A DETERMINATION OF THE RATIO OF THE SPECIFIC HEATS OF HYDROGEN AT 18° C. AND − 190° C.

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THE method for determining the ratio of the specific heats of gases originally presented by Lummer and Pringsheim[1] in 1898, and since used in modified form by Moody[2] and by Partington,[3] is generally conceded to be the most precise method thus far available, its only disadvantage being that it has seemed to require large quantities of gas. Three years ago, however, H. N. Mercer[4] obtained with the use of surprisingly small flasks some preliminary data which pointed to the possibility of using the method with small scale apparatus. Accordingly Professor Millikan suggested to the author two problems which were obviously waiting such an opportunity.

First: There are in the literature of the subject at present only two satisfactory determinations of the ratio for hydrogen at 20° C.; 1.4084, a direct determination by Lummer and Pringhseim, and 1.407, computed by Scheel and Heuse[5] from their observations on C_p by the "constant flow" method. Inasmuch as the kinetic theory affords no explanation of values so high, and experimental data generally are now under close examination from the point of view of the quantum theory, a careful redetermination of the ratio is needed to decide whether a quantum effect is actually manifested in hydrogen at this temperature.

Second: Eucken,[6] from observations on C_v, and Scheel and Heuse from observations on C_p, have announced that the hydrogen molecule loses almost entirely its two degrees of rotational freedom by the time the temperature reaches − 180° C., and becomes virtually a monatomic gas, the ratio of the specific heats being according to Eucken 1.604, and according to Scheel and Heuse 1.595. Will it be possible to confirm this by direct observation of the ratio?

This paper is an attempt to answer these two questions.

[1] Ann. d. Phys., 64: 536, 1898.
[2] PHYS. REV., 34: 275, 1912.
[3] Phys. Zeit., 14: 969, 1913.
[4] Pro. Roy. Soc. London, 26: 155, 1914.
[5] Ann. d. Phys., 40: 473, 1913.
[6] Ber. d. Preus. Akad., 1912, p. 141.

I. At 18°.

Experimental Arrangements.—The method employed for this investigation is, as stated above, essentially that of Lummer and Pringsheim. It consists in measuring the cooling attendant upon an adiabatic expansion from p_1 to p_2; the two pressures and temperatures are connected for the ideal gas by the relation,

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

and γ is therefore obtained from the equation,

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

The two modifications of the original experiment are (1) the use of a one liter flask in place of a large carboy, and (2) the substitution of a minute thermojunction for the platinum resistance thermometer, following in this respect the method already used by Moody in the Ryerson laboratory.

The thermal element was of .001 inch copper and constantan wires. It was introduced into the flask by means of two glass tubes through the rubber stopper, which were inside drawn out to fine capillaries and bent into a Y, which spread nearly to the diameter of the bulb, and could be folded together for insertion into the flask by twisting each of the tubes through 90°. It was found by repeated effort that normal values of γ could be obtained only when the couple was thus introduced with a minimum of glass as remote as possible from the junction, and the junction itself placed carefully at the center of the flask. The junctions were brazed in the edge of a Bunsen flame by holding in metal tweezers immediately back of the point to be brazed. Outside, the tubes ended in capsules containing the junctions with the copper lead-wires; these dipped into the water bath containing the bulb. The tubes were sealed by a mixture of beeswax and resin where they opened into the flask.

The arrangement by which the gas was sent into the flask is shown in Fig. 1. Air was taken from the laboratory compressed air system, passed through two bottles of concentrated sulphuric acid, then over a considerable length of solid caustic soda to remove carbon dioxide, and finally over phosphorus pentoxide. Hydrogen was obtained electrolytically and passed through the same system; further purification was deemed unnecessary, in view of the fact that the question of density is not involved in the experiment. The pressure gauge, O, on which the excess pressure was read, is of tubing 2.5 cm. in diameter, filled with light transformer oil. With cocks *a* and *c* closed, the mercury could be raised in *R* to just the right height as indicated by the accessory mercury gauge, *M*, so that on opening the cock *c*, the oil moved less than a centimeter. There is thus practically no change in the gauge reading after the bulb is filled, due to hanging of oil on the walls. The inverted U-tube through

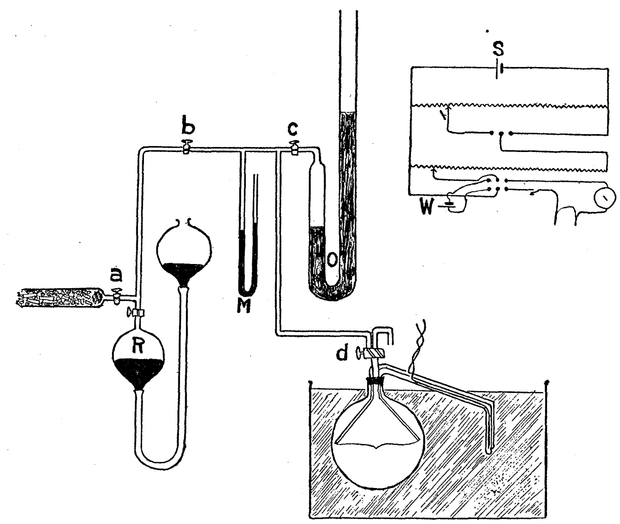

Fig. 1.

which the expansion takes place serves in the case of hydrogen as a trap to prevent air from being carried back into the bulb during the surges incident to the expansion.

The thermal E.M.F. developed by the expansion was measured by a null method with a Wolff potentiometer. An E.M.F. of the order of .002 volt was applied from a storage cell which was compared with a Weston standard before and after each series of observations. A ballistic galvanometer of the D'Arsonval type was used. It was read by a telescope and scale at a distance of 3.6 meters; the angle of deflection was doubled with practically no loss of light by the simple device of throwing the beam back upon the galvanometer mirror from a small stationary mirror about 10 cm. in front of it. Under these conditions the galvanometer sensibility was such that 3.8×10^{-8} volts corresponded to 1 mm. deflection. The constant of the thermojunction between 0° and 20° is 3.707×10^{-5} volts per degree; consequently an equilibrium temperature could be read directly to .001° and estimated to .0002°. In order to eliminate spurious motion it was found necessary to mount the galvanometer on a Julius suspension,[1] which was built very nearly

[1] Ann. d. Phys., 56: 151, 1895.

according to the original specification, the whole platform weighing about 11 kg.; the situation proved too severe a test of even this admirable device, so that observations were made only during the quieter portion of the day.

The method of procedure for a single determination was as follows: The bulb was filled and the cock *b* closed at some definite pressure, 10 to 50 cm. of oil in excess of atmospheric pressure. The potentiometer was kept balanced till it was certain that the gas had attained the temperature of the bath. Then the thermojunction circuit was opened, and the potentiometer resistance across which it is shunted changed to one or two ohms less than that which would presumably balance the E.M.F. developed by the expansion. The two-way cock, *d*, was turned to cut off the pressure gauge; then on one beat of a metronome, *d* was turned to open the bulb to the atmosphere, and on the next beat the potentiometer was closed. An instant backward throw of the galvanometer of 1 to 5 mm. is observed before it starts forward with rising temperature. The pressure gauge is read immediately, and the process is repeated for identically the same pressure with a potentiometer resistance different by an ohm. From six to ten such observations are used to fix a line from which the equilibrium resistance may be found by extrapolation. Data for one such observation are shown in Table I.

TABLE I.

p_2.	Δp.	ΔT.		T.
		Potentiometer R.	Galv. Throw.	
73.990 cm.	12.60 cm.	23 Ω	2.8 mm.	18.64° C.
	12.64	22	4.9	
	12.59	23	2.3	
	12.60	22	5.0	
	12.57	23	2.8	
73.945	12.55	22	4.6	18.68°

Temp. oil 21.7° C. 24.21 Ω = R_0

Δp = 10.88 gm./cm.^{2} 7384.3 Ω = R of Weston cell against storage

Errors Due to Inflow of Heat During Observation.—Both because the thermojunction has a finite heat capacity and because the expansion is oscillatory, it is necessary that the temperature should be measured at some definite time after the expansion is made. During this interval there is of course an inflow of heat which holds up the final temperature of the thermojunction. The effect of gas conduction and convection from the walls, which is present even in a 60 liter carboy, as shown by

Moody's work, is of course extreme in the 1 liter bulb; its magnitude, moreover, will vary in the present case with the way in which the thermo-junction is mounted in the bulb. There is also an inevitable transfer by radiation from the walls to the junction, and finally a possible inflow by metallic conduction. These errors are all proportional to ΔT, and vanish with it. It is consequently necessary that for a single thermo-junction, with a single interval between expansion and observation of temperature, sufficient data should be obtained to plot apparent values of γ as a function of Δp, or of the cooling. For expansions as small as those here employed (none are over 4 per cent.) this must be practically a linear function. Three different junctions, mounted in different tubes, were used in air with different metronome rates, and the data so plotted. Figs. 2 and 3 show that though the slopes differ widely, the intercepts are

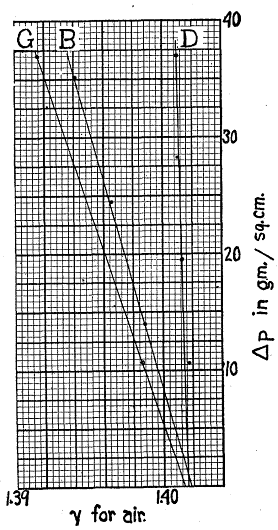

Fig. 2.

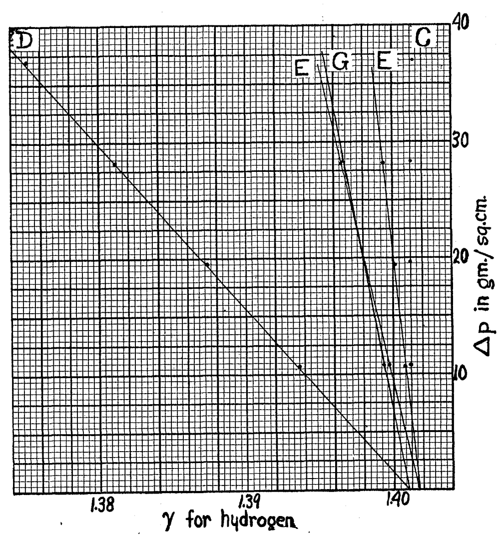

Fig. 3.

substantially the same. Two series of observations made with the same junction for t = .75 sec. and t = .62 sec. (see Table III., Junction E) indicate the extent to which the observed values depend upon the time of observation. Junction D was used with the same time interval in both air and hydrogen, and a comparison of the D lines in Figs. 2 and 3 shows how much more considerable the effect of heat inflow is in the case of hydrogen; this is partly due to the shorter time of expansion, and partly to the larger conductivity. It appears then that the data bear out satisfactorily the assertion that in the value of γ obtained by extrapolation for $\Delta p = 0$, the effect of inflow of heat by whatever means and

TABLE II.

Air.

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction B, time, .87 sec.	13.98 gm./cm.²	1,014.90 gm./cm.²	292.05°	1.133°	1.3971	
	14.00	1,007.50	292.04	1.138	1.3947	
	13.95	1,016.72	291.92	1.135	1.4000	
	14.21	1,012.46	291.20	1.156	1.3999	
	14.08	1,012.90	292.77	1.149	1.3985	
	14.01	1,011.56	292.71	1.151	1.4015	
	14.00	1,015.15	292.19	1.143	1.4010	
	14.05	1,014.82	292.18	1.140	1.3973	
	13.93	1,014.12	292.11	1.138	1.4007	
	13.91	1,019.70	291.83	1.121	1.3968	1.3988
	24.50	1,013.26	292.03	1.970	1.3953	
	24.51	1,008.00	292.02	1.986	1.3968	
	24.67	1,012.70	292.80	2.003	1.3990	
	24.49	1,011.98	292.08	1.967	1.3939	
	24.47	1,015.26	292.17	1.976	1.3985	
	24.46	1,014.00	292.13	1.969	1.3960	
	24.45	1,019.90	291.85	1.958	1.3971	
	24.46	1,018.90	292.01	1.960	1.3964	1.3966
	34.95	1,008.42	291.97	2.793	1.3929	
	35.12	1,012.68	292.79	2.812	1.3949	
	34.95	1,014.93	292.22	2.787	1.3949	
	35.00	1,012.13	292.04	2.811	1.3964	
	35.12	1,011.60	292.80	2.812	1.3943	
	35.04	1,012.86	292.66	2.805	1.3950	
	34.93	1,015.40	292.14	2.775	1.3932	
	35.02	1,019.30	291.96	2.760	1.3913	1.3942
Junction D, time, .87 sec.	10.58	1,023.31	291.16	.857	1.4013	
	10.73	1,018.60	291.25	.872	1.4008	
	10.60	1,009.80	290.81	.871	1.4028	
	10.66	1,016.82	291.12	.869	1.4021	
	10.79	1,012.50	291.40	.885	1.4027	1.4019
	19.72	1,019.70	292.24	1.602	1.4024	
	19.43	1,010.30	290.79	1.597	1.4007	
	19.50	1,016.52	291.10	1.580	1.4015	
	19.66	1,016.15	291.37	1.600	1.4031	
	19.54	1,023.76	291.34	1.569	1.3998	
	19.61	1,011.50	291.46	1.596	1.4006	1.4013
	28.14	1,021.57	291.16	2.261	1.4023	
	28.38	1,021.30	292.30	2.268	1.3971	

TABLE II.—*Continued.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction *D*, time, .87 sec.	28.12 gm./cm.²	1,010.70 gm./cm.²	290.78°	2.284°	1.4032	
	28.24	1,016.56	291.14	2.277	1.4017	
	28.39	1,016.30	291.31	2.287	1.4008	1.4010
	37.11	1,020.50	292.26	2.981	1.4025	
	36.88	1,009.35	290.82	2.954	1.3988	
	37.03	1,016.42	291.26	2.972	1.4017	1.4010
Junction *G*, time, 1.0 sec.	10.79	1,019.06	291.70	.874	1.3987	
	10.94	1,011.28	291.95	.892	1.3974	
	10.87	1,006.80	291.85	.894	1.4000	
	10.83	1,024.61	291.77	.874	1.3992	
	10.89	1,005.43	291.89	.894	1.3982	
	10.74	1,012.37	291.72	.878	1.4000	
	10.88	1,022.30	291.78	.878	1.3980	
	10.71	1,014.03	291.29	.869	1.3973	
	10.81	1,003.14	291.40	.888	1.3979	
	10.88	1,005.59	291.78	.895	1.3991	1.3986
	36.91	1,019.06	291.65	2.912	1.3929	
	37.13	1,010.07	291.90	2.945	1.3908	
	36.93	1,015.64	291.81	2.928	1.3935	
	37.13	1,013.47	291.85	2.936	1.3908	
	37.11	1,010.47	291.82	2.950	1.3921	
	37.01	1,023.96	291.40	2.890	1.3903	
	36.87	1,023.41	291.05	2.888	1.3922	
	36.81	1,017.17	291.90	2.888	1.3905	1.3916

Limiting values: $B = 1.4019$
$D = 1.4017$
$G = 1.4014$ Mean = *1.4017*

however extreme, unless the slope of the line is such as to make its intercept uncertain, is completely eliminated. Inasmuch as the errors inherent in the method are thus accounted for, it remains only to examine the observational errors.

Observational Errors.—The error in p_1, the barometric pressure read to .005 cm., would be inconsiderable were it not that a single observation requires at least an hour, and that in that time the barometer often changes by nearly a millimeter. For the smallest expansion a change of .5 mm. in p_1 is equivalent to a change in ΔT of .0003°. For this reason observations were always taken for alternately high and low points on the resistance-throw line.

Heights on the oil gauge were read to .01 cm. by means of a magnifying

TABLE III.

Hydrogen.

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction C, time, .65 sec.......	10.85 gm./cm.^{2}	999.51 gm./cm.^{2}	291.72°	.901°	1.4017	
	10.52	1,023.78	290.24	.846	1.3997	
	10.67	1,022.72	291.68	.872	1.4037	
	10.85	1,022.70	292.90	.887	1.4003	
	10.67	1,008.67	291.45	.876	1.4006	
	10.63	1,007.63	291.52	.873	1.4003	
	10.70	1,016.74	291.26	.873	1.4022	
	10.74	1,025.44	291.32	.866	1.3999	1.4011
	19.60	999.95	291.57	1.612	1.3999	
	19.60	1,017.70	291.10	1.583	1.4004	
	19.59	1,011.94	292.86	1.598	1.3994	
	19.25	1,012.20	292.72	1.589	1.4061	
	19.55	1,019.30	292.03	1.588	1.4024	
	19.69	1,021.90	292.92	1.584	1.3970	
	19.49	1,010.90	291.22	1.589	1.4017	
	19.61	1,025.44	291.32	1.578	1.4019	1.4011
	28.36	1,019.30	292.08	2.273	1.3978	
	28.27	1,008.33	291.52	2.309	1.4037	
	28.40	1,018.74	292.47	2.306	1.4043	
	28.33	1,022.02	292.30	2.276	1.4004	
	28.41	1,019.03	292.92	2.301	1.4021	
	28.40	1,014.40	291.97	2.294	1.3999	
	28.36	1,027.36	291.94	2.267	1.4012	
	28.16	1,013.80	291.12	2.276	1.4015	1.4012
	36.94	1,000.75	291.66	3.003	1.3997	
	36.88	1,014.46	291.12	2.962	1.4013	
	37.03	1,015.40	292.54	2.988	1.4018	
	37.04	1,022.02	292.32	2.977	1.4035	
	37.14	1,019.03	292.69	2.986	1.4013	
	37.14	1,021.90	292.92	2.984	1.4021	
	36.89	1,014.80	291.09	2.967	1.4020	
	36.92	1,007.63	291.53	2.982	1.4000	1.4014
Junction D, time, .83 sec........	10.79	1,013.00	291.51	.872	1.3924	
	10.74	1,000.90	291.12	.876	1.3934	
	10.62	997.24	290.62	.867	1.3902	
	10.70	1,008.95	290.92	.865	1.3929	
	10.72	1,015.20	290.62	.863	1.3963	
	10.44	1,011.80	290.35	.845	1.3962	
	10.71	1,006.35	290.77	.869	1.3941	1.3936

TABLE III.—*Continued.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction *D*, time, .83 sec........	19.61 gm./cm.²	1,003.85 gm./cm.²	291.72°	1.580°	1.3906	
	19.50	1,005.12	290.62	1.547	1.3847	
	19.61	1,016.85	290.72	1.549	1.3885	
	19.56	1,010.20	291.00	1.563	1.3900	
	19.39	1,010.45	290.40	1.523	1.3824	
	19.53	1,015.48	291.21	1.545	1.3874	1.3873
	28.28	1,003.80	291.72	2.255	1.3871	
	28.11	1,002.73	290.61	2.216	1 3830	
	28.29	1,016.45	290.70	2.190	1.3801	
	28.17	1,009.00	290.45	2.186	1.3780	
	28.19	1,006.35	290.77	2.198	1.3789	
	28.29	1,015.25	291.27	2.194	1.3792	1.3811
	37.01	1,003.75	291.77	2.869	1.3754	
	37.07	1,010.45	291.12	2.849	1.3758	
	36.98	1,015.60	290.62	2.830	1.3766	
	36.89	1,009.50	290.42	2.814	1.3725	1.3781
Junction *E*, time, .62 sec........	10.75	1,021.50	291.60	.877	1.4038	
	10.76	1,010.68	292.22	.882	1.3993	
	10.51	1,037.40	290.78	.839	1.4011	
	10.56	1,036.70	290.42	.841	1.4007	
	10.64	1,016.90	290.59	.859	1.3977	
	10.67	986.90	291.23	.898	1.4028	1.4009
	19.58	1,021.70	291.68	1.577	1.3997	
	19.66	1,015.55	291.67	1.607	1.4047	
	19.29	1,039.70	290.02	1.515	1.3981	
	19.38	1,018.90	290.81	1.561	1.3998	
	19.46	1,011.75	291.03	1.575	1.3982	1.4001
	28.20	1,022.50	291.72	2.263	1.4010	
	28.06	1,036.90	290.87	2.216	1.4015	
	28.05	1,039.75	290.02	2.194	1.3990	
	28.17	1,015.00	291.16	2.252	1.3960	
	28.08	1,038.20	290.32	2.200	1.3986	1.3992
.75 sec........	10.76	1,015.83	291.50	.877	1.4005	
	10.62	1,017.00	290.92	.861	1.3992	
	10.69	1,016.50	290.94	.867	1.3995	1.3997
	28.11	1,022.60	291.52	2.240	1.3975	
	28.04	1,035.40	290.92	2.201	1.3971	
	28.07	1,039.80	290.09	2.175	1.3938	
	28.10	1,038.40	290.32	2.190	1.3958	
	28.07	1,010.23	290.83	2.263	1.3986	1.3965

TABLE III.—*Concluded.*

	ΔP.	P.	T.	ΔT.	γ.	Mean γ.
Junction G, time, .65 sec........	10.81 gm./cm.^{2}	1,011.58 gm./cm.^{2}	292.22°	.885°	1.3988	
	10.83	1,013.05	292.12	.885	1.3988	
	10.76	1,028.84	291.21	.866	1.4008	
	10.75	1,029.40	291.25	.862	1.3992	
	10.74	1,031.36	291.41	.859	1.3985	
	10.64	1,031.24	291.03	.849	1.3979	
	10.53	1,025.31	290.17	.847	1.4009	
	10.65	1,029.04	290.41	.850	1.3983	
	10.85	1,027.92	291.40	.873	1.3999	1.3992
	28.20	1,025.75	290.69	2.239	1.3987	
	28.34	1,028.56	291.17	2.238	1.3964	
	28.27	1,029.00	291.42	2.242	1.3984	
	28.15	1,030.82	291.36	2.225	1.3977	
	28.13	1,031.48	290.77	2.208	1.3947	
	28.02	1,024.90	290.21	2.215	1.3967	
	28.13	1,025.94	290.12	2.214	1.3950	
	28.30	1,026.30	291.40	2.236	1.3950	
	28.13	1,023.41	291.14	2.233	1.3966	1.3966

Limiting values: $C = 1.4012$
$D = 1.4011$
$E = 1.4016$
$G = 1.4011$ Mean $=$ *1.4012*

glass and a small lamp to illuminate sharply the meniscus from beneath. A given pressure could be duplicated to about .05 cm. A temperature-density curve was obtained for the oil by the specific gravity bottle method which must be accurate to 1 part in 8,000. It is to be noted, however, that an error in the density of the oil, as also an error in the calibration of the thermojunction, these errors being proportional respectively to Δp and ΔT, do not appear in the final extrapolated value of γ at all. The maximum error in Δp may fairly be taken as .01 gm./cm.^{2}; this corresponds to an error in γ of .0004 for the smallest expansion and .0001 for the largest.

The water bath, while it contained no thermostat, was large enough that the temperature was constant to less than .1° during an observation, the temperature being read to .01° on a mercury thermometer which had been calibrated against a Baudin standard thermometer. The uncertainty here introduced in γ is only .0001.

The major difficulty, of course, lies in the determination of ΔT. The galvanometer throws are so rapid, particularly in hydrogen, where the conductivity is six times greater than in air, and the temperature change correspondingly rapid, that they cannot be read with precision. In each throw are involved the questions of the initial balance of the potentiometer, of the duplication of pressure, and the duplication of the time interval between opening the bulb and closing the potentiometer circuit. This last element of variation could be eliminated by the introduction of an automatic key, but in view of the other more considerable items this seemed unnecessary. The equilibrium resistance is determined from eight or ten throws, and may moreover be partially corrected if the mean slope of the line in question is already known from preceding observations. These resistances are probably obtained to the nearest .1 ohm, making a maximum uncertainty of .0006 and .0025 in γ for the largest and least coolings respectively.

The total possible error this accounted for in a single observation is larger than one would wish it. The actual mean deviation of observations in one group is, however, scarcely more than in Partington's data, and with a sufficient number of observations the slope of the γ-Δp line must be obtained with fair precision. It is also to be emphasized that several errors operate to modify the slope of the line without affecting the intercept, since for $\Delta p \doteq 0$, $\log (\theta_1/\theta_2) \doteq 0$ also. The worth of the work should therefore rather be judged by the variation in the intercepts. The three determinations for air and the five for hydrogen show a mean deviation in each instance of .0002; this may therefore fairly be taken to represent the probable error. (See summaries of Tables II. and III.)

Theoretical Correction.—The value of γ obtained from the ideal gas equation must be corrected in the case of air for departure from the ideal gas laws. The original Lummer and Pringsheim method was to compute the absolute temperature using $-272.4°$ C. as zero. This is numerically equivalent to the method used by Partington, who computes the correction from the Berthelot equation in the form,

$$\frac{1}{\gamma} = \frac{1}{\gamma i} - \frac{\frac{a}{v^2}\left(\frac{\theta_1}{(\theta_2)^2} - \frac{1}{\theta_1}\right)}{p_1 - p_2},$$

where γi is computed from equation (2), using $\theta = t + 273.09$. For the present purpose the limiting value of the correction term as $p_1/p_2 \doteq 1$ is required. This is readily found by substitution of $(p_1/p_2)^{(\gamma-1)/\gamma}$ for θ_1/θ_2, and differentiation to be

$$\frac{a}{pv^2\theta}\frac{\gamma - 1}{\gamma}.$$

Hence,

$$\frac{1}{\gamma} = \frac{1}{\gamma i}\left(1 - \frac{.4017a}{pv^2\theta}\right).$$

The mean values of the critical constants of air as determined by Olszewski and by Wroblewski give $a = .336$. It follows that for one atmosphere and 20° the correction factor is .99912 and the corrected value of γ is 1.4029. The correction for hydrogen is well beyond the limit of observation.

Discussion of Results.—The final values obtained from this investigation are for air 1.4029, and for hydrogen 1.4012.

Inasmuch as γ for air is already known with considerable certainty, the observations in air are to be regarded as a test of the precision obtainable in a small flask. A critical summary of the older work appears in Moody's paper, which points to the conclusion that neither the velocity of sound, nor the Clement and Des Ormes method, nor other direct application of Reech's theorem are capable of yielding as precise results as the Lummer and Pringsheim method. There are now three determinations by this method, as follows:

Lummer and Pringsheim	1.4025
Moody	1.4003[1]
Partington	1.4032

The close concordance between the present value and these which were obtained in large carboys, is a highly satisfactory vindication of the applicability of the method to small flasks. It is interesting to repeat in passing what others have called attention to, that, aside from the internal work, this high value for air is amply accounted for by its 1 per cent. argon content. Leduc's formula,[2] for example, gives 1.4015 for a mixture 99 per cent. of which has $\gamma = 1.400$ and 1 per cent. $\gamma = 1.67$.

The only available data for hydrogen are meager and conflicting. Oddly enough, only three attempts have been made to measure the ratio of the specific heats of hydrogen. Maneuvrier,[3] from direct application of Reech's theorem, gave for hydrogen 1.384, somewhat less than his value for air, 1.392, but he frankly states that he had not been able to secure the same consistency in hydrogen as in air. The exceedingly careful work of Lummer and Pringsheim, however, gave 1.4084 as compared with 1.4025 for air. Mercer in the same small flask found 1.398

[1] Moody's published value, 1,4011, has been increased by the theoretical correction .0012, pointed out by Partington, and it has been decreased by .0020, because the radiation error which he added had been already included, unmistakably it appears to the author, in the slope of his line.

[2] C. R., 160: 338, 1915.

[3] C. R., 123: 228, 1896.

for hydrogen and 1.392 for air. The work of Eucken on C_v and of Scheel and Heuse on C_p likewise give values of γ distinctly higher for hydrogen than for air (see Table IV.). The weight of existing evidence is therefore contrary to the present conclusion that γ for hydrogen is close to its theoretical value according to the kinetic theory. With the

Table IV.

	Observer.	γ.	c_p at 20° in 15° Cal.
a. Air............			
	Regnault[1]	1.4008	.2408
	Lummer and Pringsheim	1.4025	.2400
	Swann[2]	1.3994	.2410
	Scheel and Heuse[3]	1.4013	.2408
	Moody	1.4003	.2409
	Partington	1.4034	.2396
	Shields	1.4029	.2399
b. Hydrogen.......			
	Lummer and Pringsheim	1.4084	3.400 (16°)
	Scheel and Heuse	1.4075	3.406 (16°)
	Shields	1.4012	3.443

[1] This is after correction by Scheel and Heuse, see Ann. d. Phys. 40: 486.

[2] Phil. Trans. Roy. Soc., 210: 199, 1909.

[3] Loc. cit. Scheel and Heuse's and also Swann's values are restated, using $J = 4.187$.

idea that the discrepancy might be explained if γ were a much more rapidly changing function of the temperature in hydrogen than it is known to be in air, in which case insufficient care had been exercised in controlling the temperature of the water bath, a series of observations were taken with the bulb in an ice bath. This series yielded 1.4006, however, and there appears no reason to discredit the data of Table III. on that score.

Comparison with Data on C_p.—Alongside these direct determinations of γ it is instructive to assemble once more the values of γ obtainable from observations on C_p. These latter may be computed in either of two ways: (*a*) from the relation $C_p - C_v = R$, corrected in accordance with a chosen equation of state, as was done by Scheel and Heuse and by Partington; (*b*) from the relation,

$$C_p = \frac{1}{J}\frac{\gamma}{\gamma - 1}\theta\alpha_p p_0 \alpha_v v_0,$$

employed by Moody, which is as universally rigorous as the thermodynamic theorems out of which alone it is derived, and all factors of which are known with extreme precision. The second method has been used in the computations herewith presented, the required constants being chosen as follows:

For air:

p = 13.595 × 980.616 × 76 (Landolt-Börnstein Tables).

θ_0 = 273.09, chosen by Berthelot as the thermodynamic temperature of melting ice (Zeit. für Elektrochemie, 10 : 621, 1904) and in agreement with the more recent work of Onnes, Richards, and Witkowski on the pressure and volume coefficients of hydrogen, and of Travers on helium.

α_v = .0036700, Chappuis' value reduced from 1,000 mm. to 760 mm. (Trav. et Mem. du Bur. Int. des Poids et Mes., 13: 190, 1903).

α_p = .0036713, likewise Chappuis' with the same reduction (loc. cit.).

$J = 4.187 \times 10^7$ ergs per 15° cal. (Ames, Congres Int. d. Phys., 1: 178, 1900).

ρ_0 = .00129278, Regnault's value reduced to latitude 45°.

For hydrogen:

α_v = .00366256, Chappuis (loc. cit.).

α_p = .0036606, Chappuis, reduced to 760 mm.

$\rho_0 = 8.9876 \times 10^{-5}$, the mean of Regnault's, Jolly's and Morley's values as quoted by Berthelot (loc. cit.).

The table gives observed values in Clarendon type, computed values in ordinary type.

In the case of air the computed values of c_p are, with the exception of Moody's, lower than the observed. This may be attributed to uncertainties in the data which are the basis of the computation; it is to be noted, however, that Partington's method yields values slightly lower yet. For hydrogen the two methods are identical, as would be expected when there is no question of equation of state.

II. At – 191° C.

The same one-liter flask was placed in a liquid air bath—an open metal can well packed in cotton so that two liters of air sufficed for one and a half hours' work—and it was found that observations could be obtained with surprising ease and precision. The fixed junction was kept in ice, and in order to balance the large electromotive force due to 190°, a second potentiometer was applied to the thermojunction circuit having a fall of 1.5 volts through about 800 ohms; 3 ohms were sufficient almost to balance the thermal E.M.F., and the close adjustment was made on the Wolff potentiometer arranged as before. In this way the resistance in the thermojunction circuit was kept small, and the thermometric arrangement was quite as sensitive as at 20°. It was more difficult to reproduce pressures, and the temperature of the bath inevitably changed by about .5° between beginning and end of a complete observation. The procedure was in other respects the same as at 20°.

The temperature-E.M.F. line was obtained very simply by measuring the E.M.F. in pure oxygen (used air was accumulated until a liquid was secured which maintained its temperature to 1/4000 for seven hours) and then in new air, the temperature of the latter being obtained from Baly's data[1] by displacing the line somewhat to accord with Henning's temperature for oxygen[2] (− 183.00°), and Fischer's for nitrogen[1] (− 195.67°) C. This method was checked closely by calibrating a platinum thermometer, and then calibrating the thermojunction against it. The calibration constant of the junction in this region is 1.68×10^{-5} volts per degree.

The data obtained are shown in Table V.

Table V.

ΔP.	P.	T.	ΔT.	γ.	Mean γ.
13.84 gm./cm.²	1,011.26 gm./cm.²	81.05° A.	.394°	1.559	
14.01	1,020.51	80.35	.394	1.564	
14.39	1,018.89	81.85	.411	1.561	
14.61	1,013.50	83.33	.427	1.560	
14.20	1,006.70	82.52	.419	1.571	1.563
36.79	1,020.80	81.50	.968	1.509	
36.82	1,018.89	82.43	.978	1.506	
37.11	1,006.35	82.30	1.015	1.521	
36.56	1,007.05	82.33	1.011	1.530	
36.43	1,012.90	82.51	1.011	1.535	1.520

γ for $P \doteq 0$, **1.590**

The correction factor for hydrogen at 82° Å. is 1.0011. Hence the final value in the ideal gas state is 1.592 at a mean temperature of 82°, as compared with Scheel and Heuse's value 1.595 at 92°, and Eucken's 1.605 at 92°, or 1.624 at 82°. (These latter are computed from the relation, $C_p - C_v = R$, corrected in accordance with Berthelot's equation, as indicated by Scheel and Heuse.) The value here obtained might be slightly smaller except for the unfortunate circumstance that the mean temperature of the bath during observations at $P = 14$ gm./cm.² is lower than at 37 gm./cm.². The smaller value of γ agrees more closely than Eucken's, however, with the Planck-Einstein formula for C_v. With a specially designed thermostat, this method might well be made a more precise method of investigating specific heats of gases at low temperatures than direct measurement of either C_p or C_v.

At the conclusion of this work the author wishes to testify to her

[1] Phil. Mag. (5), 49: 517.
[2] Ann. der Phy. (4), 35: 761.
[1] Ann. der Phy. (4), 9: 1149.

appreciation of the friendly interest of all the Ryerson staff during its progress, and to her especial indebtedness to Professor Millikan for the constant encouragement and helpfulness of his oversight.

SUMMARY.

1. Observations by the Lummer and Pringsheim method in a one liter flask have been found to yield for air, $\gamma = 1.4029$, a value in close agreement with already accepted values.

2. For hydrogen, γ is found to be 1.4012 at 18° C., 5. per cent. lower than previous values, with no apparent explanation of the divergence.

3. For hydrogen at − 191° C., γ becomes 1.592, in general accordance with the quantum theory of specific heats.

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