in which Q_0 is the initial quantity and Q the quantity remaining after a time t (seconds).

$\lambda = -\frac{dQ}{Q}\frac{1}{dt}$ represents the fraction of the element transformed, reduced to the unit of time.

In the case of a double transformation, the values between brackets [ ] refer to the constants corresponding with the separate branches, the constant for both branches not being put between brackets.

The sign (?) indicates that the value has been indirectly deduced from the range of the α-rays expelled.

$\theta = \frac{1}{\lambda}$ is the average life of the radioactive atoms.

T is the period, that is, the time in which the quantity of radio element is diminished to one half.

$$\lambda T = -\log_e 0.5 = 0.69315 \text{ and } \theta = 1.443\ T$$

Radiation.—The parentheses () indicate that the radiation is relatively feeble.

a_0 is the range in centimeters of the α-rays in air at 0° and a pressure of 760 mm. of mercury.

The range at τ° and under p mm. of mercury is

$$a = \frac{a_0(273 + \tau)760}{273\,p}$$

V is the velocity of α- or β-rays relative to that of light.

To convert to cm./sec. multiply by 3×10^{10}.

For the α-rays, $V = 0.0342\ a^{1/3}$.

$\mu_{\beta \mathrm{Al}}$ is the absorption coefficient of the β-rays in aluminum, the thickness being measured in cm.

$\mu_{\gamma \mathrm{Al}}$ and $\mu_{\gamma \mathrm{Pb}}$ are the absorption coefficients of the γ-rays in aluminum and lead, respectively, the thickness being measured in cm.; the latter is given for only the most penetrating type of γ-rays.

If I_0 is the initial intensity and I the intensity after the rays have traversed x cm. of the absorbent, $I = I_0 e^{-\mu x}$; $\log_{10} \frac{I_0}{I} = 0.4343\ \mu x$.

If D is the thickness corresponding with the absorption of $^1/_2$ of the rays, $\mu D = 0.693$.

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THE SPECIFIC HEATS OF POLYATOMIC GASES AT LOW TEMPERATURES

BY RUSSELL W. MILLAR

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The specific heats of monatomic gases obey the equipartition law over a wide range of temperature[1] if we assume that the molecules have only translational energy. Even at high temperatures the specific heats of diatomic gases do not reach the value predicted by the equipartition law for all temperatures, and the experimental values decrease at first slowly, and then more rapidly, with decreasing temperature. Thus Eucken[2]

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[1] Pier, *Z. Elektrochem.*, 15, 536 (1909).

[2] Eucken, *Ber. Berl. Akad.*, 1912, p. 141.

found that the heat capacity of hydrogen reached an approximately constant value of $^3/_2\ R$ below 60° A., and Scheele and Heuse,[3] and Heuse[4] have found considerable decreases for nitrogen, oxygen and carbon monoxide, as well as for carbon dioxide. The latter authors have also confirmed Eucken's values for hydrogen as far as liquid-air temperatures. These data show that, as predicted by Lewis and Adams[5] the heat capacity of hydrogen decreases much more rapidly with the temperature than that of other diatomic gases.

By a study of the specific heats of polyatomic gases it was hoped to determine whether or not the first increase in heat capacity above $^3/_2\ R$ is due to rotational energy, as has usually been assumed, or to vibrational energy.

Method

The gas was passed through a calorimeter, or heat interchanger, so that the temperature of the gas was lowered by an amount ΔT_g and that of the calorimeter was raised by an amount ΔT_c. When N_g moles of gas were passed through the calorimeter the heat lost by the gas was $N_g C_p \Delta T_g$, where C_p is its molal heat capacity at constant pressure. Likewise, that gained by the calorimeter was $N_c C_p' \Delta T_c$, where N_c and C_p' denote the gram atoms of copper in the calorimeter and the atomic heat capacity of copper at constant pressure. Assuming Newton's law of cooling for the heat exchange between the calorimeter and its surroundings, the heat gained from this source could be calculated and subtracted from the total heat gained, so that

$$C_p = \frac{N_c C_p' \Delta T_c' - Z}{N_g \Delta T_g} = \frac{N_c C_p' \Delta T_c}{N_g \Delta T_g}$$

where Z, the correction term, may be either positive or negative, and $\Delta T_c'$ is the total temperature rise of the calorimeter.

Preparation of Materials

Air was drawn from out of doors and freed from carbon dioxide and water vapor.

Methane was prepared by the hydrolysis of magnesium methyl iodide dissolved in ether. The Grignard reagent was boiled to expel any ethane formed in its preparation. The methane was washed with conc. sulfuric acid to dissolve the ether, passed through a trap immersed in a mixture of solid carbon dioxide and ether, and condensed in liquid air from which it was distilled four times, the last portion of each fraction being discarded.

Methyl chloride was prepared from methyl alcohol and phosphorus trichloride, bubbled through sulfuric acid to remove ethers, and redistilled.

Boron trifluoride was prepared by the action of conc. sulfuric acid on potassium borofluoride ground with an excess of boron trioxide, which was prepared by the dehydration of boric acid. No hydrofluoric acid could be detected by action on the glass generating flask. The product was redistilled.

Hydrogen sulfide was formed by heating a strong solution of magnesium chloride with calcium sulfide. The product was condensed in liquid air and redistilled.

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[3] Scheele and Heuse, *Ann. Physik,* [4] **40,** 473 (1913).

[4] Heuse, *ibid.,* [4] **59,** 86 (1919).

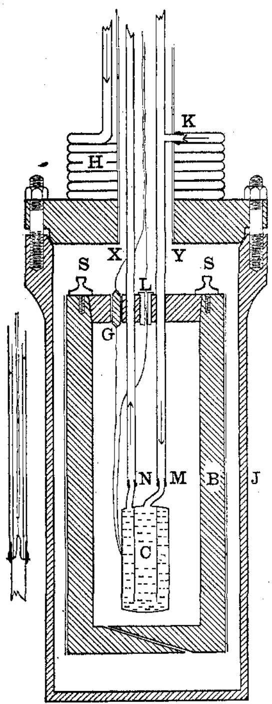
[5] Lewis and Adams, *Phys. Rev.,* **4,** 331 (1914).

Apparatus

The apparatus may be best described by references to the drawing.

Calorimeter.—The calorimeter C is a cylinder 4.4 cm. long and 2.1 cm. in diameter, fitted with a concentric baffle tube soldered to one end. The wall, ends and baffle are of 0.13 mm. copper sheet. The calorimeter is filled with 200 layers of 100-mesh copper gauze both inside and outside the baffle, so that the gas must pass through 400 layers altogether. The inlet and outlet tubes M and N are of 3mm. copper tubing about 15 mm. long.

Block.—In order to secure a constant and known temperature difference between the calorimeter and its surroundings, it was suspended within a heavy closed copper cylinder weighing 3 kg. This cylinder, or Block B, as it is usually called, is wound with Therlo wire in order to control its temperature, and enclosed in a thin copper sheath to prevent heat interchange with the surroundings, which would have been great on account of the shellac used for insulation. The constantan wire of the calorimeter thermocouple passes through the Bakelite insulator L, and the copper wire is soldered to the plug G, which is insulated from the cover with tissue paper soaked in Bakelite. Heat conducted from the outside by the copper wire is absorbed by G and communicated to the block through the thin layer of insulation, while the constantan has low heat conductivity. The block is evacuated through the diagonal hole in the bottom, and is supported by means of its cover, which is soldered to the German silver tubes X and Y passing through it. These tubes attach the calorimeter to the inlet and outlet tubes to which they are soldered.



Vacuum Jacket.—The block and calorimeter are enclosed in the jacket J, which is turned from 10cm. cold-drawn steel hydraulic tubing and welded shut at the lower end. It is 22cm. high and 9.8 cm. in outside diameter, with walls 7 mm. in thickness. The cover fits on a ball-V joint drawn tight by nuts on eight vanadium steel studs. This joint has been made and broken many times, but has not failed to hold a vacuum of less than 10^{-5} mm. of mercury.

The cover of the jacket is fitted with a 25mm. steel tube welded shut at the upper end, which served as a mechanical support, and as a conduit for the thermocouple wires and the German silver tubes X and Y. These tubes passed through the closed end of the steel tube, to which they were soldered. The German silver tubes X and Y were 3 mm. in diameter, and the walls were 0.15 mm. in thickness. Though the heat conductivity of German silver is 30 times that of glass, these tubes have about the same conductivity as tubes of glass of about the same diameter because of their thinness.

The gas was brought to the desired temperature by means of the coil H, and then passed through the apparatus in the direction indicated by the arrows. The resistance of the gas circuit, including the drying tubes, was such that one liter of air could be passed through per minute under a head of 15 cm. of mercury. All the gases except air were condensed after passing through the apparatus and used repeatedly.

Thermometers.—The temperatures of the calorimeter, the block, and the gas were measured by means of single junction thermocouples of silk-insulated No. 40 copper and

No. 36 constantan wire which had been tested for imperfections by examination for thermo-electric effects while they were drawn through liquid air. A coating of Bakelite afforded perfect insulation. These thermocouples were calibrated against the 4-junction couple of Eastman and Rodebush[6] at the temperatures of liquid air, solid carbon dioxide and ether mixture, and melting carbon tetrachloride, and were found to give e.m.f.'s 0.9606 times that of the standard.

The e.m.f. measurements were made with a commercial double potentiometer of 10,000 microvolts range, and a galvanometer of about 20 ohms resistance. The potentiometer and all lead wires were properly shielded against electrical leaks. In the case of the calorimeter thermocouple 1 mm. on the scale corresponded to 1°/2400 at room temperature and 1°/1500 at the temperature of liquid air. Less than 1 mm. could not be read with accuracy, nor was it necessary to do so.

The calorimeter and block thermocouples were led out of the apparatus through holes drilled in the closed top of the vertical steel tube. The gas thermocouple, which was used differentially, was placed with one junction in each of the German silver tubes X and Y at the points M and N. Since it was found that the temperature of a gas flowing at 1 liter per minute through the apparatus could not be measured by the thermocouples unless the tubes X and Y were smaller than 3 mm., in diameter it was found necessary to place the junctions and about 15 cm. of the adjacent wire inside glass capillaries of about 1 mm. internal diameter. These capillaries were kitted tightly with solder inside the tubes M and N of the calorimeter, and the junctions were held out of contact with the walls by tying them to wire hooks in the tubes M and N with about 1 cm. of silk thread. The thermocouple wire was then drawn taut through de Khotinsky seals at the upper ends of the tubes X and Y. This arrangement is shown at the left of the drawing.

It was found that on passing from the point K to the point M the gas took up the temperature of the block, even when the current was as rapid as one liter per minute, providing that the temperature at K was not greatly different from that of the block. The glass capillary, which did not touch the wall of the tube Y, prevented this heat interchange to a large extent in addition to enabling the junction at M to measure the temperature correctly.

When the gas flowed at less than $^1/_2$ liter per minute ΔT_g increased as the rate of flow increased, showing that the differential thermocouple was not yet measuring ΔT_g correctly. When the rate of flow was raised above $^1/_2$ liter per minute ΔT_g decreased as the current of gas increased, as we should expect, since the interchange in the calorimeter was becoming less complete. Complete heat interchange between the calorimeter and the gas was not necessary. A rate of flow of 0.8 to 1.0 liter per minute was always used in the experiments to insure correct measurement by the differential thermocouple.

Baths.—The baths used were melting ice at 273° A., the eutectic mixture of ammonium sulfate and water at 254° A., the eutectic mixture of calcium chloride hexahydrate and water at 218° A., and the eutectic mixture of ether and alcohol at about 138° A. as estimated from the melting points and heats of fusion of ether and alcohol which were assumed constant. The mole fraction of alcohol was estimated to be about 0.7. The baths were contained in a Pyrex Dewar tube 51 cm. long and 11 cm. in internal diameter.

Pumps.—The apparatus was evacuated by means of a mercury diffusion pump supported by a Nelson water-cooled 3-stage oil pump. The pressure could easily be reduced to 10^{-5} mm. of mercury; as shown by a 400cc. McLeod gage. When not in use the apparatus was filled with hydrogen at about 2cm. pressure which aided greatly in cooling the block and calorimeter, and was much more rapidly pumped out than air.

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[6] Eastman and Rodebush, THIS JOURNAL, **40,** 489 (1918).

Calibration of the Calorimeter

Since the calorimeter was soldered to the German silver tubes at M and N, and the weight of the solder used there and in soldering on the thermocouple could not be determined, it was found necessary to determine the heat capacity of the calorimeter by assuming one value for one gas. The value chosen was 6.99 calories per mole as the heat capacity at constant pressure of air at 5°, as determined by Swann[7] and by Scheele and Heuse.[8] Four determinations, which checked within 0.40% of the mean, gave the heat capacity of the calorimeter as 5.20 calories at 5° C., which corresponds to 0.897 mole of copper, taking the value of 5.80 for copper from Griffiths and Griffiths.[9] This calculation was justified by the check on methane by Heuse[4] at 200° A. The calorimeter weighed 55 g. and the solder was estimated to weigh about 2 g. Though the values for copper of Griffiths and Griffiths check those of Nernst[10] and of Naccari[11] at room temperatures, their values in the neighborhood of 140° A. appear high when compared to the specific heats of other metals by means of the usual curve[12] for these elements. Therefore, the heat capacity of copper at lower temperatures was taken from unpublished work of Mr. W. F. Giauque of this Laboratory, who determined the heat capacity of a calorimeter of sheet copper over the range from 70° A. to 300° A. The specific heat curve for copper which he obtained followed very closely the normal curve for metals of this class, and fitted well the values of Nernst[13] at low temperatures.

Experimental Procedure

The apparatus was immersed in the bath at the desired temperature, and the temperature of the gas entering the calorimeter at M determined. The sensitivity of the galvanometer in terms of centimeters of scale per microvolt was also determined.

The block and calorimeter were allowed to cool until the block had reached a temperature of about 10° above that of the gas entering at M, when the apparatus was evacuated. The temperature of the calorimeter was then about 0.5–2.0° above that of the block. The temperature of the block was then noted and the cooling rate of the calorimeter determined by readings each minute. Gas was then passed through the calorimeter until it had cooled to approximately the temperature of the block. During the time occupied by the passage of the gas, which was measured with a stop watch, the differential thermocouple was read every half minute.

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[7] Swann, *Phil. Trans. Roy. Soc.* **210A,** 199, 238 (1910).

[8] Scheele and Heuse, *Ann. Physik,* [4] **37,** 79 (1912).

[9] Griffiths and Griffiths, *Phil. Trans. Roy. Soc.* **214A,** 319 (1914).

[10] Nernst, *Sitz. Berl. Akad.,* **1910,** 247.

[11] Naccari, *Atti accad. Sci. Torino,* **23,** 107 (1888).

[12] Lewis and Gibson, THIS JOURNAL, **39,** 2554 (1917).

[13] Nernst, *Ber. Berl. Vkad.,* **1912,** p. 1160.

The temperature of the calorimeter was then measured each minute. Equilibrium, as shown by a constant rate of cooling, was attained in about two minutes. The temperature of the block was again read, and the weighings, pressure and temperature measurements necessary to determine the number of moles of gas used were made.

Sample Calculation

The calculations may be best indicated by an illustration.

Block temperature in microvolts: initial, 4232 m.v.; final, 4228. Sensitivity: calorimeter thermocouple, 7.2 cm./m.v.; differential thermocouple, 5.1 cm./m.v. Cooling rate: initial, —0.238 m.v./min.; final, 0.000. Calorimeter temperature: initial, 4270.85 m.v.; final, 4230.13 m.v.; rise, 40.72 m.v. Time of gas flow: 2.70 min.; time to attain equilibrium, 2.30 min.

Correction for heat exchange with surroundings, $2.70 \times \frac{-0.238}{2} = -0.321$ m.v. Temperature rise of calorimeter (corr.), 40.40 m.v. Average temperature of calorimeter, 4250 m.v. dE/dT at this temperature, 25.92 m.v./deg. Temperature rise of calorimeter, 1.559°. Temperature of gas: initial, 4030 m.v.; final, 4244 m.v.; drop, 214 m.v. Average temperature of gas, 4137 m.v. dE/dT at this temperature, 26.51 m.v. Temperature drop of gas, 8.07°. Molal heat capacity of copper at 4250 m.v., 4.76 cal. Heat capacity of calorimeter at 4250 m.v., 4.27 cal. Moles of gas passed through calorimeter, 0.1117.

$C_p = \frac{1.559 \times 4.27}{8.07 \times 0.1117} = 7.38$ cal. at 143° A. and 888 mm. pressure. From this result C_v was calculated, and then C_{p_0} and C_{v_0}, the heat capacities at zero pressure, by means of the well known equations $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$, and $\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$, combined with Berthelot's equation of state, $pv = RT + \left(b - \frac{a}{RT^2}\right)p$, in which R is the gas constant, and $b = \frac{v_c}{4}$, $a = \frac{27}{64}R^2\left(\frac{T_c}{p_c}\right)^3$, where v_c, p_c, and T_c are the critical volume, pressure and temperature.

We obtain the following working equations.

$C_p - C_v = R\left[1 + \frac{27}{32}\left(\frac{T_c}{T}\right)^3 \frac{p}{p_c}\right]^2$; $C_v - C_{v_0} = \frac{27}{16}\left(\frac{T_c}{T}\right)^3 \frac{p}{p_c}$; $C_{p_0} - V_{v_0} = R$. The data used are given in the following table.

TABLE I

DATA FOR CALCULATIONS

Gas	M	T_c	P_c atm.	B. p.
Methane	16.04	177.5	50	109
Methyl chloride	50.49	416	66	249
Boron trifluoride	68.00	...	..	172
Hydrogen sulfide	34.08	373	89	211

The data which were obtained are given in Tables II and III.

TABLE II

OBSERVED VALUES OF C_p

CH_4		CH_3Cl		H_2S	
T	C_p	T	C_p	T	C_p
278	8.42	278	8.89	278	9.00
278	8.29	278	8.96	278	8.91
278	8.22			278	8.85
		260	8.77		
199	8.03	259	8.66	229	9.56
199	8.00			228	9.52
199	7.93			224	9.72
199	7.91			216	9.98
		BF_3			
158	7.27	278	11.78		
158	7.19	278	11.72		
158	7.16	278	11.60		
143	7.38	190	9.96		
142	7.22	189	10.05		
139	7.12	189	9.97		

TABLE III

CALCULATED VALUES OF C_v, C_{p_0}, AND C_{v_0}, AND THE SPECIFIC HEAT RATIO

$X = \frac{C_p}{C_v}$ $\quad X_0 = \frac{C_{p0}}{C_{v0}}$

Gas	T	C_p	C_v	C_{p0}	C_{v0}	X	X_0
CH_4...........	278	8.31	6.30	8.28	6.29	1.32	1.32
	199	7.97	5.92	7.88	5.89	1.35	1.34
	158	7.21	5.11	7.04	5.05	1.41	1.39
	142	7.24	5.10	7.01	5.02	1.42	1.40
CH_3Cl.........	278	8.92	6.73	8.62	6.63	1.32	1.30
	260	8.71	6.47	8.34	6.35	1.34	1.31
BF_3............	278	11.70		Critical data are not known			
	189	10.00					
H_2S............	278	8.92	6.81	8.75	6.76	1.31	1.30
	229	9.56	7.37	9.26	7.27	1.30	1.28
	228	9.52	7.33	9.21	7.23	1.30	1.28
	224	9.72	7.51	9.39	7.40	1.29	1.27
	216	9.98	7.75	9.62	7.63	1.29	1.26

Summary

The specific heats of methane, methyl chloride, boron trifluoride, and hydrogen sulfide have been determined from temperatures near their boiling points to 5° C.

It has been shown that the heat capacities of gases do not depend on the number of atoms in the molecule alone, but upon the masses of the atoms,

the constraints, and the temperature. In the case of hydrogen sulfide the heat capacity increases with decreasing temperature, due to the heat of polymerization and to other causes.

The writer wishes to express his thanks to Professor G. N. Lewis for suggesting the problem and the method of its attack.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

AN ELECTROMETRIC STUDY OF THE NEUTRALIZATION OF PHOSPHORIC ACID BY CALCIUM HYDROXIDE

BY GERALD L. WENDT AND ALFRED H. CLARKE

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The difficulties incident to the indicator titrations of phosphoric acid and acid phosphates are well known. They are due chiefly to the instability and rearrangements of the phosphates produced in the course of the titration, and are magnified in practice both by the erroneous use of phenolphthalein as indicator, and by the use of sodium hydroxide in titration, a stronger base than is used in the commercial reactions with acid phosphates.[1] The instability of the various calcium phosphates has been indicated by numerous investigators but its application to analysis has not been clear. The electrometric method of titration is, however, uniquely adapted to the study of changes taking place during titration, and the following investigation was, therefore, undertaken to elucidate these changes. The complications produced by the instability of dicalcium phosphate are strikingly shown, and methods for their avoidance are indicated.

Several forms of exact electrotitration apparatus,[2] which were commercially available, are capable of determining the Sörensen (P_H) value within 0.01. Such accuracy, however, is unnecessary in ordinary chemical titrations and the instruments were therefore unnecessarily expensive. The apparatus used[3] was developed for the purpose, and can easily be assembled in any laboratory. It is independent of an exact potentiometer, a constant source of current, a calibrated rheostat, a standard cell, or any form of electrometer. It is based on the recommendations of J. H. Hildebrand.[4]

Phosphoric Acid with Calcium Hydroxide.—The curves shown herewith are plotted from the titrations, in the usual way, with abscissas representing cubic centimeters of alkaline or acid solution which is added, and ordinates representing the P_H value. The titration of phosphoric acid

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[1] Wadman, *J. Ind. Eng. Chem.*, **13**, 1146 (1921).

[2] Leeds and Northrup Co., Catalog 75. Arthur H. Thomas Co., Supplement 63.

[3] Bulletin 86, Central Scientific Company.

[4] Hildebrand, THIS JOURNAL, **35**, 847 (1913).