298.014	296.863	1.2966	.0000
750.213	12.606	762.819	298.034	296.899	1.2967	+.0001
743.674	12.612	756.286	297.944	296.799	1.2969	+.0003
751.052	12.257	763.309	298.004	296.902	1.2967	+.0001
747.103	12.200	759.303	298.004	296.902	1.2965	−.0001
743.299	31.333	774.632	298.074	295.294	1.2934	+.0006
747.172	31.212	778.384	298.014	295.254	1.2942	+.0014
745.398	31.266	776.664	298.014	295.254	1.2927	−.0001
750.858	31.027	781.885	298.014	295.314	1.2913	−.0015
743.574	31.035	774.609	298.014	295.254	1.2931	+.0003
751.253	30.812	782.065	298.004	295.304	1.2926	−.0002
747.103	30.575	777.678	298.004	295.309	1.2928	.0000
743.349	43.692	787.041	298.064	294.259	1.2902	−.0005
747.452	43.642	791.094	298.004	294.219	1.2907	.0000
744.887	43.673	788.560	298.024	294.212	1.2916	+.0009
750.816	43.379	794.195	298.004	294.264	1.2900	−.0007
743.574	43.462	787.036	298.014	294.214	1.2918	+.0011
751.236	43.200	794.436	298.004	294.274	1.2907	.0000
747.191	43.103	790.294	298.004	294.274	1.2899	−.0008
743.374	62.005	805.379	298.014	292.674	1.2886	+.0010
750.836	61.832	812.668	298.004	292.779	1.2878	+.0002
747.079	61.803	808.882	298.004	292.779	1.2868	−.0008
743.349	62.282	805.631	298.064	292.759	1.2873	−.0003
746.920	62.256	809.902	298.004	292.714	1.2881	+.0005
744.558	62.285	806.843	298.044	292.744	1.2875	−.0001
750.816	62.056	812.872	298.004	292.794	1.2873	−.0003
743.349	93.503	836.852	298.064	290.329	1.2852	−.0001
746.741	93.138	839.879	298.014	290.319	1.2862	+.0009
744.558	93.464	838.022	298.044	290.319	1.2854	+.0003
750.134	93.281	843.415	298.004	290.374	1.2841	−.0012
743.062	93.224	836.286	298.014	290.314	1.2850	−.0003
750.836	93.027	843.863	298.004	290.370	1.2855	+.0002
746.967	93.126	840.093	298.004	290.314	1.2862	+.0009
743.049	117.482	860.531	298.054	288.554	1.2831	+.0002
744.628	117.376	862.004	298.014	288.549	1.2842	+.0013
744.567	117.486	862.053	298.044	288.544	1.2838	+.0009
750.134	117.327	867.461	298.004	288.629	1.2820	−.0009
751.048	117.228	868.276	298.004	288.604	1.2826	−.0003
746.967	117.208	864.175	298.004	288.599	1.2820	−.0009

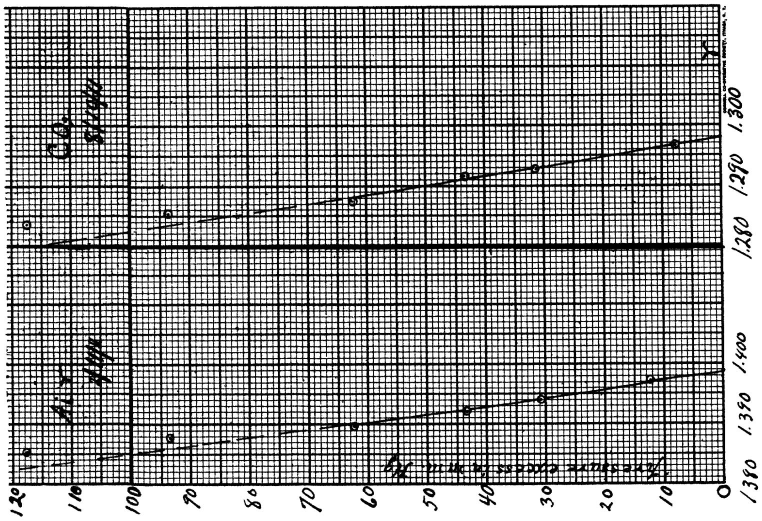
CO2
Air
Pressure excess in mm Hg
γ
120
110
100
90
80
70
60
50
40
30
20
10
0
1.380
1.390
1.400
1.280
1.290
1.300

Fig. 5.

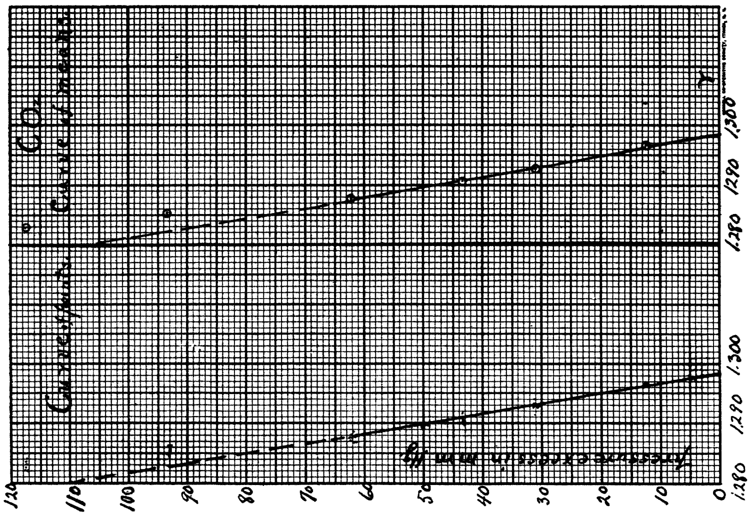
CO2
Corresponds Curve of means.
Pressure excess in mm Hg
γ
120
110
100
90
80
70
60
50
40
30
20
10
0
1.280
1.290
1.300
1.280
1.290
1.300

Fig. 4.

This was the only interval used in the case of carbon dioxide. The notation is the same as for the tables on air. Fig. 4 contains the graphs for these data.

Thinking it would be of interest to some, we have inserted Fig. 5 to show the degree of consistency which was found in most all cases. These curves are the graphs of single complete series, all points of which were determined within three of four hours of each other, so that all conditions could be maintained practically constant throughout the series.

The mean of all determinations, made in the manner described above, gives for air, $\gamma = 1.3991$, and for carbon dioxide, $\gamma = 1.2983$. Whence, upon the addition of the radiation correction, we have for air, at 25° C., 76 cm., $\gamma = 1.4011$ and for carbon dioxide, at the same temperature and pressure, $\gamma = 1.3003$, in which the probable error is ± .0005.

III. A Review of Recent Determinations of γ for Air and Carbon Dioxide.

In order to compare these values with those found by earlier observers and to draw conclusions as to the probable value of γ, for air and carbon dioxide, we may refer to the summary of A. Winkleman (6) and the critical review of M. G. Maneuvrier (7), both of which appeared about 1895. The results there given show such a wide range of variation in values that we can draw no safe conclusion. It is but natural, however, to expect that, with the improved methods and apparatus of the modern laboratory, the more recent determinations of γ should show a closer agreement. In order to see to what extent this expectation has been realized, a brief review of the work done since the time of the above mentioned summaries will be made.

Indirect Methods.—All indirect methods for the determination of γ are based upon the application of the formula for the velocity of sound,

$$V = n\lambda = \sqrt{\frac{p\gamma}{\rho}}. \tag{3}$$

(*a*) *Long Distance Measurements in Free Air.*—To this method there are the following serious objections: (1) The difficulty of making the proper corrections for the effect of humidity, (2) lack of uniform temperature throughout the path, (3) the relatively high intensity required at the source. This latter must die out as the wave recedes from the source and it is probable that the velocity of the wave diminishes with the intensity. By far the most reliable determination made by this method was that of the French Academy (8), in 1822. They found $V_0 = 331.2$ m. per sec., from which $\gamma = 1.3999$.

(*b*) *Hebb's Method.*—In 1905, Hebb (9), by a very ingenious method, suggested by Professor Michelson, eliminated the objections mentioned above as well as those which apply to the measurements made in tubes, viz., the " personal equation "[1] and the effect of the walls.

His measurements were made in the halls of Ryerson Laboratory. He applied the principle of interference by means of a system of parabolic mirrors, having a tuning fork source placed at the focus of one and a telephone receiver at the focus of the other mirror. He found $V_0 = 331.29$, with a probable error of .06 m. from which $\gamma = 1.4003$.

(*c*) *Measurements in Long and Large Tubes.*—The objections to the measurements in free air have also been eliminated by observers using long and large tubes, though they have introduced a new one, viz., the effect of the walls of the tubes. Violle and Vautier (10) made a first determination at Grenoble, in 1885, in a U-shaped conduit, 70 cm. in diameter and about 13 km. in length. In 1895, they made a second determination in another sewer conduit, just constructed, at Argentuiel; this one being a straight conduit, 3 m. in diameter and 3 km. in length. Very careful corrections were made for temperature, pressure and hygrometric conditions. They found $V_0 = 331.15$ m. per sec. with a probable error of 2 or 3 cm. A final correction for the effect of the walls was made by Violle (39), in 1900, and he gives $V_0 = 331.36$ m. per sec., whence $\gamma = 1.4009$.

(*d*) *Measurements in Short Tubes.*—Many observers have employed the interference method of Quincke with varying success. The difficulties with this method may be most easily pointed out under the discussion of the individual works. (1) J. Webster Low (11) found for air, at 10° C., $V = 330.88$, whence $\gamma = 1.3968$. The influence of the " personal equation " is evident here in the fact that he used maxima of tone strength instead of minima. Later, Stevens has corrected Low's value for humidity and effect of the size of the tubes. He gives as the corrected value, $V_0 = 331.4$, from which we get $\gamma = 1.4012$. (2) O. Buckendahl (12) found certain disturbing resonance phenomena, between the entire tube system and the body of gas, whose existence was not easily discoverable. Then, too, errors often entered because of diffusion with the outside air, so that some question holds against his results. He obtained, for carbon dioxide, at 0° C., 76 cm., $\gamma = 1.2990$. (3) E. H. Stevens (13), using this method and making very careful corrections for humidity, size of tubes, etc., found for air, $V_0 = 331.32$, from which $\gamma = 1.4006$. This seems to be the most reliable determination of all the recent ones according

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[1] This expression relates to the error in judgment involved in setting on a maximum or minimum of tone strength.

to this method. (4) R. Fürstenau (14) made some improvements on the method and was able to eliminate diffusion with outside air and the "personal equation" to some extent, still he encountered uncertainties as to the correction for the wave-length because of lack of uniformity in the heating of the tube. He, too, met with certain resonance phenomena in the surrounding tubes. He obtained for carbon dioxide, at 13.5–16.5° C., $\gamma = 1.3008$, and made no measurements on air.

Direct Methods: (*a*) *Assman's Method.*—The mechanical manipulation of this method is simple, but it cannot be considered as a serviceable method because (1) the period (about one half sec.) is so long that the process is not adiabatic and (2) because the volume of the bulbs of gas is too small. The evidence of this is found in the work of (1) Assman (15), himself, who, in 1852, obtained for air, $\gamma = 1.421$ and $\gamma = 1.427$; (2) P. A. Müller (16), who, in 1883, obtained for air, $\gamma = 1.4046$ and for carbon dioxide, at 20° C., $\gamma = 1.2653$; and of B. Hartman (17) who, in 1905, found $\gamma = 1.4137$, as a mean of readings varying from $\gamma = 1.4084$ to $\gamma = 1.4201$. He found for carbon dioxide, $\gamma = 1.3064$, as a mean of values varying from $\gamma = 1.302$ to $\gamma = 1.311$.

(*b*) *The Method of Clement and DesOrmes.*—In this classical method, the determination of γ rests upon the measurement of pressure. The results obtained by experienced observers are exceedingly discordant, varying between 1.302 (Kohlrausch) and 1.42 (Masson). Roentgen's (18) determination has usually been considered the most reliable, but since a number of unsuccessful attempts have been made to duplicate it, some of them in Ryerson Laboratory, under conditions practically identical with those under which Roentgen worked, we are inclined to attach less weight to it than has sometimes been done, and to leave out of consideration all measurements made by the Clement and DesOrmes method.

A slight modification of the above method was made by Maneuvrier and Fournier (19) when they made use of Reech's theorem and they were able to get more consistent results than earlier observers who used the method. Reech's theorem, $\gamma = \partial p_Q / \partial p_\theta$, holds only for infinitesimal changes while, in practice, the observer must work with finite changes and then extrapolate back, graphically, to the limiting values. Again, there must be surging in the body of the gas upon expansion—a fact which introduces large uncertainties into the measurement of the final pressure. These, together with the criticisms which apply to any method depending upon a measurement of pressures (see below) make it seem that their values are not entirely reliable. They obtained for air, at room temperature and atmospheric pressure, $\gamma = 1.3924$ and for carbon dioxide, $\gamma = 1.2993$.

(*c*) *Direct Application of the p-θ Adiabatic Equation.*—This is a remarkably simple and direct method, requiring only some device for the direct observation of the final temperature, θ_2, all other quantities being such that they can be measured with the highest degree of accuracy. This method possesses a great advantage over other direct methods in that it makes the determination of γ rest upon a temperature measurement rather than upon a pressure measurement. A pressure measurement is, at best, a measurement of the mean temperature throughout the vessel at the instant of measurement, while the direct temperature measurement can be made upon a small quantity of gas in the very center of the vessel. By the pressure scheme, the temperature observed is always too high because of the inflow of heat which begins at the instant of expansion, whereas the temperature at the center is not affected until a finite time after the expansion. (1) Lummer and Pringsheim (3) were the first to use the method. They used a platinum bolometer strip to indicate the temperature change by the change in its resistance, this latter being measured by means of a Wheatstone bridge. They obtained for air, at 15° C., 76 cm., $\gamma = 1.4025$ and for carbon dioxide, under the same conditions, $\gamma = 1.2995$. (2) W. Makower (4) used a platinum thermometer to detect the temperature change. While this work was very carefully done, the consistency obtained was not all that could be desired. Working under ordinary conditions of temperature and pressure, he obtained for air, $\gamma = 1.401$. (3) The author's work gives for air at 25° C., 76 cm., $\gamma = 1.4011$, and for carbon dioxide, under the same conditions, $\gamma = 1.3003$.

Summary and Tables.—Several attempts at computing the value of γ, from theoretical considerations, have been made, *e. g.*, by Boynton (20), Capstick (21), and Le Duc (22), but in all cases, because of approximations made or uncertainties in the values of certain constants needed, these results do not agree sufficiently to aid us.

In the following table will be found what seem to be the most reliable determinations made during the period covered by this review.

TABLE V.

Table of Observations on γ for Air.

Observer.	Method.	Temperature.	
Violle and Vautier..........	Velocity of sound.	0° C.	1.4009
Hebb.....................	" " "	"	1.4003
Low (corrected by Stevens)..	" " "	"	1.4012
Stevens..................	" " "	"	1.4006
Lummer and Pringsheim.....	Application adiabatic equation.	15° C.	1.4025
Makower..................	" " "		1.401
Moody....................	" " "	25° C.	1.4011

These values have not been reduced to a common temperature because in the case of air the variation of γ with temperature is inappreciable for the range covered.

TABLE VI.

Table of Observations on γ for Carbon Dioxide.

Observer.	Method.	Temperature.	
Fürstenau	Velocity of sound.	13.5:16.5° C.	1.3008
Lummer and Pringsheim	Application adiabatic equation.	13° C.	1.2995
Moody	" " "	25° C.	1.3003

If we make use of the equation developed by Wüllner (23) and reduce the above values to the same temperature, 20° C., the values of Fürstenau (14) and of Lummer and Pringsheim (3) would each be lessened by about .001, while that of the author would be increased by a like amount. These corrected values give a mean for carbon dioxide, at 20° C., $\gamma = 1.2997$.

IV. A COMPUTATION OF THE SPECIFIC HEAT AT CONSTANT PRESSURE FOR AIR AND CARBON DIOXIDE.

Upon the basis of the first law of thermodynamics, we may deduce the expression

$$(4) \qquad C_p = C_v + \frac{1}{J}\left\{\left(\frac{\partial u}{\partial v}\right)_\theta + p\right\}\left(\frac{\partial v}{\partial \theta}\right)_p.$$

(See Buckingham, § 72.) From equation (4), we have, at once,

$$(5) \qquad \lambda \equiv \left(\frac{\partial u}{\partial v}\right)_\theta = JC_p \cdot \frac{\gamma - 1}{\gamma} \cdot \left(\frac{\partial \theta}{\partial v}\right)_p - p.$$

This equation gives us a means of determiming λ, the latent heat of expansion or the internal work of free expansion. The second law furnishes us with the further relation

$$(6) \qquad \lambda = \theta\left(\frac{\partial p}{\partial \theta}\right)_v - p.$$

(See Planck, § 153.) In these equations, (5) and (6), we have two independent means of obtaining λ. In (5), the value of λ depends upon the specific heat at constant pressure, the ratio of the specific heats, and the volume coefficient of expansion. In (6), its value is determined by the thermodynamic temperature, obtained from values of the Joule-Thomson effect, and the pressure coefficient of expansion.

Now, if we make use of the defining equations,

$$\alpha_p = \frac{1}{v_0}\left(\frac{\partial v}{\partial \theta}\right)_p \tag{7}$$

and

$$\alpha_v = \frac{1}{p_0}\left(\frac{\partial p}{\partial \theta}\right)_v \tag{8}$$

we can rewrite our equations. From (5) we have

$$\lambda = JC_p \cdot \frac{\gamma - 1}{\gamma} \cdot \frac{1}{v_0 \alpha_p} - p, \tag{9}$$

and from (6) we get

$$\lambda = \theta p_0 \alpha_v - p. \tag{10}$$

When we insert the values, found, experimentally, for the different quantities, *i. e.*, $C_p = .2375$ and $\gamma = 1.401$, equation (9) gives us a relatively large negative value for λ, while equation (10) gives us a small positive value, which is as we know to be true for most real gases. If an error in γ were the cause of this, it would be necessary for $(\gamma - 1)$ to be about 2 per cent. larger, or $\gamma = 1.408$, in the case of air, in order that we obtain for λ a proper positive value. Since such a value is at variance with all recent reliable determinations of γ, and since it is even more probable that the total errors in all the other quantities is not so great, it seems certain that the generally accepted value of C_p, .2375, is much too small. For this reason, we have thought it worth while to compute it.

Upon the elimination of λ from equations (9) and (10) and the solution for C_p, we obtain an expression for C_p in terms of experimentally determined quantities, viz.,

$$C_p = \frac{\theta\gamma}{\gamma - 1} \cdot p_0 \alpha_v \cdot v_0 \alpha_p \tag{11}$$

which gives C_p in cal/(gm. × deg.). As was pointed out above, this value of C_p is just as accurate as that of γ, since the values of all other factors are known with a very high degree of accuracy.

In these equations, the symbols used are defined as in the following table:

Symbol.	**Definition.**
C_p,	Specific heat at constant pressure, in cal./(gm. × deg.).
C_v,	Specific heat at constant volume.
γ,	Ratio of the two specific heats.
θ,	Temperature on the thermodynamic scale.
θ_0,	Temperature of the freezing point of water on thermodynamic scale.
v_0,	Specific volume, in cm./gm. at the temperature θ_0.
p,	Pressure of one atmosphere in dynes.

J, Mechanical equivalent of heat.
α_p, Volume coefficient of expansion, at temperature θ.
α_v, Pressure coefficient of expansion, at temperature θ.

Since the average room temperature is 20° C., and since all the quantities needed are known more accurately at 20° C. than at 0° C., we have computed the value of C_p for 20° C. and one atmosphere's pressure. In making these computations for 20° C., it must be borne in mind that v_0, at 20° C. and one atmosphere's pressure is not equal to v_0 at 0° C. if we, as we may, arbitrarily define

$$\alpha_v = \frac{1}{p_0}\left(\frac{\partial p}{\partial \theta}\right)_v .$$

In this case, we must define

$$\alpha_p = \frac{1}{v_0'} \cdot \left(\frac{\partial v}{\partial \theta}\right)_p ,$$

where

$$v_0' = v_0 \frac{\theta_0}{\theta},$$

on the assumption that Boyle's law holds. This $v_0 = v_0$, at 0° C. and one atmosphere.

As to the available data for use in these computations, we have the following:

1. On the thermodynamic temperature of the freezing point of water, or 0° C., Makower and Noble (24), Rose Innes (25), Pellat (26), Chappuis and Harker (27), Buckingham (28), Callendar (29), and Berthelot (30) have given results, all agreeing fairly well. The more reliable of these results are, probably, those of Callendar, Berthelot, and Buckingham, from which we conclude that $\theta_0 = 273.11°$ on the thermodynamic scale, with an accuracy of $\pm .01°$. The corrections for the interval are negligible, so that 20° C. = 293.11° on the thermodynamic scale.

2. On C_p, the results for air cluster about those of Regnault (31), viz., $C_p = .2375$, as a mean value. But all these earlier observations have been taken over relatively long ranges of temperature. More recently, Swann (32) has made a determination, covering a short range, and has obtained a value higher than that of Regnault's by nearly 2 per cent. He obtained the value $C_p = .2417$, at 20° C. Just as this paper is ready for the press, an abstract has appeared in the *Physikalische Zeitschrift* of the work of Scheele and Heuse (33), who find $C_p = .2408$ at 20° C. For carbon dioxide, a better agreement is found, but, for this, γ seems to be well determined so that we have computed C_p. For carbon dioxide, Regnault (31) gives $C_p = .2025$; Lussana (34), $C_p = .2013$; Holborn and Hennings (35), $C_p = .2039$; Swann (32), $C_p = .2020$, at 20° C.

3. Values of γ have been discussed in Part III. (see above).

4. Since $v = 1/\rho_0$, we need ρ_0, the density at 0° C. The density of air at 0° C., 76 cm., and sea-level has been taken from Landolt-Bornstein's tables. From the same authority, we have taken the value of g, at sea-level, as 980.617. For CO_2 we have taken the value of ρ_0 as given by Lord Rayleigh (36).

5. For the value of J, we need only refer to the summary of Ames (37).

6. Upon the expansion coefficients, the splendid work of Chappuis (38) has been generally accepted as the best yet made, so that his values have been used in this work.

In Table VII. are given the quantities needed in equation (11) and their numerical value in the case of the two gases studied. In Table VIII., we have compared the values computed with Regnault's and the more recent determinations.

Table VII.

Table of Values Used in the Computation of C_p.

Magnitude.	Air.	Carbon Dioxide.
γ	1.401	1.300
θ_0	273.11	273.11
ρ_0	.00129278	$1.52909 \times .00129278$
J, at 20° C.	4.181×10^7	4.181×10^7
α_p, at 20° C., 76 cm.	.00367812	.00373447
α_v, at 20° C., 76 cm.	.0036722	.0037067

Table VIII.

Values of C_p, Computed and Observed.

Gas.	C_p (Computed).	C_p (Observed).
Air	.24118	.2375 Regnault. .2417 Swann. .2408 Scheele and Heuse.
Carbon dioxide	.2008	.2025 Regnault. .2020 Swann. .2013 Lussana.

It will be seen that our computed value of C_p in the case of air agrees remarkably well with the mean of the two most recent determinations. It is to be noted that the equation used in the computations is perfectly rigorous and all quantities involved are capable of measurement with the highest degree of accuracy. The one in whose value there is the largest uncertainty is γ and there can be little question but that its value is known, accurately, to the third decimal place. In the case of carbon dioxide, our value agrees within the limits of error with the value given by Lussana, though it is slightly smaller than those found by other observers. Hence it seems that the correct value of C_p for carbon dioxide must lie close about the value found by Lussana.

V. CONCLUSIONS.

1. Our work gives for air, at 20° C., 76 cm., $\gamma = 1.4011$, and for carbon dioxide, under the same conditions, $\gamma = 1.3003$, with a probable error in each of $\pm .0005$. These values agree well with the best determinations of recent years, though the value for air is smaller than some of those of earlier date which have previously been accepted.

2. We find for air, at 20° C., 76 cm., that $C_p = .24118$. This value is so reliable that there can be little doubt but that the values accepted, heretofore, are too small. In fact, a striking confirmation of the correctness of our value of γ is had in the fact that the above value of C_p agrees to within .03 of 1 per cent. with the mean of the recent determinations of Swann and of Scheele and Heuse. For carbon dioxide, at 20° C., 76 cm., we find $C_p = .2008$, which agrees within the limits of error with the value of Lussana and is slightly lower than the values given by other reliable determinations.

In conclusion, the author desires to express his appreciation to the staff of the Physics Department for their kindly interest in this work and especially to Professor Millikan, at whose suggestion and under whose direction the investigation was carried out.

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