I. A. THE OXIDATION POTENTIAL OF CEROUS-CERIC SALTS IN AQUEOUS NITRIC ACID SOLUTION.

B. THE OXIDATION POTENTIAL OF THALLOUS-THALLIC SALTS IN AQUEOUS NITRIC ACID SOLUTION.

II. AN ATTEMPT TO DETERMINE THE ELECTRODE POTENTIAL AND RAMAN SPECTRUM OF FLUORINE. THE ENTROPY OF FLUORINE.

III. A. THE CONSTRUCTION OF A LOW TEMPERATURE VACUUM CALORIMETER.

B. THE HEAT CAPACITY OF MONOFLUOROTRICHLOROMETHANE FROM 60°K TO ITS BOILING POINT. ITS HEAT OF FUSION, HEAT OF VAPORIZATION, VAPOR PRESSURE AND ENTROPY.

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California

1938

Propositions Submitted for Defense on May 13, 1938

1. The statement is made by Noyes and Sherrill (Chemical Principles. Macmillan Co., New York, 1934. Second edition, page 183):

> "By integrating Eq. 2 $\left\{(d\ln p/dT) = \Delta\tilde{H}/RT^2\right\}$ for the case that $\Delta\tilde{H}$ does not vary with the temperature, the following equation is obtained. . . . .
>
> $$\ln\frac{p_2}{p_1} = \frac{\Delta\tilde{H}}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \text{ . "}$$

In deriving this last equation it is not true that $\Delta\tilde{H}$ must be independent of the temperature, as is implied by them and by others (Millard, Physical Chemistry For Colleges. McGraw-Hill Book Co., New York, 1936; page 92. MacDougall, Physical Chemistry. Macmillan Co., New York, 1936;page 89. Fermi, Thermodynamics. Prentice-Hall, Inc., New York, 1937; page 67.), provided that a proper interpretation be given the symbol $\Delta\tilde{H}$.

2. The value of 37.29 cal./deg./mole given by Kanda (Bull. Chem. Soc. Japan 12, 511 (1937)) for the virtual entropy of ideal fluorine gas at its normal boiling point is probably low by one or two entropy units.

3. Although thallous and thallic anion complexes have been reported in the chemical literature, present experimental evidence indicates that thallous and thallic ions do not form stable complexes with nitrate, perchlorate or hydrosulfate ions in aqueous solutions in which the anion is present in moderate concentration.

4. The method for the volumetric estimation of thallium by titration of the thallous salt with a standard potassium iodate solution in the presence of iodine monochloride, as studied by Swift and Garner (J. Am. Chem. Soc. 58, 113 (1936)), possesses certain advantages over other volumetric methods proposed in the literature for the determination of thallium.

5. The statement of Noyes and Garner (J. Am. Chem. Soc. 58, 1276 (1936)) that a nitrate complex of ceric ion is formed scarcely, if at all, in nitric acid solutions 0.5 to 2f, is probably incorrect. The postulate that both cerous and ceric ions form nitrate complexes in nitric acid solutions of moderate concentration is compatible with existing experimental data.

6. The explanation advanced by G. F. Smith (Ind. Eng. Chem., Anal. Ed. 6, 230 (1934); also, the booklet, Ceric Sulfate, Vol. I, G. F. Smith Chemical Co., Columbus, Ohio, 1935, page 19) to account for the fact that ceric perchlorate cannot be obtained by oxidation of cerous perchlorate with hot, concentrated perchloric acid, is not entirely convincing. An alternative explanation can be proposed which is in agreement not only with the observed chemical facts, but also with the present view of the molecular structure of perchloric acid.

7. The assumption that the complex ions $AgCl_2^-$, $AgCl_3^{=}$, $AgCl_4^{\equiv}$, and $HAgCl_3^-$ are formed in aqueous hydrochloric acid solutions is in agreement with the solubility of silver chloride in hydrochloric acid solutions 0.005 to 16 molal, determined by Forbes (J. Am. Chem. Soc. *33*, 1937 (1911), Forbes and Cole (ibid. *43*, 2492 (1921)), and Åkerlöf and Teare (ibid. *59*, 1857 (1937)), if *one* ignores in the calculations the activity coefficients of all the ions involved.

8. The theory of overvoltage recently advanced by Lemarchands and Juda (Compt. rend. *205*, 730 (1937)) is unable to explain certain experimental facts.

9. The statements of Fermi (Fermi, *Thermodynamics*, Prentice-Hall, Inc., New York, 1937; page 139), that *all possible* states of a system at the absolute zero have the same entropy, and that the entropy of every system at the absolute zero can always be taken equal to zero, are probably too general.

10. The time has come to subdue the older idea of three sharply differentiated macroscopic states of matter ("solid", "liquid", and "gaseous"). Emphasis should be placed on the existence of many intermediate states, which tends to "smear out" the states in which gross matter exists into a"continuum".

11. Manufacturers of gas furnace equipment and heat engineers in general should make use of certain scientific principles in connection with the problem of heat losses. Standard practice in "insulating" hot-air furnace pipes often results in a very large increase in heat loss.

12. The course in Instrumental Analysis, Ch. 16, given at C.I.T., would be improved if:
    - a. it were extended to two terms,
    - b. the teaching were carried out, not by a graduate assistant, but by an instructor assigned to the course on a semi-permanent basis,
    - c. no detailed reports, involving the "sources of errors in the methods, etc.", were required, but rather preliminary question sheets to be answered in advance of each experiment, a report of numerical data and conclusions, and a final examination covering the more theoretical aspects of the course.

13. A recent method for the determination of air and carbon dioxide in beer, anonymously proposed (Ind. Eng. Chem., News Ed. *16*, 152 (1938)), can be improved upon considerably.

Respectfully submitted,

Clifford S. Garner

Clifford S. Garner

Abstract

I.A. Potential measurements made at 25 and 0°C on cells of the type

$$Pt + H_2(p\ atm.),\ HClO_4(c'), \left\{ HNO_3(c) + \begin{matrix} Ce^{IV}(c_2) \\ Ce^{III}(c_1) \end{matrix} \right\},\ Pt$$

give the value 1.6093 ± 0.0007 volts for the formal cerous-ceric oxidation potential at 25°C, substantially independent of the nitric acid concentration in the range 0.5 to 2f.

The decrease in free energy, heat content and entropy at 25°C found for the reaction

$$Ce^{IV}(1f) + E^{-I} = Ce^{III}(1f)$$

in nitric acid 0.5 to 2f are, respectively, 37,120 cal., 34, 970 cal. and -7.2 cal./deg.

Evidence is discussed for nitrate complex ions of both cerous and ceric ions in nitric acid.

B. Measurements on cells of a similar type involving thallium salts give 1.2302 ± 0.0007 volts for the formal thallous-thallic oxidation potential at 25°C, independent in the range 0.5 to 2f of the concentration of nitric acid.

For the reaction

$$Tl^{III}(1f) + 2E^{-I} = Tl^{I}(1f)$$

in nitric acid 0.5 to 2f the decrease in free energy, heat content and entropy at 25°C were found to be 56,800 cal., 30,700 cal. and -87.6 cal./deg., respectively.

II. An attempt to experimentally determine the electrode potential of fluorine met with failure because of non-reproducibility.

No Raman lines due to fluorine could be discovered when plates were exposed up to four hours to the light of a mercury arc scattered by liquid fluorine in a quartz container.

The value 48.6 cal./deg./mole has been calculated for the standard virtual entropy of fluorine from the internuclear distance and Badger's Rule. The calorimetric data of Kanda lead to a value which has been shown to be too low.

III.A. A vacuum calorimeter has been constructed for the determination of heat capacities of condensed gases from 60°K to room temperature. Descriptions of it, the manometer, electrical circuits and instruments, and of the establishment of a temperature scale are given.

B. The heat capacity of crystalline CCl_3F has been measured from 60°K to its melting point (162.54 ± 0.05°K), and the heat capacity of the liquid determined from the melting point to the boiling point.

The heat of fusion at the melting point has been determined as 1641.8 ± 3.2 cal./mole.

The vapor pressure of the liquid was determined over the pressure range 5 to 72 cm. Hg; the observations can be represented by the equation:

$$\log_{10} P\ (\text{int. cm Hg}) = -\frac{1610.04}{T} + 8.21671 - 0.0030743\ T.$$

From this equation the normal boiling point is calculated to be 296.88 ± 0.05°K, and the heat of vaporization at the boiling point to be 5905 ± 30 cal./mole after a Berthelot correction of -220 cal./mole is made. The Trouton's constant is then 19.89.

An extrapolation of the heat capacity to the absolute zero gives 71.92 ± 1.5 cal./deg./mole for the standard virtual entropy of the ideal CCl_3F gas. This value is 2.2 cal./deg./mole lower than the "spectroscopic" value.

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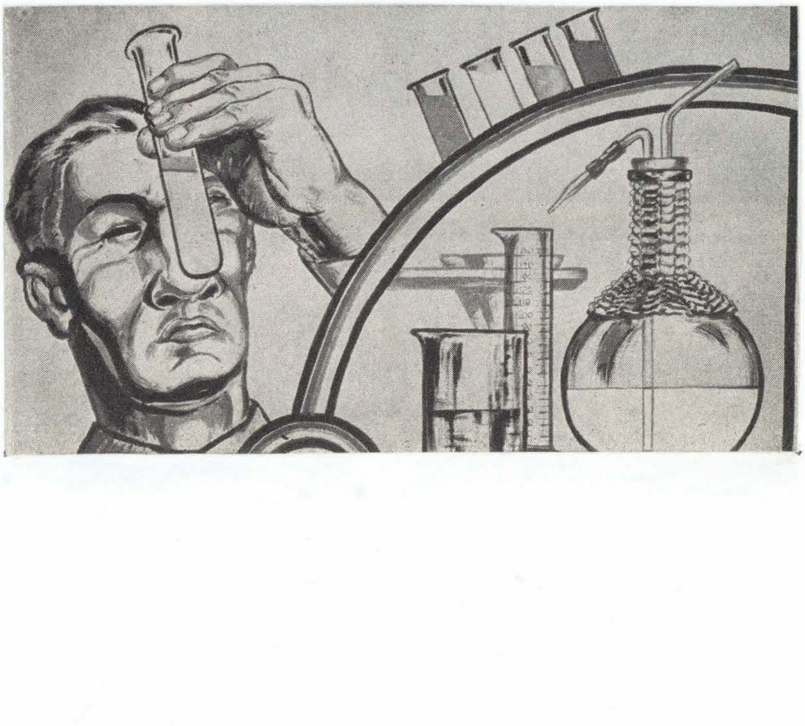

THE OXIDATION POTENTIAL OF CEROUS-CERIC SALTS IN AQUEOUS NITRIC ACID SOLUTION

Introduction

At the suggestion of Professor Arthur A. Noyes this study of the cerous-ceric oxidation potential was begun during the summer of 1935 at the Kerckhoff Marine Laboratory, Corona del Mar, California, and completed early in 1936 at the California Institute of Technology, Pasadena. The unfortunate death of Professor Noyes in June, 1936, prevented his reading this paper prior to its publication in its final form, and for this reason the junior author assumes full responsibility for such imperfections as exist in this paper.

This research is part of a series of investigations planned to determine the oxidation potentials of strong oxidizing substances in aqueous nitric acid solution in order that more accurate data may be made available for the prediction of chemical reactions involving such oxidizing substances. The data are also examined with the view of investigating the possible formation of nitrate-metal ion complexes.

[Reprint from the Journal of the American Chemical Society, **58**, 1265 (1936).]

[Contribution from the Gates and Crellin Chemical Laboratories of the California Institute of Technology, No. 546]

Strong Oxidizing Agents in Nitric Acid Solution. I. Oxidation Potential of Cerous–Ceric Salts

By Arthur A. Noyes and Clifford S. Garner

Plan of these Investigations

In connection with the recent investigations made by Noyes, Hoard, Pitzer and Dunn[1,2] of argentic salts in nitric acid solution, electromotive force measurements were made by Noyes and Kossiakoff[3] to determine the oxidation potential of argentous–argentic salts (Ag^{I}, Ag^{II}); and the result (1.914 volts) was compared with those of other strong oxidizing agents for which reliable data exist. As these data are rather limited, it seemed desirable to carry out researches on the oxidation potential of other powerful oxidizing substances; and it is the purpose of this series of papers to present the results obtained with cerous–ceric salts (Ce^{III}, Ce^{IV}), with thallous–thallic salts (Tl^{I}, Tl^{III}), and with cobaltous–cobaltic salts (Co^{II}, Co^{III}) in nitric acid solution.

The method of measurement was much the same as that used for argentous–argentic salts by Noyes and Kossiakoff, to whose article reference should be made for certain details of procedure. The conditions are simpler, however, in the case of ceric nitrate or thallic nitrate, in that these substances, unlike argentic nitrate, do not undergo at room temperature spontaneous reduction to cerous or thallous salt.

In this first paper are presented the results of measurements on cerous–ceric cells. Such cells were first measured by Baur and Glaessner.[4] They used cells containing cerous and ceric salts in nitric and sulfuric acid solutions; but carried out the work at "room temperature," and eliminated the liquid potential only to the extent that this is accomplished by inserting a saturated solution of potassium chloride between the cerium and the calomel electrodes. A satisfactory value therefore cannot be calculated for the oxidation potential from their data.

More recently, Kunz[5] studied the formal potential of cerous–ceric salts in 0.5 and 1.0 formal sulfuric acid solutions.

In order to determine the value in nitrate solution, which is likely to form complexes to a less extent, and to eliminate largely the liquid potential, we measured at 25 and at 0° cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(p\ \mathrm{atm.}),\ \mathrm{HClO_4}\,(c'),\ \left\{\mathrm{HNO_3}\,(c) + \frac{\mathrm{Ce^{IV}}\,(c_2)}{\mathrm{Ce^{III}}\,(c_1)}\right\},\ \mathrm{Pt}$$

These experiments will now be described.

Apparatus and Materials

Preparation and Analysis of Solutions.—In preparing the stock solutions of cerous and ceric nitrate, C. P. hydrated cerous nitrate was used to make up a solution approximately 0.1 *f* in cerous nitrate and 1 *f* in nitric acid (to prevent subsequent hydrolysis). A 17-cm. layer of this solution gave no absorption spectrum, showing the absence of other rare-earth elements. The solution was then divided into two nearly equal portions.

A solution of ceric nitrate was prepared by electrolytic oxidation of one of these portions with a current of 2 amperes at 6–8 volts, till samples removed and titrated with ferrous sulfate solution showed that the oxidation was nearly complete.

The ceric nitrate solution thus prepared was analyzed as

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[1] Noyes, Hoard and Pitzer, This Journal, **57**, 1221–1229 (1935).

[2] Noyes, Pitzer and Dunn, *ibid.*, **57**, 1229–1237 (1935).

[3] Noyes and Kossiakoff, *ibid.*, **57**, 1238–1242 (1935).

[4] Baur and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

[5] Kunz, This Journal, **53**, 98 (1931).

follows. Samples were weighed out, and, after adding the proper amount of water and sulfuric acid, the solutions were titrated with standard ferrous sulfate solution potentiometrically, using a vacuum-tube voltmeter. The amount of ceric cerium was thus obtained. The total cerium was determined by titration after oxidation of the cerium with ammonium peroxysulfate, using silver nitrate as a catalyst.[6] The nitric acid content was determined, after removing the cerium, by titration with standard sodium hydroxide solution, using phenolphthalein as indicator. To remove the cerium, the sample was shaken with mercury and a little potassium chloride till all the cerium was reduced to the cerous state; then sodium oxalate was added, the mixture was filtered, and the acid determined in the filtrate, tests having shown that no appreciable amount of nitric acid was adsorbed on the precipitate. The solution was diluted by weight to give a stock solution exactly 1.000 *f* in nitric acid, and check analyses were made. The ceric nitrate stock solution prepared in this manner was 0.1057 *f* in ceric nitrate and 0.004181 *f* in cerous nitrate.

The other portion of the original cerous nitrate solution was analyzed in much the same way. It was diluted by weight so as to be exactly 1.000 *f* in nitric acid, and then again analyzed. The resulting stock solution of cerous nitrate was 0.08292 *f* in cerous nitrate and contained no ceric nitrate.

The solutions of perchloric acid were prepared by dilution of C. P. 60% perchloric acid, and were standardized against a sodium hydroxide solution.

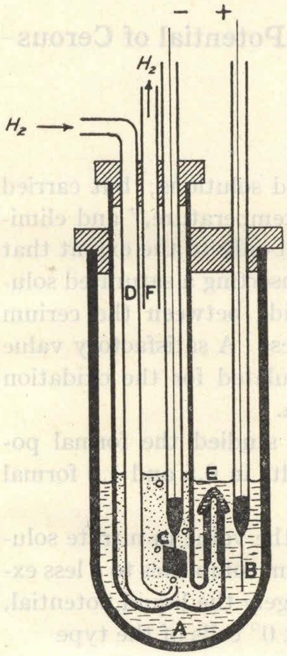

Fig. 1.

Tank hydrogen was purified by passing it successively through concentrated potassium hydroxide solution and concentrated sulfuric acid, and over solid potassium hydroxide and an electrically heated platinum wire.

The Electrolytic Cell.—The assembled electrolytic cell is shown in Fig. 1. A large test-tube served as a container A for the cerous–ceric mixture, in which was immersed the hydrogen half-cell and a platinum wire electrode B. Measurements were made with the platinum wire bright and with it platinum-blacked; there was no difference in potential, although the latter electrode came to equilibrium with the solution much more rapidly. The hydrogen half-cell vessel contained the perchloric acid solution into which dipped a platinized platinum foil electrode C and a tube D through which the hydrogen was bubbled in; the vessel was also equipped with a short vertical capillary side-arm provided with a ground glass cap E which prevented liquid diffusion while allowing electrolytic contact. Before entering the half-cell the hydrogen passed through a glass coil and a vessel containing perchloric acid of the same concentration as that used in the half-cell. In addition a small "bubbler" was provided at the hydrogen outlet F to ensure a hydrogen atmosphere in the half-cell. The apparatus was immersed in a thermostat maintained at 25.00 ± 0.01°, or in one kept at 0°.

Method of Potential Measurements.—A Leeds and Northrup Type K potentiometer was used in conjunction with a high-sensitivity galvanometer for the measurements of the electromotive force. The Weston standard cell used was carefully checked at 25° against a new laboratory standard.

Cerous–ceric mixtures containing varying amounts of nitric acid were prepared from the stock solutions and a standard nitric acid solution by weighing. While each mixture was attaining thermal equilibrium in the cell, the hydrogen electrode was checked at 25° against a 1 *N* hydrochloric acid calomel electrode which had been prepared with purified chemicals in the presence of air.[7] The hydrogen half-cell was then placed in the electrolytic cell, and the potential observed over a period of one to fifty hours. In all cases equilibrium was attained within one hour, and readings were constant thereafter to 0.3 mv. or better; stirring had no effect on the potential. The hydrogen half-cell was checked against the calomel electrode after each run; the calculated value being always obtained to within 0.1 mv.

Calibrated volumetric apparatus, thermometers and weights were employed in this research, and all weighings were corrected to vacuum.

Measurements at 0°.—One of the cells which had been measured at 25° was placed in a 0° thermostat, and measurements of the electromotive force were made over a period of several days. The readings were constant to 0.2 mv., and upon returning the cell to the 25° thermostat, it gave a value for the potential within 0.1 mv. of that previously determined.

The Observed and Computed Electromotive Forces

In Table I are recorded the electromotive forces observed at various concentrations of the substances involved, the corrections computed for reducing these to standard concentrations and eliminating the liquid potential, and the final formal electrode potential thereby obtained.

The first column of the table shows the temperature, 25 or 0°. In the next five columns are given the weight formalities *f* (the concentrations in formula weights per kilogram of water) of the substances in the cells. In the next two columns are the mean ionic strength μ of the cerous–ceric mixtures, and the observed electromotive forces $E_{obsd.}$. The activity coefficients α of the two

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[6] Willard and Young, THIS JOURNAL, **50**, 1322, 1379 (1928).

[7] The value −0.2689 volt is the molal electrode potential of the hydrochloric acid calomel electrode for the case in which oxygen is not excluded. See Randall and Young, THIS JOURNAL, **50**, 989 (1928). The activity coefficients of hydrochloric acid solutions were taken from this same source.

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$Ce(NO_3)_3$ c_1	$Ce(NO_3)_4$ c_2	Ce^{III}/Ce^{IV} c_1/c_2	Mean ionic strength, μ	$E_{obsd.}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.03284	0.03932	0.8350	2.59	1.6001	−0.0046	−0.0096	+0.0244	1.6103
	(α, 0.759)		.03284	.03932	0.8350		1.6002	− .0046	− .0096	+ .0244	1.6104
		(α', 1.295)									
										Mean	1.6104
25	1.000	1.000	.06513	.02387	2.728	1.82	1.5915	+ .0258	− .0023	− .0047	1.6103
	(α, 0.706)		.06016	.03055	1.969		1.5997	+ .0174	− .0023	− .0047	1.6101
		(α', 0.803)	.04504	.05083	0.8861		1.6197	− .0031	− .0023	− .0047	1.6096
			.04468	.05133	.8705		1.6202	− .0036	− .0023	− .0043	1.6100
			.02768	.07413	.3734		1.6412	− .0253	− .0023	− .0047	1.6089
			.02288	.08146	.2809		[illegible].6488	− .0326	− .0023	− .0051	1.6088
			.01808	.08703	.2077		1.6569	− .0403	− .0023	− .0051	1.6092
										Mean	1.6096
25	0.5000	1.000	.02191	.02624	.8351	0.89	1.6330	− .0046	− .0147	− .0051	1.6086
	(α, 0.708)		.02191	.02624	.8351		1.6328	− .0046	− .0147	− .0051	1.6084
		(α', 0.803)									
										Mean	1.6085
										General Mean	**1.6095**
0	1.000	1.000	.04468	.05133	.8705	1.83	1.6106	− .0033	− .0021	− .0040	**1.6012**
	(α, 0.706)	(α', 0.803)									

acids are given below their concentrations, the coefficients being interpolated from the data of Pearce and Nelson[8] for perchloric acid at 25° and from those of Abel, Redlich and v. Lengyel[9] for nitric acid at 25°. In the next three columns are the values of the electromotive force corrections computed as described below, and in the last column are the values of the formal oxidation potential E^0 referred to the standard molal hydrogen electrode H_2 (1 atm.), H^+ (activity 1 m.); by formal oxidation potential being meant the oxidation potential when the total concentrations, represented by Ce^{IV} and Ce^{III}, of the oxidized and reduced cerium (without reference to their ionization) are both 1.0 *f*.

This formal oxidation potential E^0 (for the reaction $Ce^{IV} + E^{-I} = Ce^{III}$) has been derived by adding to the observed electromotive force $E_{obsd.}$ (which is that of the cell formulated in the first section of this paper) the three following quantities:

(1) $E_C = (RT/F) \ln (c_1/c_2)$, in order to provide for equiformal concentrations of cerous and ceric cerium, their total concentrations c_1 and c_2 being used in this Nernst equation in place of the ion activities.

(2) $E_L = (2T_H - 1)(RT/F) \ln (\alpha c/\alpha' c')$, in order to eliminate the small liquid potential arising from the different ion activities αc and $\alpha' c'$ of the nitric and perchloric acids; it being assumed that the ion mobilities of the two acids are equal in the given concentration range. The mean transference number T_H of the cation of the two acids has been estimated[10] to have the value 0.85 at 25° and the value of 0.86 at 0°.

(3) $E_H = (RT/F) \ln (\alpha' c'/\sqrt{p_{H_2}})$, in order to refer the value to the molal hydrogen electrode standard at 25°, p_{H_2} being the partial pressure of the hydrogen gas in atmospheres.

Discussion and Summary

It is seen from Table I that the formal cerous–ceric oxidation potential E^0 changes only slightly (at most by 1.5 mv.) on varying the ratio Ce^{III}/Ce^{IV} over ten-fold at constant ionic strength. Moreover, varying the acid concentration from 0.5 to 2.0 *f* and the ionic strength correspondingly has only a small effect on the value of E^0. This shows that nitrate complexes are formed only slightly, if at all, and that a hydrolytic reaction such as $Ce^{++++} + H_2O = CeOH^{+++} + H^+$ does not occur appreciably at these concentrations. Hence the value **1.6095** ± 0.0007 volt may be regarded as the cerous–ceric oxidation potential in nitric acid at 25°, independent of the concentration of that acid between 0.5 and 2.0 formal.

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(8) Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

(9) Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

(10) This estimate at 25° is based on the considerations that the two acids have equal conductances at 2.0 *f*, that the nitric acid solution contains less than 10% as much cerium as acid, so that its conductance does not differ greatly from that of pure nitric acid, and that the latter has the values recorded in "International Critical Tables" (Vol. VI, pp. 241, 310 (1929)). For the 0° measurement, the same activity values were used as at 25°, since none are available at 0°.

The value of this potential at 0° was found to be 1.601 volts (in 1.0 *f* HNO_3).

It is interesting to note that in sulfate solution Kunz[5] obtained much smaller values, namely, 1.461 and 1.443 volts at 25° in 0.5 *f* and in 1.0 *f* H_2SO_4, respectively. This indicates that complex formation between the ceric ion and sulfate ion (or hydrosulfate ion) takes place to a large extent. It is probable therefore that the value obtained in nitric acid represents much more nearly the *molal* oxidation potential of cerous–ceric *ions*.

It may also be noted that the cerous–ceric potential in nitrate solution is of the same order as that (1.59 volts)[11] for the reaction $MnO_4^- + 4H^+ + 3E^- = MnO_2(s) + 2H_2O(l)$. Correspondingly, on adding permanganate solution to a nitric acid solution of cerous nitrate, manganese dioxide was found to form; and on adding ceric nitrate solution to freshly precipitated manganese dioxide, the color of permanganate was developed.

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(11) Brown and Tefft, THIS JOURNAL, 48, 1128 (1926).

PASADENA, CALIFORNIA

RECEIVED MAY 12, 1936

values are presented in Table II.

Additional Calculated Results

Table II

Observed and Recomputed Electromotive Forces at 25 and 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$E_{obsd.}$	E_C	E_L	E_H	$E°$
25	2.000	2.000	1.6001	-0.0046	-0.0051	+0.0187	1.6091
	$(\alpha, 0.774)$	$(\alpha', 1.039)$	1.6002	- .0046	- .0051	+ .0187	1.6092
						Mean	1.6092
25	1.000	1.000	1.5915	+ .0258	- .0022	- .0045	1.6106
	$(\alpha, 0.715)$	$(\alpha', 0.811$	1.5997	+ .0174	- .0022	- .0045	1.6104
			1.6197	- .0031	- .0022	- .0045	1.6099
			1.6202	- .0036	- .0022	- .0041	1.6103
			1.6412	- .0253	- .0022	- .0045	1.6092
			1.6488	- .0326	- .0022	- .0049	1.6091
			1.6569	- .0403	- .0022	- .0049	1.6095
						Mean	1.6099
25	0.5000	1.000	1.6330	- .0046	- .0147	- .0049	1.6088
	$(\alpha, 0.715)$	$(\alpha', 0.811)$	1.6328	- .0046	- .0147	- .0049	1.6086
						Mean	1.6087
						General Mean	1.6093
0	1.000	1.000	1.6106	- .0033	- .0020	- .0038	1.6015
	$(\alpha, 0.715)$	$(\alpha', 0.811)$					

Table III

$-\Delta F_{298}$	$-\Delta H_{298}$	$-\Delta S_{298}$
37,120 cal./mol ion	34,970 cal./mol ion	-7.2 cal./deg./mol ion

Additional Discussion

Subsequent to the publication of this paper, there appeared in the Landolt-Börnstein Tabellen (1) revised values of the activity coefficients of nitric and perchloric acids. If these more recent and probably more precise activity coefficients are used, the values of E_L and E_H will be found to be changed appreciably; however, due to the fact that the changes partially cancel one another, the values of E° obtained using these new activity coefficients are not greatly different from those given in Table I. The recomputed values are presented in Table II.

The approximate validity of the formula and assumptions used to calculate the values of the small liquid-junction potentials in the cells measured has been established by Noyes and Deahl (2).

Values for the decrease in free energy, heat content and entropy at 25° for the reaction $Ce^{IV}(1f)+E^{-I} = Ce^{III}(1f)$ in nitric acid solutions 0.5 to 2f have been calculated and are presented in Table III.

Since publication of this paper, it has come to the attention of the author that a nitrate complex is formed with ceric ion, at least in nitric acid solutions 2.5f and more concentrated. Briefly, the evidence for such a complex ion is as follows:

Excess nitric acid does not salt out a ceric salt from a nitric acid solution of $(NH_4)_2Ce(NO_3)_6$, but excess ammonium nitrate does salt out the ceric salt. Cerium can be separated cleanly from nitric acid solutions of the other rare-earths, with the exception of thorium (which also forms a nitrate complex), which indicates that ceric ammonium nitrate has a structure different from the other rare-earths which form "double" salts with ammonium nitrate (3,4). Manganous nitrate precipitates $MnCe(NO_3)_6 \cdot 8H_2O$ from a strong nitric acid solution of ceric nitrate; when this salt is dissolved in dilute acid solution, the manganese is oxidized to manganese dioxide with the reduction of cerium, and hence the ceric nitrate complex ion in strong nitric acid solution must be relatively undissociated or manganese dioxide would be produced there since it is insoluble in concentrated nitric acid (5). The author has carried out preliminary transference experiments on ceric nitrate in 6f nitric acid which indicate that some of the cerium migrates toward the anode; experiments made with 1f nitric acid were not conclusive.

Other evidence has also been cited by Smith, Sullivan and Frank (3). Namely, crystalline $(NH_4)_2Ce(NO)_6$ when dissolved in water does not hydrolyze to insoluble ceric salts, whereas $(NH_4)_2Ce(SO_4)_3$, a "double" salt does so hydrolyze in water. A solution of $(NH_4)_2Ce(NO_3)_6$ in water (2.5n.) has about the same color as a solution 0.1n. in $(NH_4)_2Ce(SO_4)_3$ and 1n. in H_2SO_4. When ferrous salts are titrated with ceric salts in the presence of much nitric acid the rate of oxidation near the equivalence point is noticeably slower than is the case when sulfuric acid is used in place of nitric acid. These statements cannot be accepted as legitimate evidence for a ceric nitrate complex ion, for ceric ion undoubtedly forms a sulfate, or hydrosulfate, complex ion in 1f sulfuric acid, which is more stable than the nitrate complex, as shown by the difference between the cerous-ceric potentials in the two acids. That $(NH_4)_2Ce(SO_4)_3$ does hydrolyze may be interpreted as evidence that the complex in sulfuric acid is a hydrosulfate, and not a sulfate complex. As far as the color of the solutions mentioned is concerned, there is no a priori reason to suppose that the color will be less intense because a complex is formed, or vice versa.

That a nitrate complex is formed with ceric ion is thus definitely established, and it seems likely that it has the formula $Ce(NO_3)_6^{=}$, although further experiments should be made to remove any doubt, as well as to ascertain its stability.

It may be mentioned here that there are other nitrate complex ions known. Thoric ion forms a similar complex with nitrate ion (4,6). (This occasioned some fear that thorium salts might have been present in the cerium nitrate used in this investigation, but experiments carried out in this laboratory by Mr. Philip Smith showed the absence of thorium.) Another nitrate complex is that of argentic silver (7,8). The formulas of these nitrate complexes have not been definitely established.

In view of the fact that a ceric nitrate complex ion may be formed under certain conditions, one is faced with the necessity of explaining why the formal potential of cerous-ceric salts in nitric acid is practically independent of the concentration of nitric acid over the range 0.5 to 2 f. The most obvious answer is that nitrate complex formation is simply not occurring in this range of nitric acid concentration, since all of the evidence for a ceric nitrate complex ion was obtained with solutions more concentrated in nitric acid. Against this hypothesis, however, is the fact that the formal cerous-ceric potential in 2f perchloric acid is about 1.71 volts (9), 0.10 volt more oxidizing than the formal potential in nitric acid. Since this represents nearly a one hundred-fold change in the ratio of the activities of cerous and ceric ions, and since the activity coefficient ratios would not be expected to differ much in perchloric and nitric acid solutions of the same ionic strength, it is very likely that the ratio of the ion concentrations has been changed by complex-formation. One explanation which is compatible with the experiments is that cerous ion also forms a nitrate complex in such a way that the effect of increasing nitrate concentration is offset by a shift in the two complex-ion equilibria and perhaps by a change in the ratio of the activity coefficients also. This may be stated more clearly in another way. The potential measurements indicate that under the stated conditions, $\frac{a_{Ce^{+++}}}{a_{Ce^{++++}}} = (\text{a constant}) \frac{\sum Ce^{III}}{\sum Ce^{IV}}$.

But $$\frac{a_{Ce^{+++}}}{a_{Ce^{++++}}} = \frac{\gamma_{Ce^{+++}}}{\gamma_{Ce^{++++}}} \cdot \frac{(Ce^{+++})}{(Ce^{++++})} =$$

$$\frac{\gamma_{Ce^{+++}}}{\gamma_{Ce^{++++}}} \cdot \frac{\sum Ce^{III} - (\text{cerous nitrate complex})}{\sum Ce^{IV} - (Ce(NO_3)_6^{=})},$$ where

$\underline{a}$ refers to the ion activity, γ the ion activity coefficient, $\sum$ the total formal concentration of cerium salts of the given oxidation state, and the assumption has been made that the ceric nitrate complex has the stated formula. As the nitric acid concentration is increased, more of each nitrate complex is formed, so that the ratio can remain nearly constant. Since the ceric complex is probably more stable than the cerous complex, the ratio may tend to increase slightly. This could probably be offset by a corresponding small change in the activity coefficient ratio. (Present theories do not allow an evaluation of how this ratio would actually change.) Sufficient data to settle this matter are not available at present; an investigation of the effect of nitrate ion concentration upon the potential of a half-cell involving cerium metal and cerous nitrate would give the information needed. Transference experiments made with cerous nitrate in both 6f and 1f nitric acid were not conclusive; there was practically no transference of cerium at all. In the case of cerous perchlorate in 2f perchloric acid there was a more definite evidence of cerium migration to the cathode. This may be interpreted to mean that in nitric acid part of the cerium is transferred towards the cathode and part towards the anode. Unfortunately, the ion-mobilities of hydrogen and nitrate ions are much greater than those for cerous ion or any nitrate complex of cerium.

The possibility that hydroxide may participate in the complex formation with ceric ion to the same extent as nitrate would also explain the observed potentials in nitric acid. To decide this, experiments should be made in which the nitrate and hydrogen ion concentrations are not varied simultaneously. Since the ceric nitrate complex already known is relatively stable and since it contains no hydroxide, the former explanation is believed more likely.

Summary

Potential measurements have been made at 25° and 0°C on cells of the type $\mathrm{Pt} + \mathrm{H_2}(p\ \mathrm{atm}),\ \mathrm{HClO_4}\ (c'),\ \left\{ \mathrm{HNO_3}\ (c) + \begin{matrix}\mathrm{Ce^{IV}}(c_2)\\ \mathrm{Ce^{III}}(c_1)\end{matrix} \right\},\ \mathrm{Pt}.$ The formal cerous-ceric oxidation potential E° changes by only 1.5 mv. at most on varying $\mathrm{Ce^{III}/Ce^{IV}}$ over ten-fold at constant ionic strength; moreover, there is almost no dependence of this potential on nitric acid concentration between 0.5 and 2f. The calculated formal oxidation potential is 1.6093 ± 0.0007 volts at 25°C in this range of nitric acid concentration. The value at 0°C was found to be 1.601 volts (in 1f $\mathrm{HNO_3}$).

The decrease in free energy, heat content and entropy at 25°C attending the reaction $\mathrm{Ce^{IV}(1f)} + E^{-I} = \mathrm{Ce^{III}(1f)}$ in nitric acid 0.5 to 2f are, respectively, 37,120 cal., 34,970 cal., and -7.2 cal./deg., for one mol ion.

Evidence is discussed which makes it likely that ceric ion forms a nitrate complex (probably $\mathrm{Ce(NO_3)_6^{=}}$), even in the more dilute nitric acid solutions. The constancy of E° when the nitric acid concentration is varied may be qualitatively explained by the assumption of a cerous nitrate complex ion, or by a hydroxide nitrate complex of ceric ion; the former is thought to be the more likely explanation. Transference experiments are mentioned which tend to support this view.

The formal potential in nitric acid, hence, does not approximately represent the molal potential, as was originally supposed by us. It is likely that the molal potential is considerably higher, being perhaps close to that of the cerous-ceric formal potential in perchloric acid; namely, about 1.71 volts, as determined by preliminary experiments.

Additional References

(1) Landolt-Börnstein Physikalisch-chemische Tabellen, Dritter Ergänzungsband; Julius Springer, Berlin, 1936; page 2144.

(2) Noyes and Deahl, J. Am. Chem. Soc. 59, 1341 (1937).

(3) Smith, Sullivan and Frank, Ind. Eng. Chem., Anal. Ed. 8, 449 (1935).

(4) Meyer and Jacoby, Z. anorg. Chem. 27, 359 (1901)

(5) Private communication from Professor G. F. Smith.

(6) Cuttica and Tocchi, Gazz. chim. ital. 54, 628 (1924), through Professor Smith.

(7) Weber, Trans. Am. Electrochem. Soc. 32, 391 (1917).

(8) Noyes, DeVault, Coryell and Deahl, J. Am. Chem. Soc. 59, 1326 (1937).

(9) Preliminary experiments of the author. Time was not available to find the effect of varying perchlorate concentration, but it is thought unlikely that a perchlorate complex of cerium is formed. Further experiments, to be carried out with Professor E. H. Swift and Mr. D. Nicholson, are planned.

THE OXIDATION POTENTIAL OF THALLOUS-THALLIC SALTS IN AQUEOUS NITRIC ACID SOLUTION

Introduction

This investigation of the thallous-thallic oxidation potential in aqueous nitric acid solution was carried out at the Kerckhoff Marine Laboratory, Corona del Mar, California, in the summer of 1935. The problem was undertaken under the guidance of the late Professor Arthur A. Noyes, whose inspiration and advice were responsible for a large part of this work.

Data concerning the oxidation potentials of powerful oxidizing substances are rather limited, and as it is desirable to have such information readily available for predicting the direction and extent of various chemical reactions, a series of investigations was planned of which this research is a part. The possibility of the formation of nitrate complexes of metal ions is also examined.

[Reprint from the Journal of the American Chemical Society, 58, 1268 (1936).]

[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 547]

Strong Oxidizing Agents in Nitric Acid Solution. II. Oxidation Potential of Thallous-Thallic Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Previous and Proposed Investigations

The thallous–thallic oxidation potential has been studied by several investigators. Its determination was first undertaken by Spencer and Abegg[1] who studied the potential in nitric, hydrochloric and sulfuric acids, and in the presence of various salts with the view of investigating complex-ion formation. Their measurements were made at 25° against a 0.1 *N* calomel half-cell as a reference electrode, and their potentials were not corrected for liquid-junction potentials. Grubb and Hermann[2] later obtained values for the thallous–thallic potential in sulfuric acid solutions. Measurements by them were made at 18° against either a normal calomel electrode or a mercurous sulfate electrode, and liquid-junction corrections were not applied. Partington and Stonehill[3] recently measured at 25° cells of two types

$$\mathrm{Pt}, \left\{ \mathrm{H_2SO_4}\,(c) + \frac{\mathrm{Tl_2SO_4}\,(c_1)}{\mathrm{Tl_2(SO_4)_3}\,(c_2)} \right\}, \mathrm{H_2SO_4}\,(c), \mathrm{H_2}\,(1\ \mathrm{atm.}) + \mathrm{Pt}$$

and

$$\mathrm{Pt}, \left\{ \mathrm{H_2SO_4}\,(c) + \frac{\mathrm{Tl_2SO_4}\,(c_1)}{\mathrm{Tl_2(SO_4)_3}\,(c_2)} \right\}, \mathrm{Hg_2SO_4}\,(\mathrm{satd.}), \mathrm{Hg}, \mathrm{Hg_2SO_4}\,(\mathrm{satd.}), \mathrm{H_2SO_4}\,(c), \mathrm{H_2}(1\ \mathrm{atm.}) + \mathrm{Pt}$$

These investigations showed that the oxidation potential of thallous–thallic salts varies greatly with the nature of the anion present, doubtless owing to the formation of anion complexes; and as these complexes are probably produced in minimum quantity with monobasic oxyacids, such as nitric acid and perchloric acid, thereby yielding a molal potential approximating most closely that of the simple thallous and thallic ions, we have measured and describe in this paper cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \mathrm{atm.}), \mathrm{HClO_4}\,(c'), \left\{ \mathrm{HNO_3}\,(c) + \frac{\mathrm{Tl^{III}}\,(c_2)}{\mathrm{Tl^{I}}\,(c_1)} \right\}, \mathrm{Pt}$$

During the progress of our investigation an article upon the thallous–thallic potential in perchloric acid solution has been published by Sherrill and Haas,[4] thereby making possible a comparison of the potential in the two monobasic oxyacids.

Apparatus and Materials

Preparation and Analysis of the Solutions.—A weighed quantity of C. P. thallous nitrate, dried in an oven at 140°, was dissolved in a definite weight of distilled water, and the resulting solution was divided into two nearly equal portions.

(1) From one of these portions a thallic nitrate solution was prepared by oxidation with a gas mixture containing 5% by volume of ozone (Noyes, Hoard and Pitzer[5]), thereby avoiding the introduction of foreign substances into the solution. To it had previously been added the amount of strong nitric acid (freed from nitrogen dioxide by bubbling air through it) required to leave the oxidized solution 0.5 *f* in nitric acid. It was thought that this acid would suffice to prevent the hydrolysis of the thallic nitrate formed, but during the oxidation dark-brown thallic hydroxide precipitated, and it was necessary to add more nitric acid to the oxidized mixture. The excess of ozone was blown out with oxygen, and the thallic nitrate solution was analyzed in the following way.

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[1] Spencer and Abegg, *Z. anorg. Chem.*, **44**, 379 (1905).

[2] Grubb and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1357 (1935).

[4] Sherrill and Haas, THIS JOURNAL, **58**, 952 (1936).

[5] Noyes, Hoard and Pitzer, *ibid.*, **57**, 1223 (1935)

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$TlNO_3$ c_1	$Tl(NO_3)_3$ c_2	Tl^I/Tl^{III} c_1/c_2	Mean ionic strength, μ	$E_{\text{obsd.}}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.07264	0.04720	1.5392	2.17	1.2096	+0.0055	−0.0096	+0.0244	1.2299
	(α, 0.759)	(α', 1.295)	.06499	.05819	1.1194		1.2138	+ .0014	− .0096	+ .0244	1.2300
										Mean	1.2300
25	1.000	1.000	.04999	.00406	12.314	1.09	1.2048	+ .0323	− .0023	− .0056	1.2292
	(α, 0.706)	(α', 0.803)	.04133	.01643	2.5148		1.2273	+ .0119	− .0023	− .0056	1.2313
			.03574	.02445	1.4617		1.2346	+ .0049	− .0023	− .0056	1.2316
			.02874	.03442	0.8351		1.2407	− .0023	− .0023	− .0056	1.2305
			.02146	.04484	0.4786		1.2489	− .0095	− .0023	− .0056	1.2315
			.00514	.06817	0.0754		1.2708	− .0332	− .0023	− .0056	1.2297
										Mean	1.2306
25	0.5000	1.000	.01624	.01455	1.1155	0.55	1.2499	+ .0014	− .0147	− .0056	1.2310
	(α, 0.708)	(α', 0.803)	.00691	.02788	0.2479		1.2677	− .0179	− .0147	− .0056	1.2295
										Mean	1.2303
										General Mean	**1.2303**
0	1.000	1.000	.02874	.03442	0.8351	1.09	1.203	− .0021	− .0021	− .0051	**1.193**
	(α, 0.706)	(α', 0.803)									

To a weighed sample solid potassium chloride and mercury were added, the mixture was shaken for two minutes and filtered through a Jena glass filter. The filtrate with washings was then titrated with standard sodium hydroxide solution to determine the nitric acid content. It was necessary to reduce the thallic salt in this way, since otherwise it separated out as the hydroxide and obscured the end-point. The content in thallic nitrate was determined on separate samples by reducing the thallic thallium to thallous thallium with sulfur dioxide, blowing out the excess of sulfur dioxide with carbon dioxide, and determining the thallium by two independent methods. However, it was found that the large amount of nitrate present interfered with these determinations; so the samples were first fumed with concentrated sulfuric acid to convert the nitrate to sulfate. Two determinations were made by the iodate method using the iodine monochloride end-point,[6] and these agreed to better than 0.1% with two determinations by the bromate method using methyl orange as an oxidation indicator.[7] The absence of thallous thallium in the thallic nitrate solution was proved by making a sample 5 *f* in hydrochloric acid, adding a small amount of iodine monochloride solution and shaking with carbon tetrachloride; no iodine color was perceptible. The thallic nitrate stock solution thus prepared was 0.1835 *f* in thallic nitrate and 2.430 *f* in nitric acid.

(2) To the other portion of the thallous nitrate solution was added enough nitric acid to make the resulting solution of the same acidity as the thallic nitrate stock solution. Analyses for both thallium and acid checked the values obtained by the direct synthesis of the solution. The thallous nitrate stock solution was 0.1284 *f* in thallous nitrate and 2.430 *f* in nitric acid.

The Electrolytic Cell.—The electrolytic cell used for the electromotive force measurements was that described in the preceding paper. The platinum wire electrode gave the same potential whether it was bright or platinum-blacked; however, equilibrium was more rapidly attained in the latter case.

Method of Potential Measurements.—The equipment used and the method of making the electromotive force measurements were those previously described in detail. The potential of a given cell was observed over a period of one to seventy hours. Equilibrium was reached within an hour, and subsequent readings were constant to 0.1 mv., stirring having no effect on the potential.

Measurements at 0°. One of the cells which had been measured at 25° was transferred to a 0° thermostat, and its potential observed over a period of three days. Equilibrium was much more slowly attained than at 25°, and the readings were sensitive only to about 0.5 mv. The cell was afterward returned to the 25° thermostat, and gave substantially the same electromotive force as before. The probable error of the formal potential at 0° is about one millivolt.

The Observed and Computed Electromotive Forces

In Table I are shown the concentration data, the observed electromotive forces, $E_{\text{obsd.}}$, the corrections applied to these, and the computed formal oxidation potentials E^0 resulting thereby, all in just the same form in which these quantities are presented in Table I of the preceding article. The activity coefficients α and α' of the two acids are as before taken from the data of Pearce and Nelson[8] and of Abel, Redlich and v. Lengyel,[9] the same values being used at 0° (where data are lacking) as at 25°.

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[6] Swift and Garner, THIS JOURNAL, **58**, 113 (1936).

[7] Kolthoff, *Rec. trav. chim.*, **41**, 172 (1932); Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 278 (1926); see also Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1231 (1935).

[8] Pearce and Nelson, *ibid.*, **55**, 3080 (1933).

[9] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

Summary and Discussion

Measurements have been described above of the electromotive forces at 25 and 0° of cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(p\ \mathrm{atm.}),\ \mathrm{HClO_4}\,(c'),\ \left\{ \mathrm{HNO_3}\,(c) + \begin{matrix}\mathrm{Tl^{III}}\,(c_2)\\ \mathrm{Tl^{I}}\,(c_1)\end{matrix} \right\},\ \mathrm{Pt}$$

From these measurements presented in Table I the formal oxidation potential E^0 of the reaction $\mathrm{Tl^{III}} + 2\mathrm{E^{-I}} = \mathrm{Tl^{I}}$ has been computed to have the value **1.2303** ± 0.0007 volt at 25° and the value **1.193** ± 0.001 volt at 0° in nitric acid solution. This value is shown to remain substantially constant when the ratio $\mathrm{Tl^{I}}/\mathrm{Tl^{III}}$ is varied one hundred-fold and when the concentration of nitric acid is varied from 0.5 to 2 *f*. This constancy of the potential shows that neither hydrolysis of the thallic nitrate (by a reaction like $\mathrm{Tl^{+++}} + \mathrm{H_2O} = \mathrm{TlOH^{++}} + \mathrm{H^+}$), nor formation of nitrate complexes occurs to a considerable extent with thallic salts in nitric acid solutions between 0.5 and 2.0 formal.

This value, 1.230 volts, of the formal potential is slightly lower than those found by Sherrill and Haas[4] for the thallous–thallic potential in perchloric acid solution, who obtained at 25° 1.260 volts for the formal potential in 1.0 *f* perchloric acid and 1.247 volts for the extrapolated molal potential for thallous–thallic ions.

Noteworthy is the fact that the thallous–thallic potential in sulfuric acid solution, determined by Partington and Stonehill[3] to be 1.20 to 1.22 volts, is of about the same magnitude as the potentials in nitric and perchloric acids indicating that the formation of sulfate complexes by thallic sulfate is not very extensive.

PASADENA, CALIF. RECEIVED MAY 12, 1936

Additional Calculated Results

Table II

Observed and Recomputed Electromotive Forces at 25 and 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$E_{obsd.}$	E_C	E_L	E_H	E°
25	2.000	2.000	1.2096	+0.0055	-0.0051	+0.0187	1.2287
	(α,0.774)	(α',1.039)	1.2138	+ .0014	- .0051	+ .0187	1.2288
						Mean	1.2288
25	1.000	1.000	1.2048	+ .0323	- .0022	- .0054	1.2295
	(α,0.715)	(α',0.811)	1.2273	+ .0119	- .0022	- .0054	1.2316
			1.2346	+ .0049	- .0022	- .0054	1.2319
			1.2407	- .0023	- .0022	- .0054	1.2308
			1.2489	- .0095	- .0022	- .0054	1.2318
			1.2708	- .0332	- .0022	- .0054	1.2300
						Mean	1.2308
25	0.5000	1.000	1.2499	+ .0014	- .0147	- .0054	1.2312
	(α,0.715)	(α',0.811)	1.2677	- .0179	- .0147	- .0054	1.2297
						Mean	1.2304
						General Mean	1.2302
0	1.000	1.000	1.203	- .0021	- .0020	- .0050	1.194
	(α,0.715)	(α',0.811)					

Table III

$-\Delta F_{298}$	$-\Delta H_{298}$	$-\Delta S_{298}$
56800 cal./mol ion	30,700 cal./mol ion	-87.6 cal./deg./mol ion

Additional Discussion and Summary

As in the case of the cerous-ceric oxidation potential, the revised values of the activity coefficients of nitric acid and of perchloric acid give slightly different values of the formal potential of thallous-thallic salts in nitric acid. The recomputed values are presented in Table II.

It has been thought worthwhile to record the values of the decrease in free energy, heat content and entropy at 25° for the reaction $Tl^{III}(1\ f) + 2E^{-I} = Tl^{I}(1\ f)$ in nitric acid solutions 0.5 to 2 f. These data appear in Table III.

One may wonder if the constancy of this potential in solutions of varying nitrate ion concentration really does indicate that no very stable nitrate complexes of thallium are formed under the experimental conditions, for in the case of cerium the constancy of the values of the potential proved so misleading at first in regard to complex formation (see the portion of this thesis dealing with the cerous-ceric oxidation potential). However, in view of the very constant values of the potential in the case of thallium salts and in view of the relatively good agreement among the values of the thallous-thallic potentials in such different solutions as sulfuric acid, nitric acid and perchloric acid, it seems extremely unlikely that either thallous ion or thallic ion forms a nitrate complex to any appreciable extent in nitric acid as concentrated as 2 f.

For a summary of this research see page 18 of this thesis, substituting for the values given there for the formal oxidation potential of the reaction $Tl^{III}(1\ f) + 2E^{-I} = Tl^{I}(1\ f)$ the probably better value of 1.2302 ± 0.0007 volts at 25° and the value 1.194 volts at 0°C. The decrease in free energy, heat content and entropy attending the above reaction at 25° are respectively, 56,800 cal., 30,700 cal. and -87.6 cal./deg. per mol ion in nitric acid solutions 0.5 to 2 f.

AN ATTEMPT TO DETERMINE THE ELECTRODE POTENTIAL AND RAMAN SPECTRUM OF FLUORINE. THE ENTROPY OF FLUORINE

[Reprinted from the Journal of the American Chemical Society, **59**, 2738 (1937).]

An Attempt to Determine the Electrode Potential and Raman Spectrum of Fluorine. The Entropy of Fluorine

By Clifford S. Garner and Don M. Yost

The Electrode Potential of Fluorine

Although the normal electrode potential of fluorine has been estimated to have the value −2.88 v.,[1] the thermodynamic constants of aqueous hydrogen fluoride are not known accurately. Consequently, investigations were undertaken in which cells of two types were measured

F_2 (p atm.), KF(c f in HF(l)), PbF_2(s) + Pb(s)

H_2 (1 atm.), HF(c f), KF(c' f in HF(c f)), PbF_2(s) + Pb(s)

for which the cell reactions (neglecting liquid-junction effects) presumably would be

$$\mathrm{Pb(s)} + \mathrm{F_2}(p\ \mathrm{atm.}) = \mathrm{PbF_2(s)}$$

and

$$\mathrm{H_2\ (1\ atm.)} + \mathrm{PbF_2(s)} = \mathrm{Pb(s)} + 2\mathrm{HF}(c\ \mathrm{f})$$

respectively. From the electromotive forces and temperature coefficients of these cells, together with data on the partial pressures of hydrogen fluoride above solutions of potassium fluoride in liquid hydrogen fluoride at the temperatures of interest[2] (needed in order to calculate the partial pressure of fluorine in the first cell), the thermodynamic constants of solid lead fluoride[3] and of aqueous hydrogen fluoride, as well as the normal electrode potential of fluorine, could be obtained. In this note only measurements of the first cell are treated.

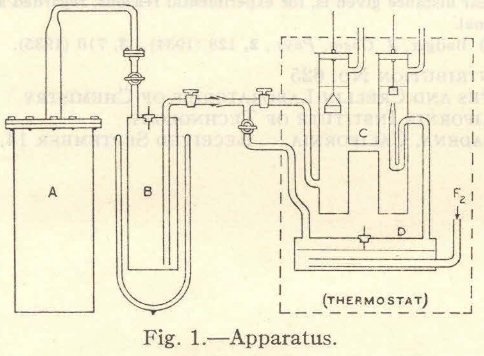

Fig. 1.—Apparatus.

Experimental Procedure.—All chemicals used were of a high grade of purity. The fluorine was generated by the electrolysis of molten anhydrous potassium hydrofluoride. The liquid hydrogen fluoride was prepared by heating anhydrous potassium hydrofluoride to 600° in a copper still (A) and condensing the distillate in a tared silver trap (B). The trap and contents were weighed and a known amount of dried potassium hydrofluoride added, after which the mixture was well shaken at 0° and then forced by a current of dry nitrogen into the platinum cell (C) and the silver saturator (D) which were thermostated at 0°. While the solution was being mixed, the platinum electrode was blacked, and the lead–lead fluoride electrode prepared and put in place. Fluorine was bubbled into the cell from the saturator, and potential readings were taken over a period of four to eight hours.

Results and Discussion.—In the four runs made, the potentials fluctuated irregularly from about 0.5 to 3 v. The rate of flow of fluorine was reasonably constant during each run, but varied from run to run. The amount of potassium fluoride added was changed and also the extent of stirring of the solution in the cell without any large effect. At the end of each run the container was found to be corroded and the black removed from the platinum electrode; in one case the electrode was not blacked, but the results were no better. No conditions were found which would give constant readings. In a somewhat different cell Simons and Hildebrand[4] were also unable to get reproducible and constant e. m. fs. This is probably because of the reaction of the fluorine with the electrode and container in the presence of liquid hydrogen fluoride.

The Raman Spectrum of Fluorine

Spectroscopic data for fluorine in the normal electronic state do not exist,[5] and consequently no accurate value for the entropy of fluorine is available. To obtain this information it was decided to determine the Raman spectrum of liquid fluorine.

Experimental Procedure.—The fluorine was prepared as previously, and was purified by being

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[1] Latimer, This Journal, **48**, 2868 (1926); Yost and Hatcher, *J. Chem. Ed.*, **10**, 330 (1933).

[2] Cady, This Journal, **56**, 1431 (1934).

[3] ΔH^0 for PbF_2 (s) has been determined to be −156,000 cal. and −155,600 cal., respectively, by v. Wartenberg and Fitzner, *Z. anorg. allgem. Chem.*, **151**, 313 (1926), and Jellinek and Rudat, *ibid.*, **175**, 281 (1928). Since the present work was completed a value of −147,300 cal. for ΔF^0 has been estimated by Jahn–Held and Jellinek, *Z. Elektrochem.*, **42**, 401 (1936), from measurements on certain cells.

[4] Simons and Hildebrand, This Journal, **46**, 2223 (1924). They reported that platinum, iridium, gold, nickel and graphite all react with fluorine at room temperature in the presence of liquid hydrogen fluoride; they did not state the extent of such reaction.

[5] Gale and Monk, *Astrophys. J.*, **59**, 125 (1924); **69**, 77 (1929), have analyzed a band spectrum of fluorine, and they give a value of 1130.1 cm.$^{-1}$ for the fundamental frequency of vibration of the molecule in the normal state. It is not certain, however, that their spectra arise from transitions involving the normal state of the F_2 molecule.

passed through a tube filled with sodium fluoride (to remove hydrogen fluoride) and condensed in a Pyrex trap surrounded by fresh liquid air. A portion of the condensate was allowed to escape and about one-half of the remainder was distilled into an evacuated Raman tube which previously had been well heated while evacuated to remove any moisture. The Raman tube held about 25 cc. of liquid and was closed by means of a brass and steel needle valve joined to the tube with a thin layer of sealing wax or by a copper–Pyrex seal. While being filled, and during the exposure to radiation, the Raman tube was surrounded by a Dewar flask (silvered except for one portion where light was admitted to the tube) filled with fresh liquid air. The liquid air was filtered to remove any ice crystals; the Dewar flask was closed off from the atmosphere by a cork which supported the Raman tube, and it was provided with means for adding liquid air during the exposure. As exciting radiation the 5461 Å. line of mercury was used. The light was concentrated on the Raman tube by a cylindrical aluminum reflector, and radiation below 3700 Å. was removed by a filter of sodium dichromate solution.[6] In addition a filter of neodymium nitrate solution was used to cut down the intensity of the "yellow" lines of mercury, since it was expected from the evidence at hand that the Raman line would fall in the region adjacent. The plates used were Eastman, type I-C.

Results and Discussion.—In the first attempt a Pyrex Raman tube was used, and after about fifteen minutes of illumination a white precipitate began to form in the fluorine. The tube was later found to be etched, and following this a quartz Raman tube was used. Two photographs were taken with the quartz tube, one of one hour and one of four hours' exposure. Longer exposures seemed impractical because of the gradual attack of the container by the fluorine, and because of the formation of ice crystals in the liquid air with resulting optical difficulties. No Raman lines could be found on either plate. The absence of a Raman line may be attributed to poor scattering ability of liquid fluorine, or to the possibility of the line falling near or on a mercury line and being thus obscured.

The Entropy of Fluorine

Recently, Brockway[7] has taken electron-diffraction photographs of gaseous fluorine, and a value of 1.46 Å. has been obtained for the internuclear distance of the fluorine molecule in its normal electronic state. If one assumes that Badger's rule[8] holds here, the value 836 cm.$^{-1}$ is obtained for the fundamental frequency of vibration. Making use of these two data, a calculation gives 48.6 cal./deg. for the standard entropy, S^0_{298}, of fluorine at 25° and one atmosphere.

The authors wish to express their thanks to the National Research Council for a grant which defrayed in part the cost of this investigation.

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[6] According to v. Wartenberg and Taylor, *Nach. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 119 (1930), fluorine gas at 1 atm. absorbs radiation below about 4500 Å. We found that if the dichromate filter was removed at the end of an exposure, a white precipitate appeared in the liquid fluorine in two to three minutes when the container was of Pyrex, and fifteen minutes when of quartz.

[7] Private communication from Dr. L. O. Brockway. **The internuclear distance given is, for experimental reasons, regarded as provisional.**

[8] Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

CONTRIBUTION NO. 625
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The Entropy of Fluorine. Additional Discussion and Summary

Shortly following the publication of the above note, there appeared a paper by Kanda (1) describing the results of heat capacity measurements on fluorine, and giving a value of 37.29 $\frac{\text{cal.}}{\text{deg.}}$ for the virtual entropy of ideal fluorine gas at its normal boiling point. That the reported value is probably about 4 % low is indicated by the following argument.

In order to calculate the standard virtual entropy of fluorine gas from Kanda's value, one must compute the change in entropy, ΔS, in going from 85.19 to 298.1°K. The translational molal heat capacity at constant volume is 3/2 R, and the rotational heat capacity is R for a diatomic molecule. The vibrational contribution is a somewhat complicated function of the vibrational frequency and the temperature; below about 150°K it is entirely negligible for fluorine, and even at 298°K it amounts to about 0.6 cal./deg. only, if one assumes the fundamental vibrational frequency to be 836 cm.^{-1} (A larger value for the fundamental frequency, such as 1071 cm.^{-1} proposed by Gale and Monk, would give about 0.3 cal./deg. at 298°K.) Taking as the average vibrational molal heat capacity, in the range 85.19 to 298.1°K, the value 0.3 $\frac{\text{cal.}}{\text{deg.}}$, and neglecting the very small contribution due to vibro-rotatory terms, we get

$$\Delta S = \int_{85.19}^{298.1} \widetilde{C}_p \, d\ln T = \int_{85.19}^{298.1} (\widetilde{C}_v + R)\, d\ln T = \int_{85.19}^{298.1} (3/2\ R + R + 0.3 + R)\, d\ln T = \underline{9.0\ \frac{\text{cal.}}{\text{deg.}}}$$

Whence, $S^\circ_{298.1} = 37.3 + 9.0 = \underline{46.3}\ \frac{\text{cal.}}{\text{deg.}}$ Now the Sackur-Tetrode formula permits one to calculate the rotational entropy of fluorine gas from the above value, for $S^\circ = S(\text{trans.}) + S(\text{rot.}) + S(\text{vib.}) - 2.299$, or since $S(\text{trans.}) = 3/2\ R\ln M + 5/2\ R\ln T - R\ln p = 39.13\ \frac{\text{cal.}}{\text{deg.}}$, and $S(\text{vib.}) = 0.18\ \frac{\text{cal.}}{\text{deg.}}$ (as calculated from the tables of Gorden and Barnes (2) for $\omega_0'' = 836\ \text{cm.}^{-1}$), we get $S(\text{rot.}) = 46.3 - 39.13 - 0.18 - 2.30 = 4.7\ \frac{\text{cal.}}{\text{deg.}}$ From this result the moment of inertia of the normal fluorine molecule is calculated to be $3.2 \times 10^{-40}\ \text{g.cm.}^2$ The internuclear distance in the normal fluorine molecule would then be 0.45 Å ! This is obviously much too small, and it must be concluded that Kanda's value is too low.

Kanda determined the amount of fluorine in his experiments by measuring its volume in a mercury gas-burst in which glycerol was placed on the mercury. It has been shown (3) that both chlorine and bromine react with glycerol containing water. It is very likely that fluorine reacts with glycerol, even if the very hydroscopic glycerol be rendered anhydrous; such a reaction would probably result in an apparently smaller amount of fluorine that was actually present in the calorimeter during the heat capacity measurements. This would cause the calculated molal heat capacity to be too large. On the other hand, if the fluorine gas were measured before being condensed into the calorimeter, other gases might be present during the heat capacity measurements. This difficulty could have been eliminated by the use of a metal container and a metal diaphragm manometer for measuring the amount of fluorine.

One might also remark that the thermometer used by Kanda was a resistance thermometer of platinum wound directly onto a bakelite lacquered copper cylinder, and its resistance-temperature relationship was determined in advance by comparison with a gas thermometer. Since there must be a strain set up in the thermometer by the differential thermal expansion, it may be that Kanda's temperature scale is not an accurate one.

The question of the purity of the fluorine used is a matter of some importance. Also, the method of calculating some of the results is not clearly defined; recalculation of the results, insofar as the data permit, lead to a value of the virtual entropy of fluorine at its normal boiling point 0.3 $\frac{\text{cal.}}{\text{deg.}}$ lower than that recorded by Kanda.

Probably the most significant aspect of the work of Kanda is that it represents a pioneering attempt in this difficult problem of ascertaining the entropy of fluorine by heat capacity measurements. With some refinements in technique this method of attack should be a fruitful one.

To summarize the results of this investigation: The electromotive forces of certain cells were measured in an attempt to evaluate the normal electrode potential of fluorine. Failure was met with because of the lack of constancy and reproducibility of the potentials. Next, an attempt was made to secure the Raman spectrum of liquid fluorine; no fluorine lines could be detected on the plates under the experimental conditions involved. From the tentative value of 1.46 Å for the internuclear distance of the fluorine molecule in its normal electronic state, as determined by Dr. L. O. Brockway, the value 48.6 cal./deg. was calculated for the standard virtual entropy of fluorine. The experimental value of 37.29 cal./deg. obtained by Kanda for the virtual entropy of fluorine at its boiling point, is shown to lead to a value of the standard virtual entropy too small by several entropy units.

Additional References

(1) Kanda, Bull. Chem. Soc. Japan <u>12</u>, 511 (1937).

(2) Gordon and Barnes, J. Chem. Physics <u>1</u>, 297 (1933).

(3) Hlasiwetz and Habermann, Annalen der Chemie u. Pharmacie <u>155</u>, 131 (1870).

THE CONSTRUCTION OF A LOW TEMPERATURE VACUUM CALORIMETER

Introduction

The construction of an apparatus for low temperature calorimetry and the measurement of vapor pressures of condensed gases was undertaken about two years ago for the purpose of measuring the heat capacities, heats of fusion and heats of vaporization of certain inorganic chemical compounds which are of interest for one reason or another. From such measurements, by means of the Third Law of Thermodynamics, it is possible to evaluate the entropies of substances, as well as their free energies when the heats of formation are known.

There are at present other calorimetric devices being built by men in the Department of Chemistry which are intended for measuring heat capacities of gases directly and by the adiabatic method; the program, including this work, is under the direction of Professor Don M. Yost, whose constant advice and encouragement have played no small part in bringing to fruition this research.

The design selected for this calorimeter is one which follows certain conventional features of vacuum calorimeters made by other investigators and which is, to a certain extent, also a product of experiment. To say that it has been completely successful would be misleading, and, indeed, there are certain improvements which should be made on the finished device.

Auxiliary apparatus, such as the manometer, time-measuring device and electrical instruments are also described and discussed in the immediately following pages, as is the establishment of a temperature scale.

Description of the Calorimeter and Manometer; Constructional Details

A full-scale drawing of the calorimeter is shown in Fig. 1. The calorimeter vessel itself, to be known as copper calorimeter No. 1, is represented at p in the diagram. It was machined from a single rod of copper, and has a wall thickness of 0.5 mm. Inside are ten perforated disks, q, of 0.3 mm. thick copper, equally spaced and having flanges which press tightly against the calorimeter wall. These are for the purpose of obtaining better thermal equilibrium in the condensed material inside the calorimeter. These, as well as the calorimeter, were gold plated separately and then placed in the calorimeter and the tightly fitting bottom soldered on, after which an extra plating of gold was deposited on the whole vessel. The total weight of the vessel is approximately 100 grams. Attached to the calorimeter by a copper-Pyrex seal, j, is a thin-walled Pyrex tube, a, of inside diameter 4 mm., which is used for filling and emptying the calorimeter. A heater of number 30 DSC constantan wire, not shown in the diagram, is closely wound over the greater portion of the inlet tube. Gas may be kept from condensing in the tube by energizing this coil, which is supplied with copper leads at 10 cm. intervals to serve as thermocouples.

The outside of the calorimeter was painted with electrician's enameling fluid which was baked on. It was decided to follow the example set by Eucken (1) and use a combination resistance thermometer heater. Number 40 DSC annealed copper wire was wound non-inductively on the lacquered calorimeter, covering substantially the whole cylindrical surface, and a coat of electrician's enameling fluid applied and baked on. Current leads, k, of number 36 DSC copper wire were soldered onto the number 40 potential leads, m, at the end of the coil, and the junctions were thoroughly tied onto the lacquered calorimeter wall and lacquered in place to eliminate possible small

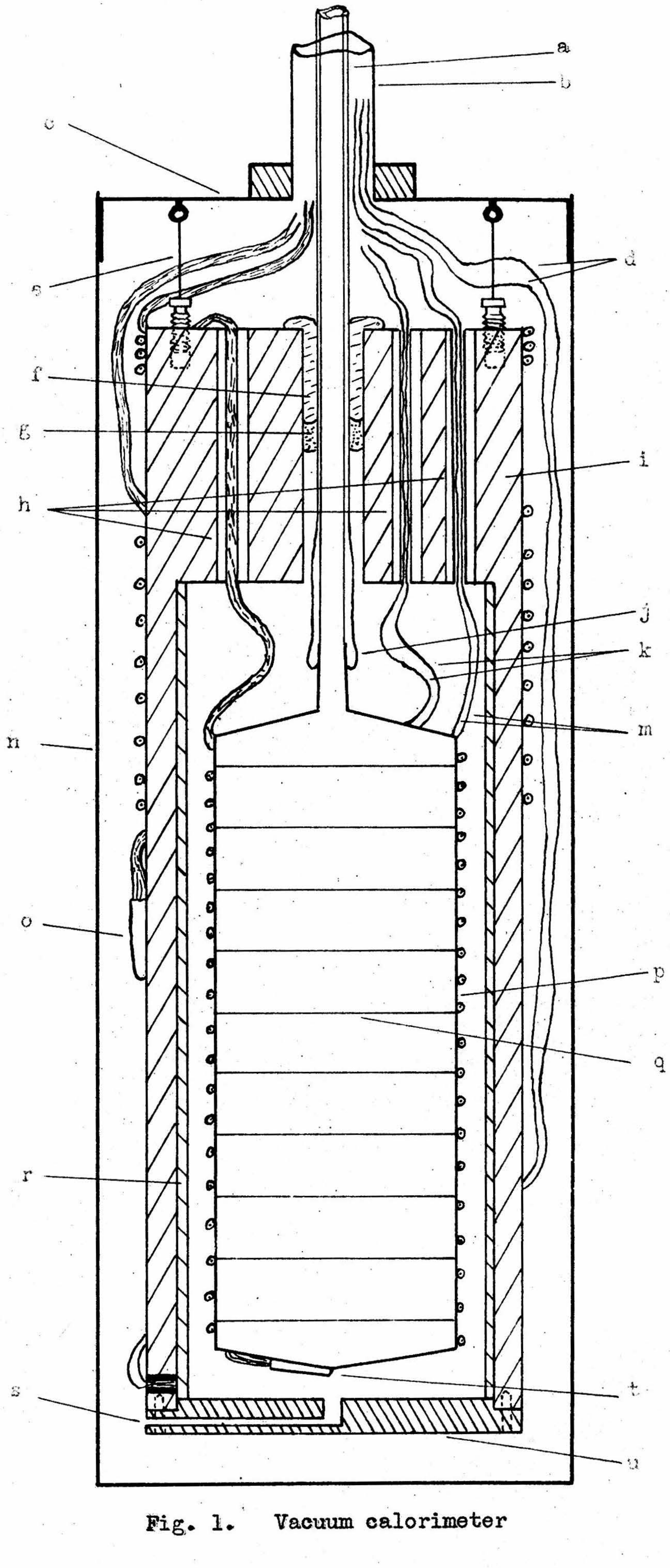

Fig. 1. Vacuum calorimeter

thermocouple effects. The resistance of the thermometer heater at room temperature is about 180 ohms. Gold leaf was applied to the entire exterior of the calorimeter with a very light coating of enameling fluid to reduce the heat interchange due to radiation.

A copper-constantan thermocouple, designated as couple No. 7, has one of its junctions inserted into a small copper tube, t, filled with Wood's metal; the tube itself is soldered onto the bottom of the calorimeter. About 50 cm. of the thermocouple are wrapped tightly around the calorimeter and lightly paraffined in place. The possibility of thermal gradients near the junction is thus greatly reduced. The length of the thermocouple between the calorimeter and the block is about 5 cm.

The calorimeter is suspended within the block by means of the Pyrex inlet tube, the outside of which was brought into good thermal contact with the block by means of Wood's metal, f, poured around it after it was in place. (A plug of cotton, g, prevented the molten Wood's metal from running down the tube too far.) The block itself is a heavy cylinder of copper, i, weighing 2165 grams, which is used to give an approximately constant temperature environment of any desired temperature. It is provided with a copper resistance heater, similar to that on the calorimeter, wound on a copper sleeve, r, which was cemented in place inside the block. A bright aluminum-foil radiation shield was attached to the face of the sleeve facing the calorimeter. Leads, d, for the heater come out through bakelite insulators in the block. A copper-constantan thermocouple, designated as couple No. 11, has one of its junctions soldered into a tube, o, on the outside of the block, and about 90 cm. are wound tightly around the block. (It would have been better to put the thermocouple junction on the sleeve facing the calorimeter.) A cap, u, is provided for the block which is fastened on by four machine-screws, and which is easily removable to allow insertion and centering of the calorimeter during assembly. Four radial holes, s, in the cap allow the space around the calorimeter to be evacuated. Bakelite insulators, h, were set into the block at the top to provide for the exit of leads from the calorimeter, the leads being wrapped around the block before leaving the apparatus. The block is suspended by three strong cords, e, of fish-line from the lid, c, of the container.

The container, n, is a strong brass cylinder with a brass bottom silver-soldered on. The vacuum-tight joint between it and the lid is a tight fit soldered with a relatively low-melting bismuth solder. The lid and container are supported by a German silver tube, b, of diameter 14 mm. and wall thickness 0.2 mm.

The assembled calorimeter and cryostat are shown in Fig. 2, scaled to one-fifth actual size. The German silver tube, d, supporting the calorimeter is fastened securely to a hard rubber lid, j, to which the cryostat can be attached by bolts and wing-nuts. The cryostat itself consists of a highly evacuated, silvered, Pyrex Dewar, m, supported by Celotex pads, p, inside a stout brass can, k, which is itself housed in a wood case, n, partially filled with kapok insulating material, o. The case is provided with sliding clamps which fasten onto an upright rod, allowing the cryostat to be lowered from the calorimeter when desired.

Liquid air is introduced through the vacuum-jacketed, German silver transfer tube, h, which is equipped with a cap, i, which closes off the tube when the can is under reduced pressure. A German silver tube, g, provided with a rubber tube and clamp gives an indication when the liquid air level has reached its maximum in the Dewar by blowing off liquid air at that point. There is also a large bore tube with stop cocks which permit the can and contents to be opened to the air at f, to a small manometer, e, and/or to a high speed rotary

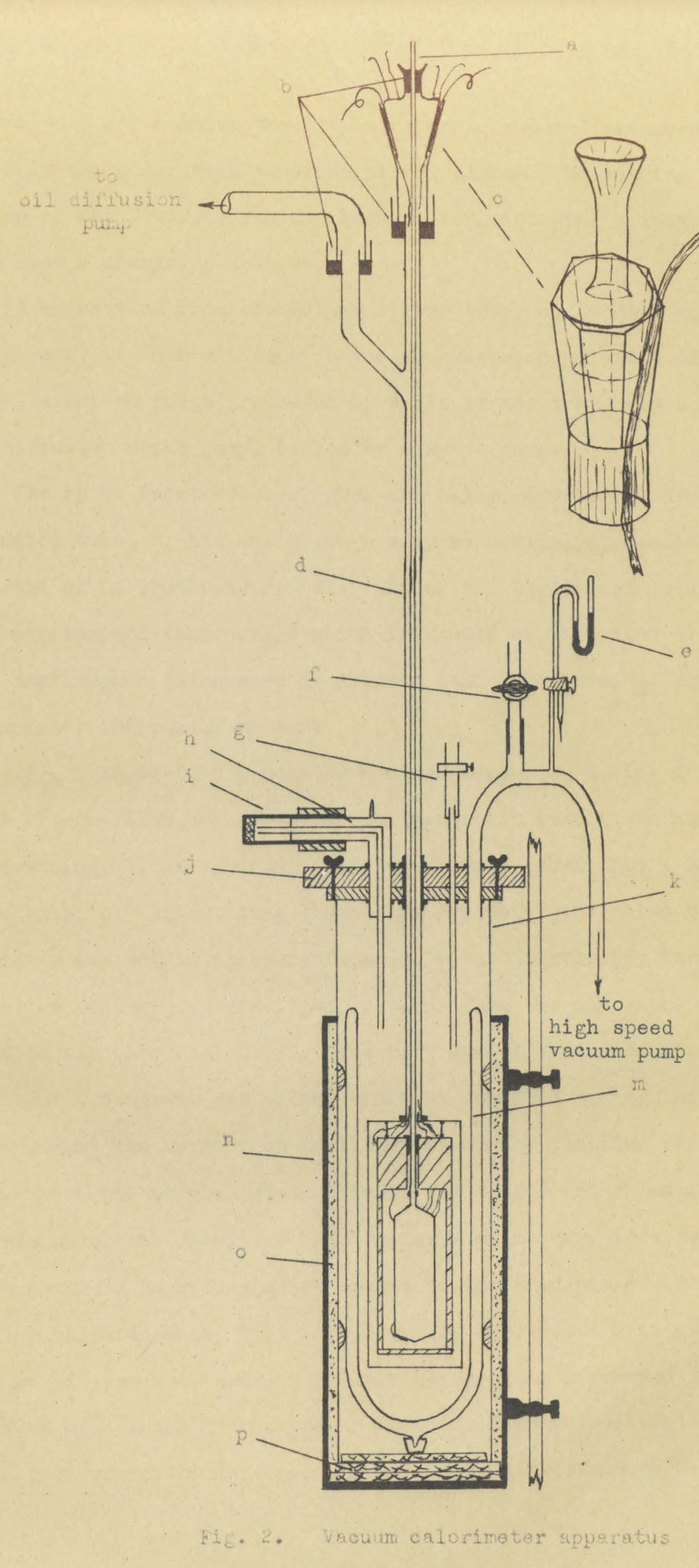

Fig. 2. Vacuum calorimeter apparatus

vacuum pump for cooling the apparatus under reduced pressure. Not shown in the diagram is a German silver siphon tube running to the bottom of the Dewar, which can be used for siphoning out any liquid bath when a change is desired.

A connection from the German silver tube, d, leading into the calorimeter is made with a high vacuum system, consisting of a Pirani gauge, a McLeod gauge protected by a liquid air trap, and a large oil diffusion metal pump, backed by a Hyvac pump.

The Pyrex inlet tube, a, from the calorimeter comes up through the metal tube, d, and out through a Pyrex device, c, sealed at b by means of De Khotinsky cement. All of the electrical leads also come out through this device which is fluted so that each wire lies in a small space surrounded by Apiezon wax. The tube, a, leads to a manometer and vacuum system.

Fig. 3 shows this manometer and gas measuring device drawn to a scale of one-fifth actual size. The manometer itself was made from Pyrex tubing, c, of internal diameter 19 mm., blown onto a 300 ml. round bulb, o. After being thoroughly evacuated and baked out, the manometer was set in plaster-of-paris, r, and previously thrice distilled mercury was distilled in vacuo into the manometer through a, which was then sealed off. The left arm of the manometer was so made that a constant gas volume could be obtained during the measurements by bringing the mercury up to the upper of the platinum contacts shown at h, whereupon an electrical circuit was closed and a lamp, q, lighted. Adjustment of the level was made by means of mercury in a reservoir, k, which could be evacuated or opened to the atmosphere through a calcium chloride tube, i; a stop-cock, n, lubricated with graphite and a trace of vaseline, and a capillary connection, p, served to control the flow of mercury. In order to keep the line volume small, the major portion of the left arm and all connecting lines were made of

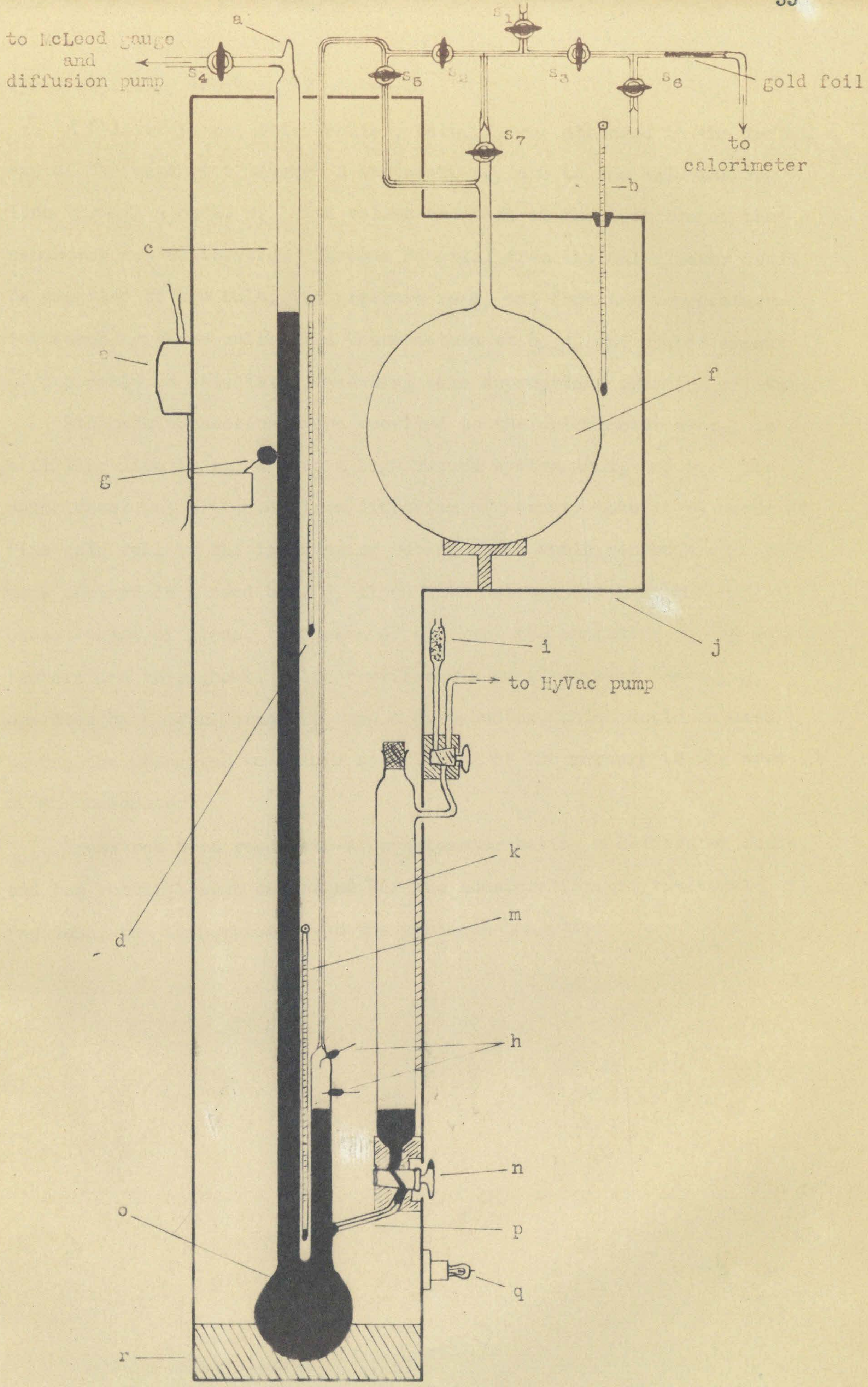

Fig. 3. Manometer and gas measuring device

Pyrex capillary tubing of 2 mm. bore.

A 5 liter Pyrex, thick-walled, bulb, f, was attached to the left arm of the manometer through a stopcock, s_5, and to the calorimeter line through a cock, s_7. Its volume and that of the left arm of the manometer was calibrated. Gaseous material from the calorimeter could be admitted to the bulb, its pressure read, and from the temperature (obtained by three calibrated thermometers at b, d, and m) the amount of gas could be calculated, assuming some appropriate equation of state.

Stopcock connections were provided to the calorimeter at s_3, to a filling line at s_6, and to a high vacuum system at s_4 and s_1. The calorimeter was protected from diffusion of mercury into it by means of fine gold foil in the intervening tubing. The whole manometer and bulb were encased in a wood box, j, lined with Celotex and provided with a plane window of glass. A stream of air kept the manometer at the same temperature throughout. Also provided was an electrical hammer, g, operated by a transformer, e, and a push-button, which could be used to tap the manometer to ensure no sticking of the mercury in the arms of the manometer.

Pressures were read with a cathetometer having a calibrated scale, and the readings were corrected for the acceleration of gravity at Pasadena, the temperature, and the meniscus-heights.

Electrical Circuits, Apparatus and Method of Measurements

Since all electrical measurements made in heat capacity determinations are measurements of electromotive force essentially, it is important that one have some reliable standard of electromotive force. For this present research an unsaturated Weston type cell was used. A Bureau of Standards certificate, dated 1930, was available, and in addition, the electromotive force was kindly checked by Dr. F. Dunnington of the Physics Department against a new Bureau of Standards certified cell. The values obtained by him in 1935 and in 1937, along with the original value, were extrapolated to give the value now used, since it has been found by Dr. Dunnington that cells of this type have a fairly constant potential decrease with time of 4 to 5 microvolts per month. The value taken for the cell used in this work was 4.7 microvolts per month, and the EMF was 1.018306 international volts at 23°C on April 16, 1937. Fortunately, for this work the electromotive force need be known only to about 50 microvolts. In order to prevent hysteresis effects (2), and to keep the temperature of the cell constant at a known value, an air thermostat was constructed for the standard cell. Fig. 4a shows this thermostat drawn to scale one-fourth actual size. It consists of an outer wood box, g, lined with Celotex, k, an aluminum box, f, and an inner aluminum box, e; air spaces, a, separate the three boxes. The standard cell, h, rests on a felt pad, j, inside the innermost box. Leads, o, of number 40 DSC copper wire are taken out through bakelite insulators, i, and are conducted inside small diameter glass tubing directly to the potentiometer. The larger metal box has a 100 ohm resistance heater of number 28 Chromel "A" wire wound on it, which is supplied with alternating current controlled by a vacuum tube relay and a regulator, d, in a pocket attached to the box. A thermometer at b, indicates the temperature. The regulator itself is shown one-half size in Fig. 4b. It consists of 10 thin-walled glass arms, a, connected together and filled with acetone, and a mercury column, c, which closes and opens an electrical circuit by means of the platinum contacts b and d.

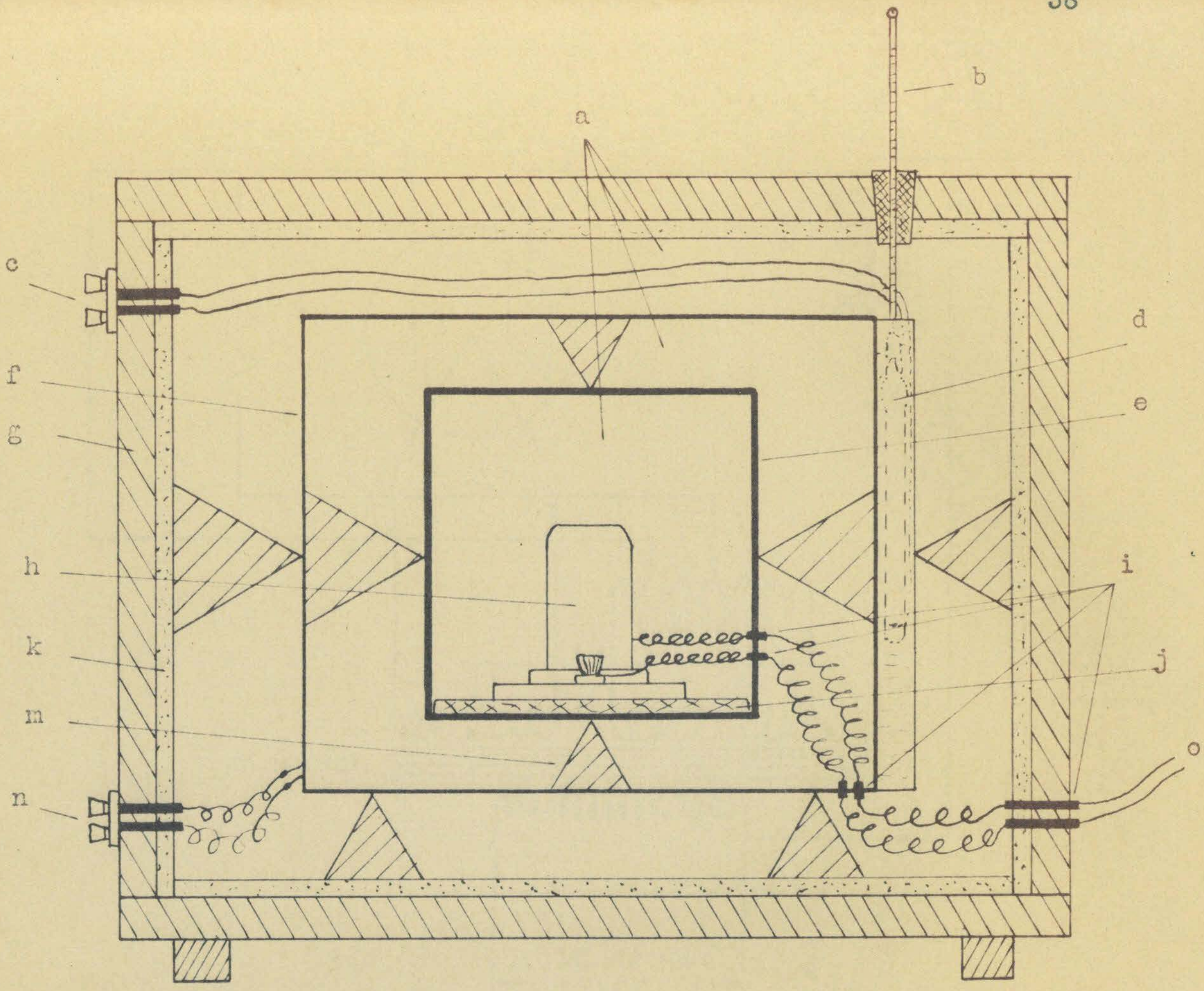

Fig. 4a. Thermostat for standard cell

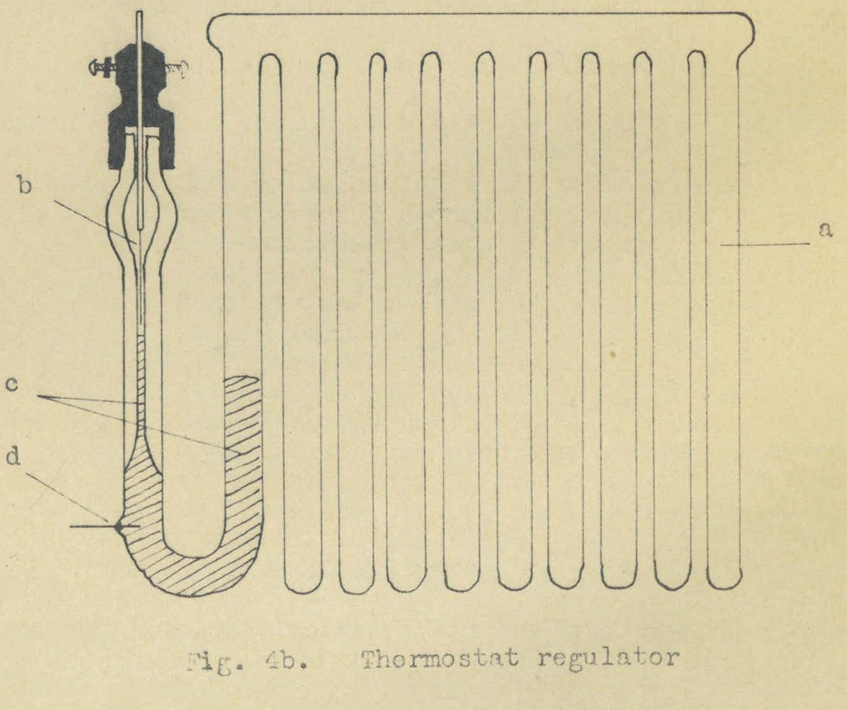

Fig. 4b. Thermostat regulator

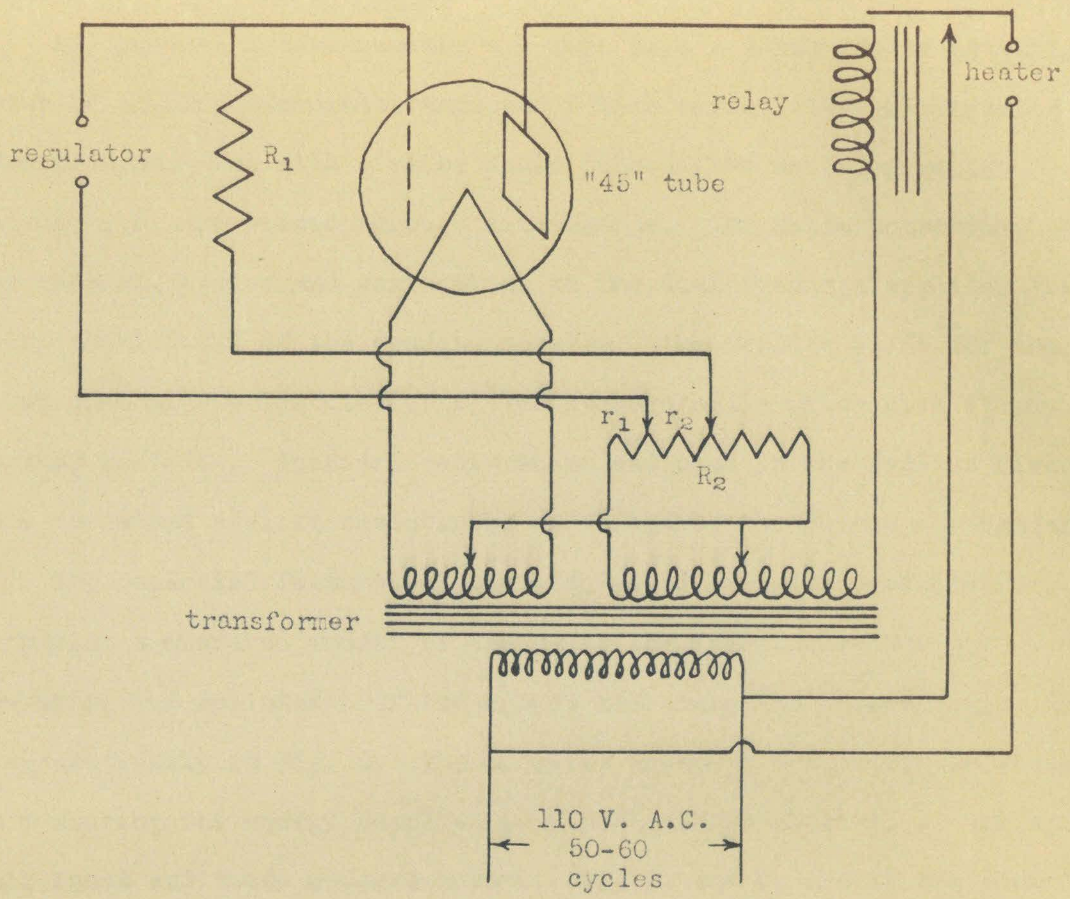

Fig. 5. Circuit diagram of A.C. vacuum tube relay

The above circuit is a modification of the one proposed by Ellis (3), and it was suggested by Mr. G. Keighley, Technical Assistant in Biology at this Institute. The device has performed very satisfactorily for over a year without any attention. The parts are as follows:

Transformer:	Inca C-31, having a 110 volt primary, 660 volt center-tapped secondary, and 2.5 volt center-tapped filament supply winding.
Relay :	Leach A.C. relay, type 1307; DPST single break; normally open. 115 volt coil consumes 4 watts on 110 volt, 50-60 cycle, input.
Tube :	"45" power amplifier tube.
Resistor R_1:	Fixed grid-leak resistor; 20,000 ohms, 10 watts.
Resistor R_2:	Semi-variable resistor; 50,000 ohms, 50 watts. With the tube removed and the device connected to the A.C. supply, the P.D. across R_2 should be 325 volts, and r_1 should be adjusted to give a P.D. of 50 volts and r_2 a P.D. of 65 volts approximately, depending on the relay used.

The power consumption, exclusive of the heater, is about 35 watts.

The vacuum tube relay referred to is discussed on page 39.

All potential measurements are made with a White double potentiometer of 100,000 microvolt range and a high sensitivity galvanometer used in connection with a meter scale placed five meters from the galvanometer and viewed through a telescope. The White potentiometer was auto-calibrated and corrections to the dial readings applied, these being about 0.01% of the reading usually. The working cells for the potentiometer are low discharge type storage cells which give steady working currents. Standard resistances employed in the various circuits were rechecked against resistances certified by the Bureau of Standards.

The essential features of the electrical circuits employed for supplying a measured amount of energy to the calorimeter and for measuring the resistance of the copper resistance-thermometer are shown diagramatically in Fig. 6. The circuits shown in red are those involved in measuring the energy supplied to the resistance-heater, R; during this input and these measurements S_1, S_2, S_3 and S_4 are in the "down" position and S_5 in the "up" position. The energy is supplied by a battery of storage cells which can be connected so that an electromotive force of 2 to 12 volts may be used, depending upon the resistance of the heater-thermometer at the particular temperature of interest; these cells are brought to a steady state for about ten minutes before each energy input by throwing switch S_5 to an "exercising" resistance, which is made approximately equal to the resistance of the heater-thermometer. The potential measured with the Q potentiometer, E_C, measures in effect the current flowing through the heater, while E_V, measured with the P potentiometer, essentially measures the potential drop across the heater. Those circuits shown in blue are involved in measuring the resistance of the resistance-thermometer before and after energy input; during the "temperature" measurements the switches S_1, S_2, S_3, and S_4 are in the "up" position and S_5 in the "down" (before energy input)

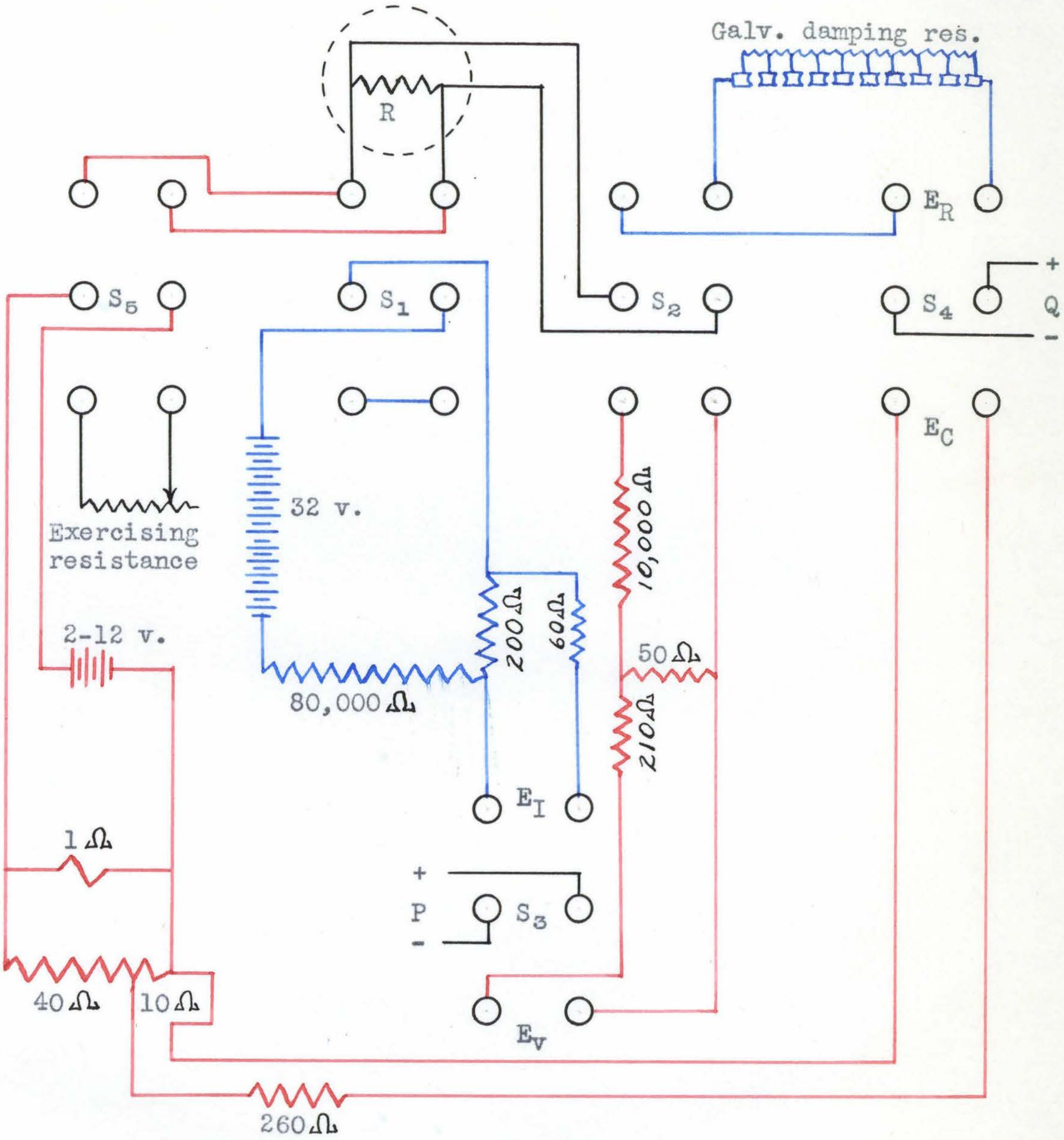

Fig. 6. Electrical circuits for calorimeter

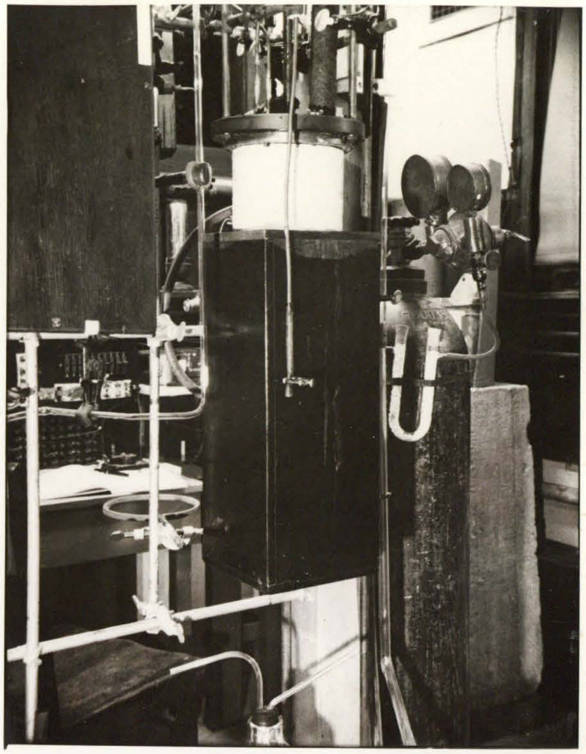

Fig. 7. Calorimeter and cryostat

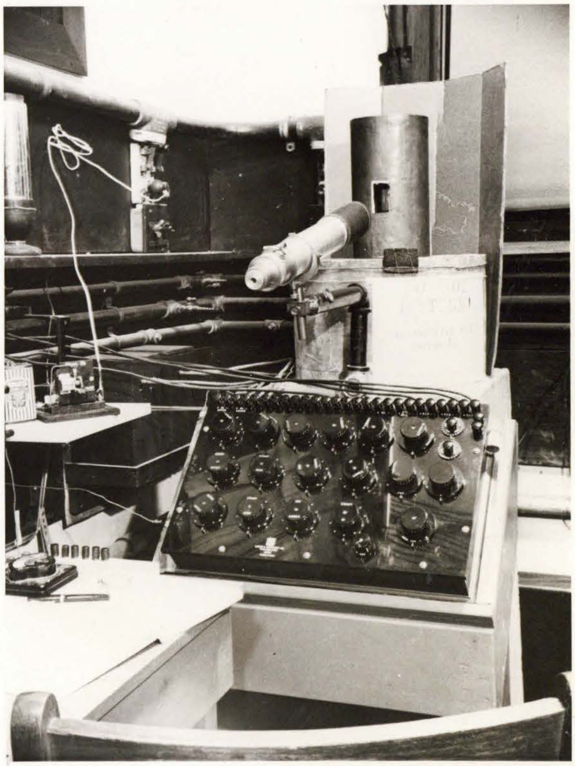

Fig. 8. Potentiometer and galvanometer

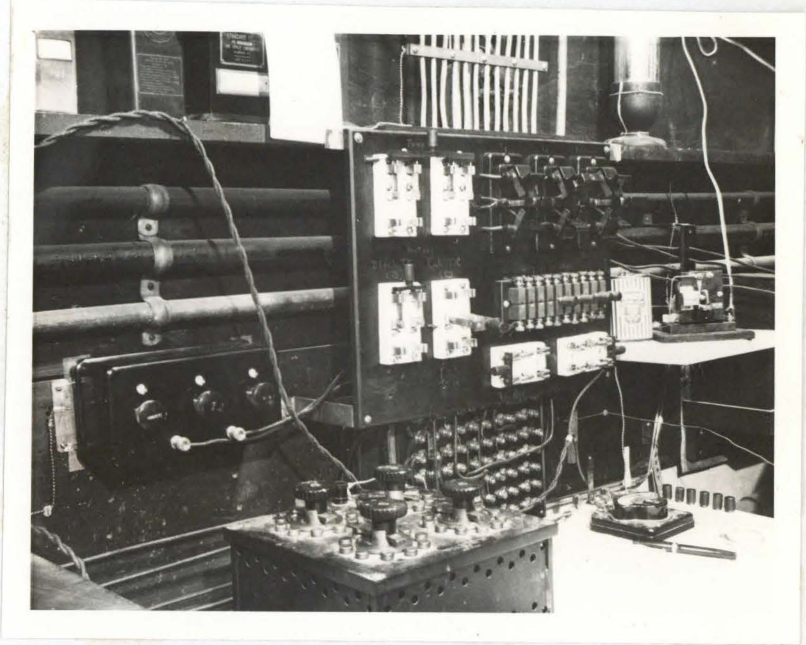

Fig. 9. Arrangement of switches for electrical circuits

or "open" (after energy input) position. An extremely constant current of about 4 x 10^{-4} ampere flows through the resistance-thermometer continuously, except during energy input; the energy generated in the thermometer is about 5 x 10^{-4} cal./min., which produces a negligible heating effect. The potential E_I, obtained with the P potentiometer, measures in effect this small thermometer current, and the potential E_R measures the potential drop across the thermometer. The nominal value of each resistance, standard or otherwise, is indicated in the diagram. Not shown in the diagram are the thermocouple circuits and the block and inlet tube heater circuits. Photographs of the calorimeter-cryostat, potentiometer and switch arrangements appear on pages 42, 43 (Fig. 7, 8, 9).

The method of determination of a heat capacity is as follows. Having cooled the calorimeter to the desired temperature, the can surrounding it is evacuated. Current is passed through the block heater until its temperature is a predetermined amount above that of the calorimeter. A small current is usually allowed to flow continuously through the block heater to maintain its temperature constant. The heating rate of the calorimeter is then taken by means of the resistance-thermometer over a period of about five minutes. Approximately 0.1 ampere is then passed through the calorimeter heater for about 10 minutes, this energy input being timed to within about 0.05% by means of a 15 watt synchronous clock motor run by the precisely-controlled frequency of Boulder Dam power and geared to a Veeder-Root counter which records seconds and which actuates an electrical device which gives a signal every second. (The switch controlling the energy input can be thrown in or out with the signal to a precision of about 0.1 second) Five potential readings are made during the energy input, three of E_c and two of E_V, at predetermined exact times depending on the time of energy input. The rise in temperature resulting from this energy is usually about 4°, which, in the case of measuring the heat capacity of a solid or liquid of low vapor-pressure is about 2° above the block temperature, but which is definitely below the block temperature when measurements are being made on liquids of moderate vapor-pressure to prevent distillation from the calorimeter into the inlet tube. The cooling (or warming) rate is followed for 20 to 30 minutes, equilibrium apparently being obtained in from 10 to 20 minutes usually. At the end of each determination, the resistance thermometer is calibrated against the thermocouple on the calorimeter.

To correct for the heat interchange between the calorimeter and surroundings Newton's law of cooling is assumed, the energy measurements furnishing sufficient data to calculate the external temperature of the calorimeter during the energy input. Correction is also made for the fact that a thermal head between the resistance-thermometer and contents of the calorimeter exists during the energy input. Further corrections are also made for the heat developed in the leads between the calorimeter and block and for the change in block temperature if it changes appreciably. (For a discussion of the theory of these "corrections" see the Ph.D. thesis of Mr. Darrell Osborne, 1938.) The total of these corrections amounted to about 0.2% at the lower temperatures and increased to as much as 1% at the higher temperatures for the measurements made on CCl_3F and discussed in section III B of this thesis.

It was found that the current during the energy input could be represented very well as a quadratic function of time, and by making use of a modification of the method proposed by Gibson and Giauque (4) a tedious graphical process of obtaining the average current was avoided.

The average resistance of the thermometer was obtained by a simple calculation involving a factor read off a graph (Fig.10), and the total

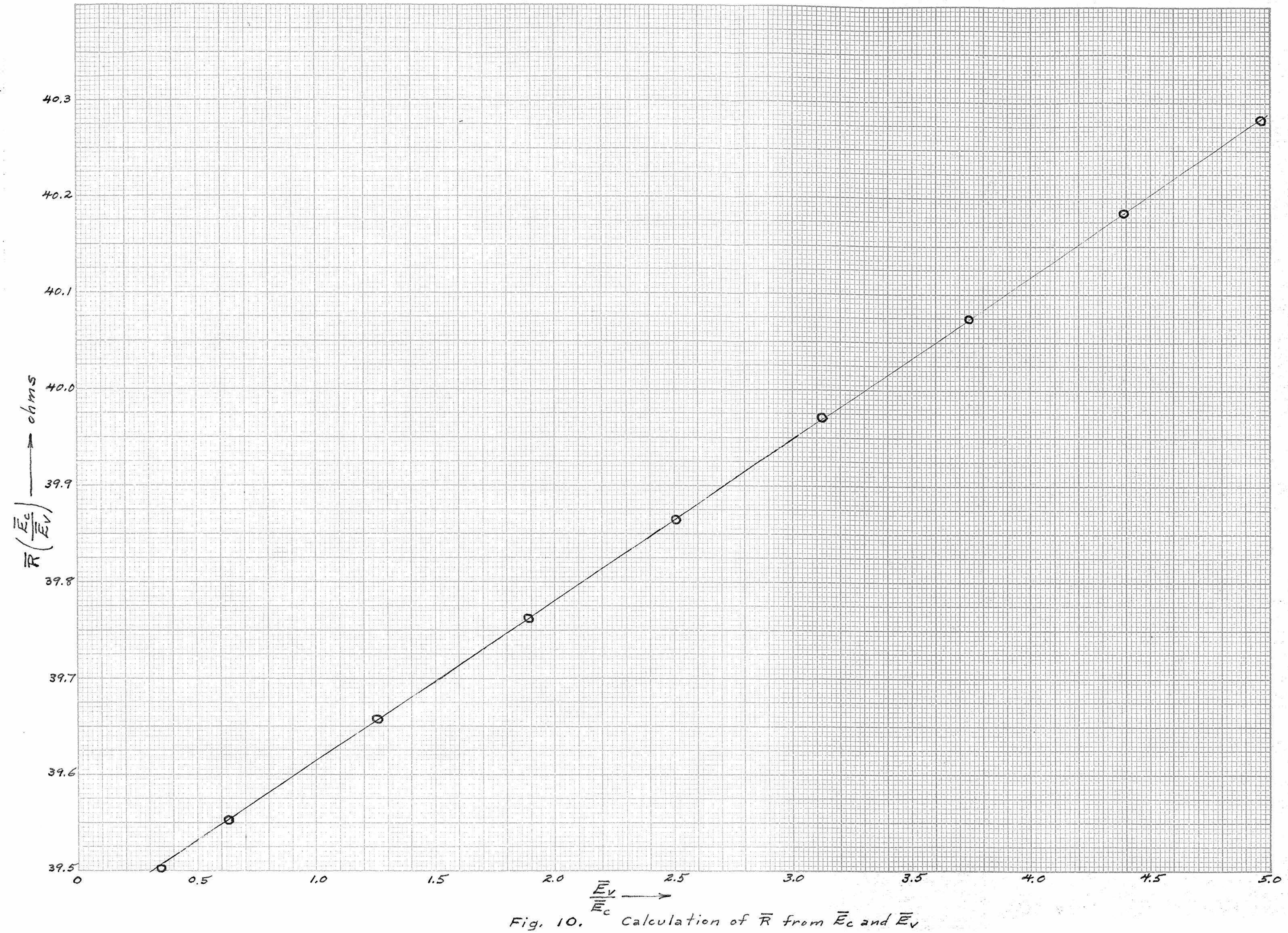

Fig. 10. Calculation of $\overline{R}$ from $\overline{E}_c$ and $\overline{E}_v$

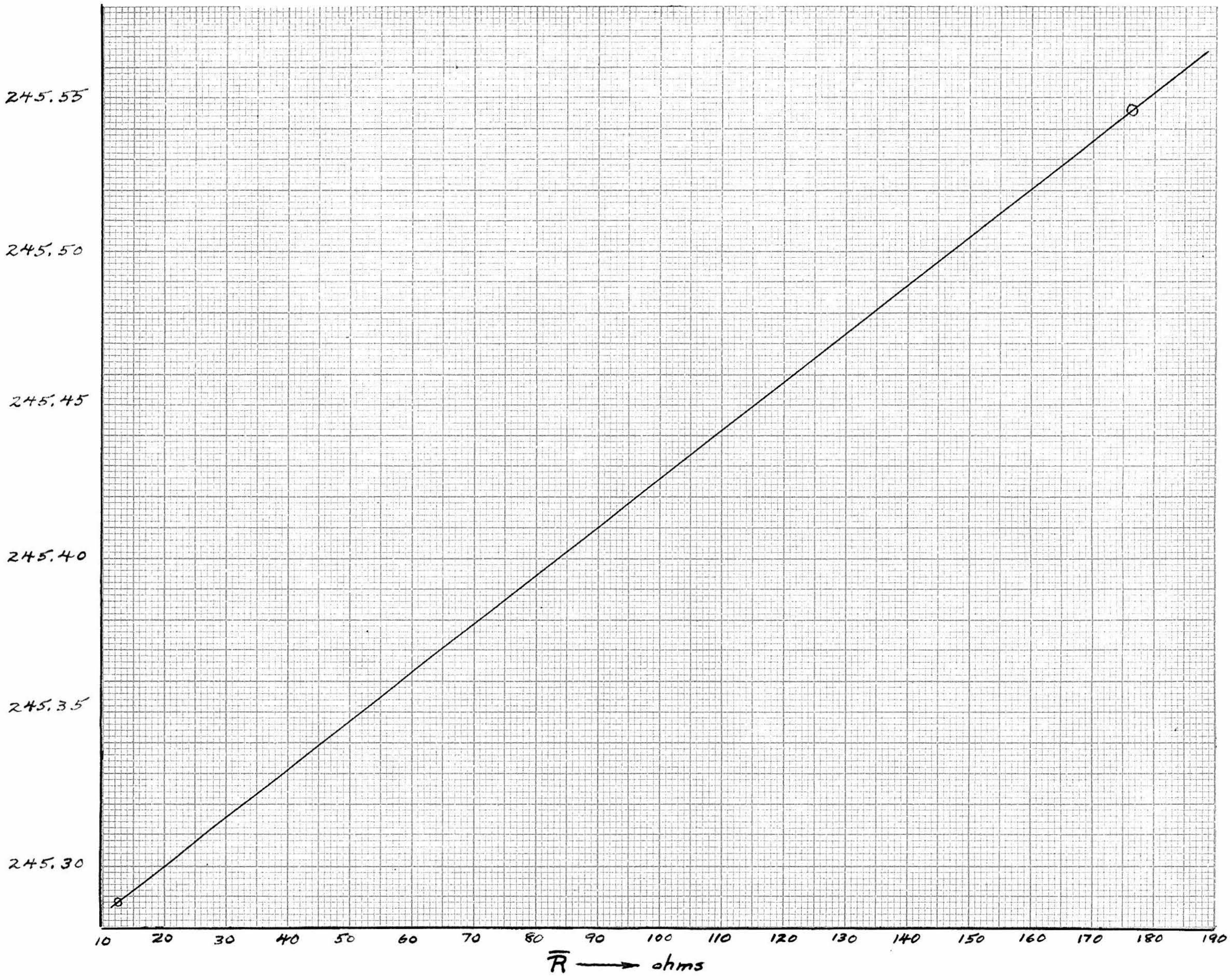

Fig. 11. Conversion of $\overline{E}_c \overline{E}_v t$ into calories

energy added was obtained by another calculation involving a second factor from another graph (Fig. 11). From the change in resistance of the thermometer and from a large graph of $\frac{dR}{dT}$ against R as determined by the calibration of the resistance thermometer against the thermocouple, the rise in temperature can be calculated. (Between 60° and 80°K the slope of the curve mentioned changes rapidly and the precision obtained is not as good as at higher temperatures. Rather detailed calculations eventually give rise to the total heat capacity. For the higher temperatures corrections must be made for the gradual vaporization of material into the inlet tube.

The amount of material whose heat capacity is being determined is ascertained by measuring it in the manometer and gas-measuring device shown on page 35 if it be a gas, or by weighing it in a special glass container if it be a liquid at room temperature. The apparatus is not designed for solid substances.

Preparation of Thermocouples; Establishment of a Temperature Scale

Before the calorimeter was assembled, thermocouples No. 7 and No. 11 had to be made and calibrated. A considerable portion of the preparation and inter-comparison of the couples was done by Mr. Darrell Osborne, to whose Ph.D. thesis (1938) reference should be made for a more detailed discussion.

Twelve thermocouples were made altogether, only two of which were selected for actual present use in the calorimeter. Driver-Harris number 30 DSC constantan wire and Anaconda number 36 DSC annealed copper wire were used. The constantan wire was kindly given us by Dr. H. Huffman; it was from the same lot as that used by Giauque, Buffington and Schulze (5). (Both the constantan and the copper wire were tested for homogeneity by drawing a loop through liquid air and noting the EMF produced, which was less than 1 microvolt with this very large temperature gradient.) The thermocouples were made with one strand of copper wire and five strands of constantan to give rigidity to each couple and to tend to average out any small inhomogeneities; the heat conduction of the five constantan wires is about the same as that of the single copper wire. Each couple was bound together with silk thread and lightly lacquered with electrician's enameling fluid over the greater amount of the couple. The variable junction was soft-soldered, and the "ice-end" constantan wires were all soldered to a number 24 DSC copper wire as was the "ice-end" copper wire of the couple. (Each bundle was drawn through liquid air fifteen times after which further homogeneity tests were made on the five combined constantan wires which showed the EMF due to this large temperature gradient to be 0.3 microvolt or less.) The "ice-end" junctions were placed in thin glass tubes which were then filled with paraffin; these tubes were then inserted in a large Dewar flask containing the crushed ice-water mixture, the temperature of which was noted with a precision Beckmann thermometer and which never varied more than 0.005° from the ice-point during all our investigations.

A comparison was made of six of these couples with a similar couple loaned us by Dr. Huffman and which had been calibrated against the Giauque, Buffington and Schulze temperature scale which was based on the helium and hydrogen gas thermometers and oxygen vapor pressure measurements (5,6). This comparison was made in the calorimetric device, the calorimeter being replaced by a heavy copper block to which all seven couples were soldered with Wood's metal. Due to the possibility that the standard couple might have "aged" and because a break occurred in the copper wire of this couple, it was recalibrated against one of our own couples which was calibrated against the oxygen vapor pressure thermometer. (The standard couple was repaired by replacing the entire copper wire and testing the couple at liquid air temperature.)

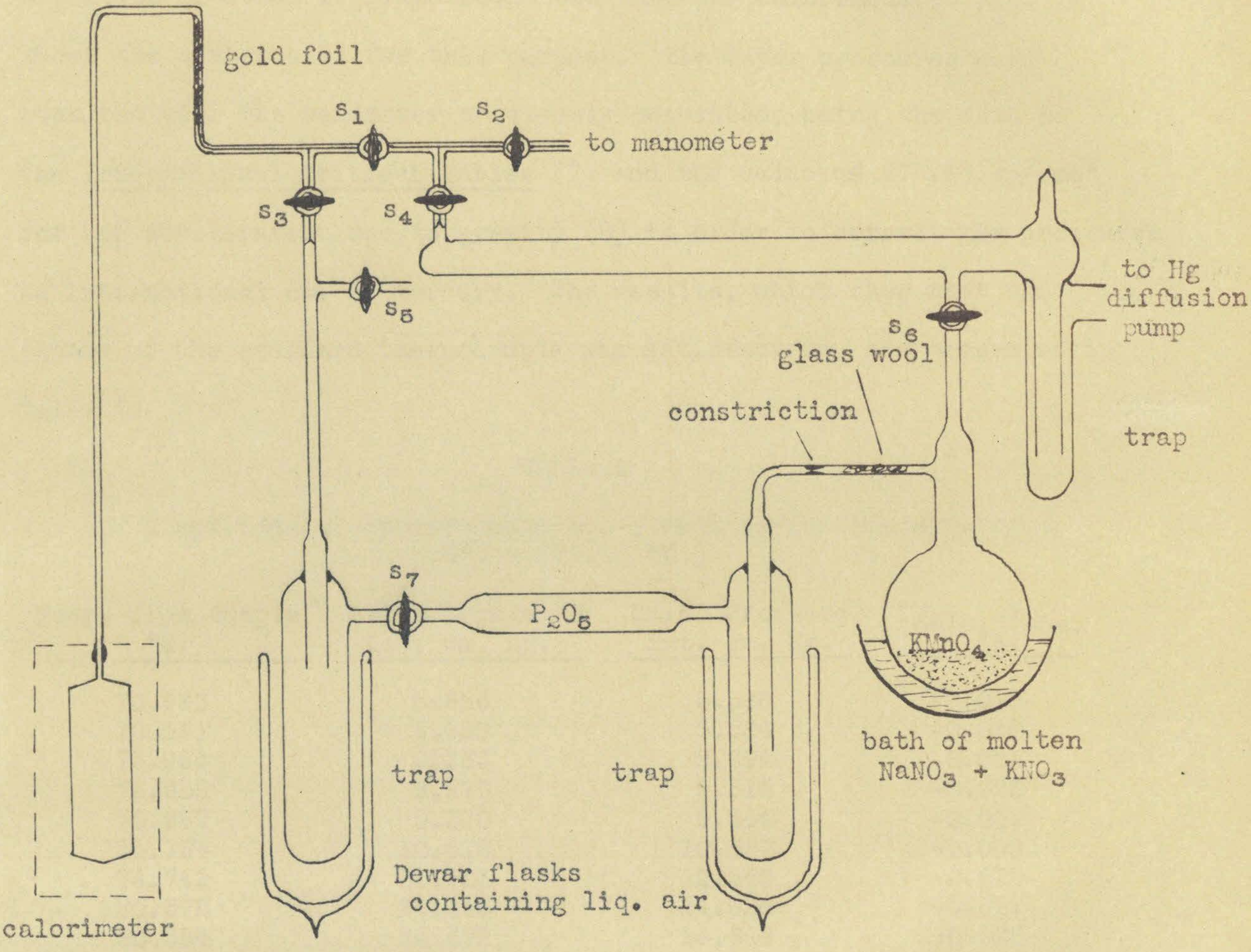

Fig. 12. System for preparation of oxygen

The calibration of one of our couples with the oxygen thermometer was made in our calorimeter. The oxygen was prepared from pure potassium permanganate; it was dried by passage through a tube containing anhydrous phosphorous pentoxide, after which it was "fractionated" and a portion of about 70 grams condensed into the calorimeter. Fig. 12 shows the system used for this purpose. The vapor pressures were measured with the manometer previously described, using the data in the International Critical Tables (7) and the value of 979.57 cm/sec^2 for the acceleration due to gravity (8) in order to correct the pressures to international cm. of mercury. The results, which show that the repair of the standard thermocouple was satisfactory, are presented in Table I.

Table I

Comparison of thermocouple No. 7 with oxygen thermometer
(0°C = 273.10 °K.)

Temp. from couple °K.	Exptl. Pressure int. cm. Hg.	Calc. Pressure int. cm. Hg.	$T_{calc.}-T_{obs.}$ °K.
70.923	5.556	5.566	-0.010
70.941	5.559	5.584	-0.026
73.954	9.263	9.294	-0.021
73.968	9.276	9.315	-0.026
73.987	9.330	9.344	-0.009
74.734	10.518	10.527	-0.003
74.742	10.523	10.540	-0.013
80.578	24.665	24.624	+0.012
80.584	24.672	24.644	+0.008
84.575	40.866	40.870	-0.001
84.580	40.903	40.895	+0.002
86.255	49.696	49.785	-0.016
86.258	49.738	49.801	-0.011
89.853	74.00	73.87	+0.017
89.857	74.04	73.90	+0.017
90.083	75.63	75.68	-0.004
90.086	75.66	75.68	-0.003
90.327	77.54	77.60	-0.008
90.331	77.56	77.63	-0.009

The calculated pressures given in column 3 are computed from the equation of Cath (9): $\log_{10}P(\text{int.cm.Hg}) = -\frac{419.31}{T} + 7.1173 - 0.00648\,T.$

The values of $T_{calc.} - T_{obs.}$ given in column 4 are obtained by subtracting the temperature read with the thermocouple from that calculated by inserting the experimentally determined corresponding pressure in Cath's formula. Two sets of measurements were made of the oxygen vapor pressures, the second set being made after about two-thirds of the oxygen in the calorimeter was pumped out; the close agreement between the two sets indicates the purity of the oxygen.

A table was constructed with which the EMF of thermocouple No. 7 could be easily and precisely converted into temperature by interpolation over a very small EMF interval. It is believed that the temperature scale from 60° to about 290°K is accurate to about 0.05° and probably to 0.1° from 290° to 300°K.

Acknowledgements

It is desired to acknowledge here the help of many, and, in particular, of the following:

Professor Don M. Yost, for encouragement and assistance throughout this work; Mr. Darrell Osborne, who has worked with the author on a large part of this particular investigation; Dr. Hugh Huffman, for his many helpful suggestions and his kindness in loaning us a calibrated thermocouple, as well as supplying us with certain materials; the late Mr. Searle, instrument maker, and Mr. Newton, Chemistry Division instrument maker, for their valuable help in fabricating certain parts of the apparatus.

Summary

An apparatus for calorimetric and vapor pressure measurements on condensed gases between 60°K and room temperature has been described in some detail. The calorimeter is of the "isothermal environment" type, similar in some respects to the type used by Giauque and his coworkers. Energy is supplied and measured electrically, and the temperatures are

obtained by a copper resistance thermometer wound directly on the gold-plated copper calorimeter and calibrated with a standard copper-constantan thermocouple with each heat capacity determination.

The various electrical circuits are described, and the general method of measurement is outlined.

Preparation of the thermocouples and their calibration against a standard couple and against the oxygen vapor pressure thermometer is discussed.

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(3) Ellis, Science 81, 568 (1935).

(4) Gibson and Giauque, J. Am. Chem. Soc. 45, 93 (1923).

(5) Giauque, Buffington and Schulze, ibid. 49, 2343 (1927).

(6) Giauque, Johnston and Kelley, ibid. 49, 2367 (1927).

(7) International Critical Tables, McGraw-Hill Book Co., New York, 1926. Vol. I.

(8) Measured at C.I.T. by the Coast Geodetic Survey. The acceleration due to standard gravity was taken as 980.67 cm/sec^2.

(9) Cath, Comm. Phys. Lab. Univ. Leiden, No. 152 (1918).

THE HEAT CAPACITY OF MONOFLUOROTRICHLOROMETHANE FROM 60°K TO ITS BOILING POINT. ITS HEAT OF FUSION, HEAT OF VAPORIZATION, VAPOR PRESSURE AND ENTROPY

Introduction

Because of the increasing use of the fluorochloromethanes as refrigerants and because of the interesting structural comparisons which can often be made with similar compounds, it seems desirable that the thermodynamic properties of monofluorotrichloromethane, one of these substances mentioned, be determined in a precise manner.

For the purpose of obtaining the standard virtual entropy of CCl_3F gas, the heat capacity of solid CCl_3F has been measured from 60°K to its melting point, the heat of fusion has been determined, the heat capacity of the liquid measured up to its boiling point, and the heat of vaporization determined by measurements made of the vapor pressure. An extrapolation of the heat capacity to 0°K allows a value for the entropy to be obtained.

As far as the present investigation is concerned, a precise determination of the entropy of CCl_3F gas is difficult to make because of the uncertainties involved in extrapolating the heat capacities from 60°K to the absolute zero. For this reason a further investigation of the heat capacities from 60° down to at least 20°K is planned, after which a good value for the entropy will be abailable.

Comparison of the calorimetrically obtained entropy is made with the entropy calculated from the internuclear distances and the Raman frequencies.

This entire investigation has been jointly carried out with Professor Don M. Yost and Mr. Darrell Osborne.

Purification of Monofluorotrichloromethane

A sample of partially purified monofluorotrichloromethane was kindly given us by Dr. L. O. Brockway who received it from Mr. R. J. Thompson of the Kinetic Chemicals, Inc., Wilmington, Del. It was distilled and after standing over calcium chloride for several days it was fractionated with a glass column packed with glass helices. The middle fraction was collected in a glass bulb. A portion of this purified sample was distilled (in a vacuum) from the bulb through a tube containing anhydrous phosphorus pentoxide and then condensed in a glass trap. The sample was then alternately cooled to liquid air temperature, pumped on with a diffusion pump, and allowed to melt; in this way the last traces of air and of low boiling material were removed. Part of the CCl_3F was then distilled into another trap and this process repeated. Finally, about 100 grams of the purified material were distilled into the calorimeter which had been previously well evacuated.

The weight of sample was obtained by weighing the filling bulb with the sample and the evacuated bulb after removal of the sample. Calibrated weights were used and a correction to vacuum weight was made.

The impurity in the sample was 0.01 mole per cent. as estimated from the melting point range.

Heat Capacities

The method of heat capacity measurement and the temperature scale have been discussed elsewhere (1). In calculating energy, one calorie was taken equal to 4.1852 absolute joules and one international joule to 1.0004 absolute joules (2). The ice-point was taken as 273.10°K in conformity with the value given in the <u>International Critical Tables</u> (3).

The molal heat capacities are given in Table I and Fig. 1. The molecular weight of monofluorotrichloromethane was taken as 137.38 in agreement with the 1938 International atomic weights (4).

Table I

Molal Heat Capacity of Monofluorotrichloromethane

Temp., °K	$\tilde{C}_p$ cal./deg./mole	Series number
62.22	11.68	I
65.25	12.09	I
68.08	12.34	I
70.53	12.56	I
75.85	12.90	I
79.85	13.22	I
85.37	13.69	I
89.02	13.94	I
89.29	13.96	II
92.86	14.28	I
96.36	14.53	I
99.68	14.82	I
103.0	15.12	I
106.6	15.46	I
110.3	15.75	I
114.0	16.12	I
117.9	16.46	I
122.4	16.85	II
126.2	17.30	I
131.2	17.77	I
135.3	18.13	I
137.3	18.38	II
139.1	18.58	I
141.0	18.83	II
141.9	18.92	III
143.2	19.06	I
144.7	19.32	II
145.9	19.36	III
147.0	19.49	I
148.3	19.75	II
152.0	19.97	II
156.4	21.66	P
156.5	21.12	P
157.1	21.92	P
159.5	25.90	P
160.0	26.74	P
160.1	28.20	P
162.54	Melting point	
165.9	26.10	I
169.2	26.11	II
171.2	26.10	I
173.0	26.18	II
175.8	26.29	I
180.2	26.45	I
183.3	26.37	III
190.9	26.59	I
196.4	26.66	I
201.7	26.63	I
207.0	26.70	I
212.9	26.93	III
222.0	27.05	III
225.0	27.19	III
231.8	27.17	II
241.3	27.42	III
247.9	27.55	III
254.7	27.70	III
260.2	27.73	III
261.0	27.87	I
266.3	27.91	III
272.5	28.07	III
279.3	28.21	III
283.5	28.38	II
285.6	28.41	III
290.5	28.60	I
291.8	28.56	III
296.88	Boiling point	

The measurements of series I were taken after the CCl_3F had been kept at 60°K for about three hours. Series II and III were obtained after the CCl_3F had been warmed to room temperature and then recooled to 65°K and held there for about six hours. In general, the measurements were not made continuously but extended over a period of many weeks.

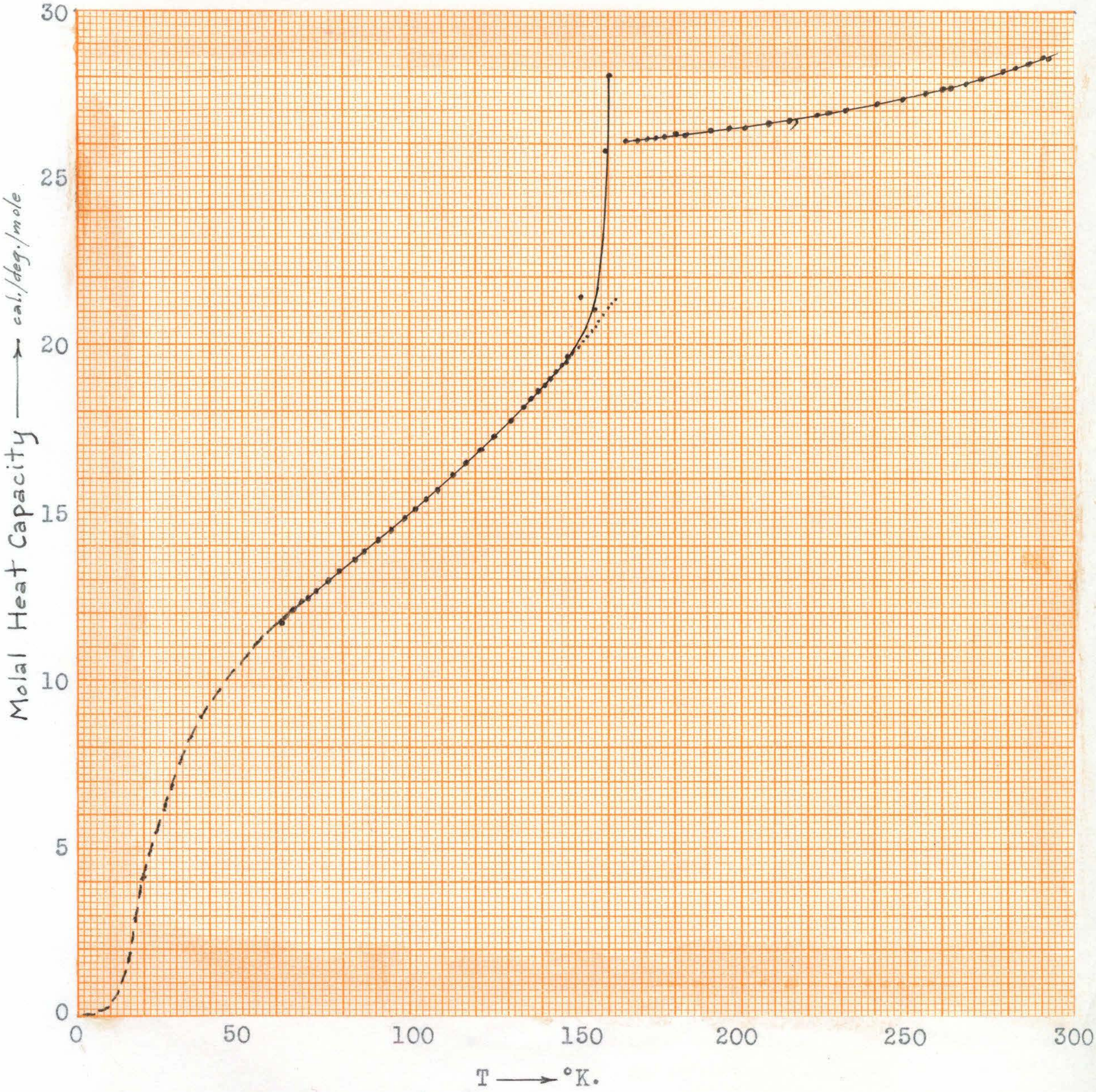
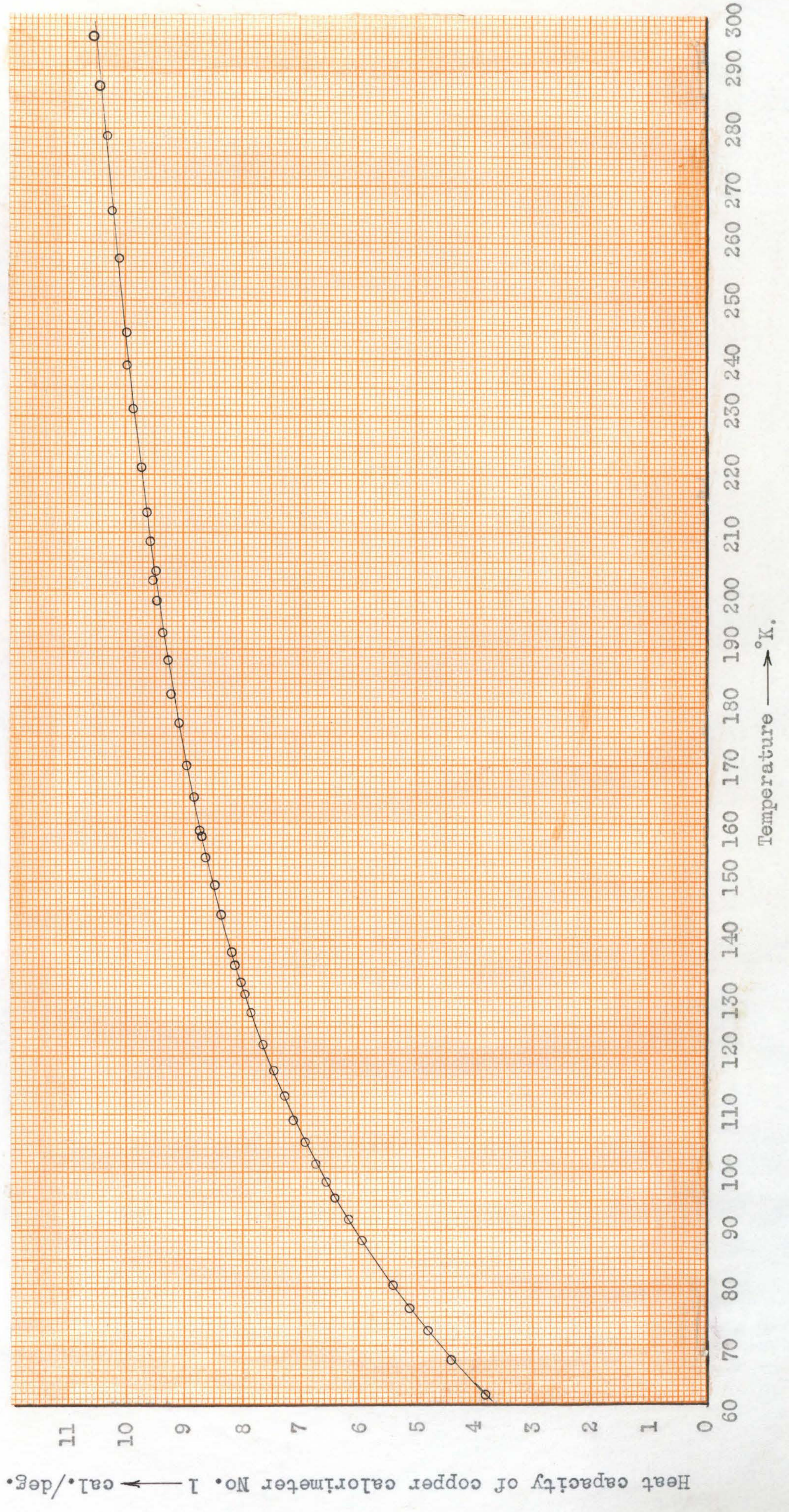


Fig. 1. Heat Capacity of Monofluorotrichloromethane


Heat capacity of copper calorimeter No. 1 ⟶ cal./deg.
0
1
2
3
4
5
6
7
8
9
10
11
Temperature ⟶ °K.
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300

In series P the tabulated heat capacities require correction for heat absorbed in premelting; the correction is made with the thermodynamic freezing point equation and the heat of fusion at the melting point, an estimate being made of the amount of material melted. The heat capacities of the liquid have been corrected for material vaporized into the space above the liquid in the calorimeter and into the filling tube. This volume was known from the known amount of CCl_3F (0.7660 mole) and the volume of the empty calorimeter and filling tube which was determined by an expansion method. In the calculation the density taken for the liquid was that given (as a function of temperature) by Ruff and Keim (5), and the heat of vaporization used was that obtained from our vapor pressure measurements; the correction amounted to 0.5 cal./deg. at 295°K and diminished rapidly with decreasing temperature.

It should be remarked that Fig. 1 is not intended to reproduce carefully the experimental points; the plot was roughly made merely to enable one to see the general behavior of the heat capacity with temperature. The dotted extension of the curve for the solid represents an extrapolation to the melting point to obtain heat capacities used in calculating the heat of fusion. The dashed extension of the same curve indicates the extrapolation made to the absolute zero.

The heat capacity of the CCl_3F is about three times that of the empty calorimeter throughout the range of these measurements. This, as well as the general precision of measurement for the empty calorimeter, is shown in Fig. 2. In determining the heat capacity due to the CCl_3F a large plot was made of the empty calorimeter heat capacity from which could be read the value corresponding to the temperature at which the total heat capacity was found.

The error in these measurements from all the various sources is dependent on the temperature. Between 60° and 75°K the results may be in error by 0.4% due to the rapid change of dR/dT for the copper resistance thermometer in this range; from 75° to 165°K the error probably does not exceed 0.2%. In the case of the liquid the error may rise to 0.5% due to the increased heat leak correction (the drifts were often non-linear and had to be treated in a special way) and the correction for vaporization into the filling line.

The Melting Point

Observations were made of the equilibrium temperature when the sample was melted to the extent of approximately 50%, 70% and 85%, the temperatures at these places being 162.538°, 162.541° and 162.542°, respectively. As estimated from the melting point range, the impurity present probably does not exceed 0.01 mole per cent. (It should be stated, however, that an estimate of the impurity from the amount of premelting as judged by the area between the upper and lower curves for the heat capacity of the solid (Fig. 1) led to the value of 0.1 mole per cent. or less. This is not compatible with the observed melting point range, and the explanation is probably to be sought in the fact that equilibrium was only slowly if at all established in the heat capacity measurements in the premelting range.) Hence, the melting point of pure monofluorotrichloromethane is taken to be 162.54 ± 0.05°K. The only value recorded in the literature seems to be that of Ruff and Keim (5), namely 162°K.

The Heat of Fusion

The method used for the determination of the heat of fusion at the melting point consisted in adding a measured amount of energy sufficient to heat the calorimeter and contents from a temperature somewhat below that at which premelting begins to a temperature a few degrees above the melting point, correcting this energy input for heat interchange between the calorimeter and surroundings, and taking into account the integral $\int C_p dT$ on both sides of the melting point.

The results are presented in Table II.

Table II

The Molal Heat of Fusion of Monofluorotrichloromethane

Temp. interval, °K	Energy input, cal.	Heat interchange, cal.	$\int C_p dT$ cal.	ΔH, cal.	$\Delta \tilde{H}$, cal./mole
150.73 - 166.35	1652.3	4.0	399.3	1257.0	1641.0
150.59 - 163.90	1585.1	5.2	332.0	1258.3	1642.7
				Mean	1641.8 ± 3.2

In the above table, column 2 gives the energy added electrically and column 3 gives the energy which was received by the calorimeter and contents from the surroundings. $\int C_p dT$ refers to the energy which was used in heating the calorimeter and contents up to the melting point (a correction was made to the heat capacities in the premelting range) and in heating the calorimeter and liquid contents to the final temperature. Column 5 gives the heat of fusion for the amount of CCl_3F actually present, namely 0.7660 mole. The molal heat of fusion is recorded in column 6; the error assigned to the mean value arises from possible errors of 0.1% in the amount of CCl_3F present and 1 cal. in $\int C_p dT$.

The Vapor Pressure Measurements

The vapor pressure of the liquid was measured by means of a Henson cathetometer with a calibrated scale and the manometer previously described (page 34 ff). The observations have been represented by the following equation:

$$\log_{10} P \text{ (int. cm Hg)} = -\frac{1610.04}{T} + 8.21671 - 0.0030743\, T.$$

The observed and calculated values are compared in Table III.

The temperatures have been given to 0.001° because of the high relative accuracy; there may be an error of 0.05° in the absolute temperature recorded. By means of data given in the International Critical Tables (3) and additional observations of the menisci heights, the observed readings were corrected to International cm. of mercury. The standard acceleration due to gravity was taken as 980.67 cm/sec^2 and the acceleration for this location as 979.57 cm/sec^2(6).

Table III

The Vapor Pressure of Liquid Monofluorotrichloromethane
(0°C = 273.10°K)

Temp., °K	Exptl. Pressure int. cm Hg.	Calc. Pressure int. cm Hg.	$P_{obs.} - P_{calc.}$ int. cm Hg.
236.640	4.851	4.848	+0.003
236.680	4.854	4.858	-0.004
239.742	5.781	5.807	-0.026
239.812	5.781	5.830	-0.049
251.489	11.019	11.003	+0.016
251.526	11.040	11.024	+0.016
251.571	11.052	11.050	+0.002
265.183	21.398	21.381	+0.017
265.229	21.410	21.426	-0.016
274.799	32.509	32.578	-0.069
274.809	32.510	32.592	-0.082
280.918	41.869	41.853	+0.016
280.938	41.884	41.887	-0.003
280.945	41.894	41.901	-0.007
282.229	44.120	44.088	+0.032
282.268	44.192	44.156	+0.036
285.980	51.027	51.006	+0.011
285.987	51.035	51.019	+0.014
291.103	61.802	61.793	+0.009
291.109	61.840	61.807	+0.033
291.211	62.046	61.040	+0.006
293.844	68.205	68.253	-0.048
293.893	68.376	68.371	+0.005
295.330	71.937	71.962	-0.025
295.381	72.125	72.093	+0.032

The only other vapor pressure data on monofluorotrichloromethane are those of Ruff and Keim (5), who measured the vapor pressure at three temperatures which were recorded to the nearest degree only. Their values agree reasonably well with the values calculated for their temperatures from our vapor pressure equation.

The Boiling Point

The normal boiling point calculated from our vapor pressure equation is 296.88 ± 0.05°K. During the distillation of the same sample, after it had been purified, the boiling point remained constant to within 0.1° and the normal boiling point calculated from the distillation data is 296.8°K.

Previous values which have been reported for the normal boiling point are 298.0° (7) and 297.3°K (5), these being high presumably because of impurities in the samples used or because of inaccuracies in the temperature scales employed by these other investigators.

The Heat of Vaporization

From the vapor pressure equation representing our measurements and the Clapeyron equation the heat of vaporization at the normal boiling point can be obtained. For this purpose the density of liquid CCl_3F given by Ruff and Keim (5) was used to calculate the molal volume of the liquid, and the molal volume of the gas was calculated with the Berthelot equation:

$$P\tilde{V} = RT\left[1 + 9PT_c(1 - 6T_c^2/T^2)/128P_cT\right] .$$

The critical temperature of CCl_3F has not been measured apparently, but an inspection of the data in the International Critical Tables (8) indicates that the ratio of T_c/T_b is substantially constant for a given homologous series, where T_c is the critical temperature and T_b the normal boiling point on the absolute scale. Using the value 1.597 for the ratio (this is the mean of the closely agreeing values for CCl_4 and $CHCl_3$), one calculates that T_c = 474 °K. The critical temperature, P_c, is 50 atm., obtained by substituting the above critical temperature into our vapor pressure equation. (This value is about the same as that for carbon tetrachloride.)

The heat of vaporization at the normal boiling point, thus calculated, is 5905 cal./mole, the Berthelot correction amounting to -220 cal./mole. The Trouton's constant calculated from this value and the boiling point is 19.89. The constants given for CCl_4, CCl_2F_2 and $CClF_3$ are 20.55 (9), 19.3 (5) and 18.4 (5), respectively; as is seen, the Trouton's constant for these compounds increases more or less regularly as chlorine is substituted for fluorine.

The Entropy from the Calorimetric Data

Table IV gives a summary of the entropy calculation from the calorimetric data.

Table IV

The Entropy of Monofluorotrichloromethane from Calorimetric Data

0-60.00°K, extrapolation	10.12 ± 1.5 cal/deg/mole
60.00-162.54°K, crystals, graphical	15.26 ± 0.05
Fusion 1641.8/162.54	10.10 ± 0.02
162.54-296.88°K, liquid, graphical	16.34 ± 0.10
Vaporization 5905/296.88	19.89 ± 0.10
Entropy of actual gas at boiling point	71.71
Correction for gas imperfection	0.14
Entropy of ideal gas at 1 atmosphere and 296.88°K	71.85 ± 1.5
296.88-298.10°K, gas, calculated	0.07
Entropy of ideal gas at 1 atmosphere and 298.10°K	71.92 ± 1.5

The extrapolation of the measured heat capacities to the absolute zero was attempted in several ways. The "n" formula method developed by Lewis and Gibson for solid elements of "class II" (10) was applied to carbon tetrachloride from 60°K on down, but the entropy increment so obtained disagreed with the value obtained from calorimetric work down to 10°K (11) by some three or four entropy units; for this reason it was thought inadvisable to use this method for CCl_3F. The treatment of Kelley, Parks and Huffman (12) was also tried on CCl_4 using their "class I" standard substance, but the agreement was poor again. Using their treatment on CCl_3F assuming CCl_4 as the "standard" substance led to values for the extrapolation constants in their formula which varied considerably with the temperature above 60°K. Still another procedure which could be tried is to fit the experimental heat capacity curve with a combination of Debye and Einstein functions; it is doubtful whether this method would give a more reliable answer than that finally adopted, and it is certainly much more laborious to apply. In view of these considerations, and because the heat capacity of CCl_3F probably behaves in a way similar to that of CCl_4 below 60°K, the plan adopted was to plot the heat capacities of CCl_4 (data of Blanchard and Blue, see ref. 11) against lnT on a large scale and then displace the entire curve along the lnT axis until it coincided with the CCl_3F curve at 60°K. (The fit of the two curves was not a bad one, although there was apparently some tendency for the CCl_3F curve to continue at slightly higher heat capacities for a short ways than did the curve for CCl_4. For this reason it is felt that the value given in Table IV for the extrapolation to 0°K represents a lower limit, and may well be off by as much as 1.5 cal./deg./mole.) The entropy increment to 60°K was then obtained by a graphical integration in part and partly from the data of Blanchard and Blue. It is planned to measure the heat capacity of CCl_3F crystals down to at least 20°K later on; an extrapolation from this point on will be uncertain by only some hundredths of an entropy unit.

The correction for gas imperfection given in the table was made using the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ and Berthelot's equation of state, which lead to $S_{ideal} - S_{actual} = (27RT_c^3P)/(32T^3P_c) = 0.14$ cal./deg./mole.

The entropy of ideal monofluorotrichloromethane at one atmosphere and 298.10°K was calculated from the entropy at the boiling point with the aid of the Sackur-Tetrode equation and the spectroscopic data of Yost and Osborne (13).

It is of interest to compare the value for the entropy obtained in this investigation with that calculated from the internuclear distances, determined by electron-diffraction experiments of Brockway (14), and the Raman frequencies (13). The "spectroscopic" value thus obtained is 74.10 cal./deg./mole for the gas at 1 atmosphere and 298.10°K. The discrepancy of 2.2 entropy units may be attributed to errors arising in the extrapolation of the heat capacity data and to the possibility that the assignment of the Raman frequencies may not be correct. It is hoped that the additional experiments planned on CCl_3F heat capacities will reduce greatly the uncertainties in the extrapolation to the absolute zero.

Acknowledgements

The author extends his thanks to Professor Don M. Yost and Mr. Darrell W. Osborne for their splendid cooperation in this research.

Summary

The heat capacity of crystalline CCl_3F has been measured from 60°K up to its melting point, and the heat capacity of the liquid determined from the melting point to the boiling point. The heat of fusion at the melting point has been determined to be 1641.8 ± 3.2 cal./mole. The vapor pressure of the liquid was determined over the range of pressures 5 to 72 cm of mercury; the observations can be well represented by the equation:

$$\log_{10} P \text{ (int. cm Hg)} = -\frac{1610.04}{T} + 8.21671 - 0.0030743\,T.$$

From this equation the boiling point at one atmosphere pressure is calculated to be 296.88°K, and the heat of vaporization at the normal boiling point to be 5905 cal./mole, a Berthelot correction of -220 cal/mole being made. The Trouton's constant is then 19.89.

A reasonable extrapolation of the measured heat capacity to the absolute zero allows a Third Law computation of the entropy of CCl_3F gas at 1 atmosphere and its boiling point; the value 71.85 ± 1.5 cal./deg./mole is obtained after correcting for the gas imperfection. A calculation gives 71.92 ± 1.5 cal./deg./mole for the standard virtual entropy of CCl_3F gas.

A comparison of the calorimetric entropy with the "spectroscopic" entropy gives rise to a discrepancy of 2.2 cal./deg./mole, for which a partial explanation can be offered.

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Acknowledgements

I wish to express my sincere appreciation for the interest and counsel of Professor Don M. Yost and the late Professor Arthur A. Noyes throughout these investigations.

I wish to thank also my wife, Mrs. Ellen Louise Garner, for typing the major portion of this thesis.

Clifford S. Garner
May, 1938