indicate that the value $3R$ is reached at about $-51°$. These small discrepancies are to be expected when high temperature data are used for extensive extrapolations. The estimated accuracy of the integrated entropy values is $\pm 0.3\%$ above 200°K., although the reproducibility of and deviation from the smooth heat capacity *vs.* temperature plot is somewhat better than this. The entropy below 20°K. was estimated to be 0.049 cal. mole^{-1} deg.$^{-1}$ by aid of the Debye relation. The molal entropy at 298.16°K. was calculated to be 8.89 $\pm$ 0.03 cal. mole^{-1} deg.$^{-1}$.

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Thermodynamic Properties of Technetium and Rhenium Compounds. V. Low Temperature Heat Capacity and the Thermodynamics of Potassium Perrhenate and the Perrhenate Ion[1]

By J. W. Cobble,[2] G. D. Oliver and Wm. T. Smith, Jr.

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The low temperature heat capacity of potassium perrhenate has been measured from 16° to 300°K., and the molal entropy has been calculated to be 40.12 $\pm$ 0.08 cal. mole^{-1} deg.$^{-1}$ at 298.16°K. When combined with solubility data and heat of solution measurements, the entropy of the perrhenate ion has been found to be 48.3 cal. mole^{-1} deg.$^{-1}$. The free energy of formation of the ion has been calculated to be $-167{,}100$ cal. mole^{-1}.

Introduction

The molal heat capacity of crystalline potassium perrhenate has been measured from 16° to 300°K. as part of a study on the thermodynamics of technetium and rhenium. The molal entropy of potassium perrhenate has been calculated from the data. When combined with the solubility measurements of Smith[3] and the calorimetric heats of solution of Roth and Becker,[4] the partial molal entropy of the perrhenate ion can be calculated. This value together with an experimentally determined value for the entropy of rhenium[5] has been used in calculating the thermodynamic functions for the perrhenate ion.

Experimental

Materials.—The potassium perrhenate was furnished by the University of Tennessee and was specified as $\geq 99.9\%$ pure. The crystals were ground to *ca.* 100-200 mesh, dried at 100° and placed in the calorimeter. The calorimeter was then evacuated to 10^{-6} mm., flushed repeatedly with dry helium, and then sealed at a helium pressure of $\sim ^1/_3$ atm. During the measurements it became apparent that an unusual absorption of energy was taking place near 273°K. After the measurements, the salt was removed and fused. A loss of 0.30% was observed on the initial fusion, and no further loss occurred upon re-fusion. Since this weight loss corresponded closely to the calculated amount of water which would account for the observed energy involved in the transition (0.305%), it was concluded that drying at 110° and flushing with helium had not been sufficient to remove the water, and the data have been so corrected.[6] The corrected weight of the sample was 99.5466 g. (*in vacuo*).

Apparatus and Methods.—The adiabatic cryostat together with the temperature measuring equipment and the energy measuring apparatus has been previously described.[7] The previously calibrated calorimeter was made of copper and was provided with a hole at the top for filling and emptying of the solid. The hole could be capped with a copper disc and sealed with soft solder.[5] Liquid and solid nitrogen and liquid and solid hydrogen were used as the refrigerants.

Experimental Results

The corrected experimental molal heat capacity data are given in Table I, and the smoothed thermodynamic functions are given in Table II.

Table I

Observed Molal Heat Capacities of $KReO_4$(c)

Molecular weight, 289.406; 0°C. = 273.16°K.

T_m, °K.	C_p	T_m, °K.	C_p	T_m, °K.	C_p
15.94	1.452	75.88	13.759	180.85	23.729
17.14	1.715	80.66	14.426	184.10	23.924
18.37	1.922	82.23	14.630	187.98	24.140
19.95	2.260	86.30	15.222	191.95	24.400
21.55	2.601	90.18	15.736	193.79	24.502
23.60	3.027	93.83	16.170	197.38	24.662
26.26	3.680	97.39	16.657	203.38	25.009
29.13	4.386	103.90	17.369	212.50	25.546
32.38	5.182	113.70	18.416	223.76	26.108
36.36	6.165	121.78	19.258	231.45	26.438
40.80	7.220	129.19	19.885	239.04	26.788
45.76	8.311	137.66	20.696	246.55	27.088
51.30	9.524	145.86	21.381	255.05	27.473
53.07	9.836	151.81	21.997	264.58	28.045
56.66	10.475	161.57	22.504	284.73	28.363
61.07	11.321	170.06	23.061	290.67	29.036
65.84	12.146	179.29	23.656	299.68	29.392

Abnormally high values near 273°K. due to water have been omitted from Table I. The entropy below 16°K. was estimated from the Debye relation and amounted to 0.533 cal. mole^{-1} deg.$^{-1}$. At 298.16°K. the molal entropy for potassium perrhenate is 40.12 $\pm$ 0.08 cal. mole^{-1} deg.$^{-1}$. For purposes of calculation we have taken the

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[1] This work was performed for the Atomic Energy Commission.

[2] The Radiation Laboratory, University of California, Berkeley, Calif.

[3] W. T. Smith, Jr., This Journal, **68**, 394 (1946).

[4] W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932).

[5] W. T. Smith, Jr., G. D. Oliver and J. W. Cobble, This Journal, **75**, 5785 (1953); paper IV of this sequence.

[6] The residual water in potassium perrhenate is held very strongly since the sample lost no weight at 110° and did not rapidly lose weight until melting occurred (555°). It was further observed that the sample could be heated well above 273°K., then cooled as much as 40 degrees below the ice point without causing the transition to occur. Cooling to much lower temperatures for eight hours or so would cause it to reappear.

[7] G. D. Oliver and J. W. Grisard, This Journal, **73**, 1688 (1951).

TABLE II

THERMODYNAMIC FUNCTIONS FOR $KReO_4(c)$

T, °K.	C_p	$S°$	$\left(\frac{H° - H_0°}{T}\right)$	$-\left(\frac{F - H_0°}{T}\right)$
10	0.400	0.137	0.104	0.033
15	1.290	.441	.329	.112
20	2.320	.950	.689	.261
30	4.596	2.298	1.609	.689
40	7.032	3.968	2.662	1.306
50	9.225	5.781	3.763	2.019
60	11.154	7.636	4.836	2.800
70	12.842	9.481	5.858	3.623
80	14.344	11.294	6.888	4.406
90	15.694	13.068	7.793	5.275
100	16.921	14.786	8.645	6.141
120	19.078	18.067	10.209	7.858
140	20.906	21.150	11.611	9.539
160	22.412	24.044	12.871	11.173
180	23.670	26.758	14.002	12.756
200	24.840	29.312	15.028	14.284
220	25.887	31.730	15.968	15.762
240	26.830	34.027	16.838	17.189
260	27.778	36.211	17.642	18.569
280	28.660	38.303	18.388	19.915
298.16	29.303	40.123	19.032	21.091
300	29.364	40.305	19.097	21.208

calorie equal to 4.1840 joules (absolute). The mean deviation was observed to be about ±0.1%, but the over-all accuracy of the data was estimated to be ±0.2% except at the very low temperatures. There was no indication of a transition in potassium perrhenate between 16 and 300°K. The heat capacity is approximately a linear function of temperature above 230°K.

Roth and Becker[4] have reported the calorimetrically determined heat of solution of potassium perrhenate to give a dilute solution (0.04 *M*) as 13,800 cal. mole^{-1} at 18°. Neglecting any further heat change on dilution from that concentration to infinite dilution, and considering the heat of solution to be constant in this range of temperature as observed by Smith,[3] the value of 13,800 cal. mole^{-1} for the heat of solution at 25° was assumed.

From the data of Smith[3] the calculated value for the solubility at 25° is 0.0406 mole liter^{-1}. The activity coefficient of potassium perchlorate at this concentration[8] is $\gamma_{\pm} = 0.81$, while the value calculated for $KReO_4$ from the Debye–Hückel limiting law is 0.791. Using $\gamma_{\pm} = 0.81$ and $K_{sp} = 1.082 \times 10^{-3}$, the free energy of solution is then 4047 cal. mole^{-1} and the entropy of solution, 32.71 cal. mole^{-1} deg.$^{-1}$. Using the value of 24.5 ± 0.2 e.u. for the entropy of K^+, aq,[9] and the value given above for the entropy of $KReO_4(c)$ (40.12 e.u.) the entropy of ReO_4^-, aq, was calculated to be 48.3 ± 0.3 e.u. Using 8.89 for the entropy of Re(c),[5] the entropy of formation of the ReO_4^-, aq, ion from its elements at 25° becomes[10] −74.2 e.u. Using the revised heat of formation[11] of the perrehenate ion as −189,200 ± 800 cal. mole^{-1}, the free energy of formation of ReO_4^-, aq, then becomes −167,100 ± 800 cal. mole^{-1}.

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(8) G. Scatchard, S. S. Prentiss and P. T. Jones, THIS JOURNAL, **56**, 805 (1934).

(9) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

(10) Auxiliary thermodynamic data from U. S. Bureau of Standards. "Selected Values of Chemical Thermodynamic Properties," 1949.

(11) J. W. Cobble, W. T. Smith, Jr., and G. E. Boyd, THIS JOURNAL, **75**, 5783 (1953); paper III of this sequence.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Separation of Technetium from Molybdenum, Cobalt and Silver[1]

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In order to study the chemistry of technetium formed by the neutron bombardment of molybdenum the technetium had to be separated from its molybdenum matrix. This also involved the separation of radioactive trace impurities. The separation was accomplished by means of the Amberlite ion-exchange resins IRA 400 and IR 120. Cobalt and silver were identified as the trace impurities by determining approximately the energies of their beta particles and by carrying the radioactivity on inert cobalt and silver compounds to constant specific activity. The technetium was obtained as ammonium pertechnetate free from radioactive impurities. Quantitative analysis by counting techniques showed that the concentration of technetium in this sample of molybdenum was about ten micrograms per gram. This method is an example of the separation and determination of a radioelement formed in trace amounts by bombardment of large amounts of another element.

One of the methods available for preparing technetium is the neutron–gamma reaction on molybdenum.[2a]

$$\mathrm{Mo^{98}(n,\gamma)\,Mo^{99}} \xrightarrow{\beta^-} \mathrm{Tc^{99m}} \xrightarrow{\gamma} \mathrm{Tc^{99}}$$

In order to obtain pure technetium, this would, ideally, demand only a separation of technetium from molybdenum. Such a separation can be accomplished to a relatively high degree by successive distillations of ditechnetium heptoxide from concentrated sulfuric acid slurries of oxidized molybdenum.[2b] However, for microscopic and ultramicroscopic concentrations of technetium, as might occur naturally, such distillative techniques become impracticable. Also, metallic molybdenum targets for thermal neutrons are not free from impurities; hence, a procedure was needed for the separation of various radioactive species which might co-occur with technetium.

Recently, Fisher and Meloche[3] reported a separa-

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(1) Supported in part by funds supplied by the Wisconsin Alumni Research Foundation.

(2a) E. Segrè and G. T. Seaborg, *Phys. Rev.*, **54**, 772 (1938).

(2b) G. W. Parker, J. Reed and J. W. Ruch, AECD-2043, Jan. 9, 1948.

(3) S. A. Fisher and V. W. Meloche, *Anal. Chem.*, **24**, 1100 (1952).