

RESULTS OF ANALYSES

Subject	Mg. of iodine in 24-hour urine No iodized salt used	Subject	Mg. of iodine in 24-hour urine Iodized salt used
1	0.008	1	0.068
2	.008	2	.082
3	.009	3	.085
4	.0095	1	.102
5	.01	4	.112
5	.01	4	.128
2	.011	1	.128
6	.011	4	.182
		1	.205 ^a
Average	0.00956	Average	0.1214

^a Day following heavy exercise.

Summary

1. Foodstuffs and urine are burned with oxygen in a silica or pyrex tube furnace, using an atomizer for oils and a screw feed device for solid substances. Heat is applied from the outside by gas burners or from the inside by electrically heated platinum wires or oxy-gas torches. Urine is freed from urea with urease and burned in a pyrex tube furnace.

2. Sodium sulfite solution is used to absorb the iodine, and hydrazoic acid to free it from excess nitrite. The iodide is oxidized with a known quantity of nitrite to iodine and shaken out with carbon tetrachloride.

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THE HEAT CAPACITY AND ENTROPY OF POTASSIUM PERCHLORATE FROM 12 TO 298° ABSOLUTE. THE HEAT OF SOLUTION OF POTASSIUM PERCHLORATE. THE ENTROPY AND FREE ENERGY OF PERCHLORATE ION

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This work is a continuation of the program^{1a} for the evaluation of entropies of aqueous ions and constitutes an example of the application of these values to the determination of the free energy of a negative ion which is not readily obtained by the ordinary equilibrium or electromotive-force methods.

The following measurements were made: (1) the heat capacity of po-

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^{1a} For references to the general theory see (a) Latimer and Buffington, *THIS JOURNAL*, **49**, 2297 (1927); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); (d) Latimer and Kasper, *ibid.*, **51**, 2293 (1929); (e) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927).

tassium perchlorate from 12 to 298°K., (2) the heat of solution of potassium perchlorate at 298.1°K. These values have been used in the calculation of the entropy of potassium perchlorate and the entropy and free energy of perchlorate ion.

Material.—The potassium perchlorate used was Baker's "C. P.," which was recrystallized four times and dried for 100 hours under vacuum. Analysis indicated the purity to be at least 99.9%.

Measurement of Heat Capacity.—The experimental method follows the general plan used by Latimer and Greensfelder^{1c} and reference may be made to their paper for a description of the experimental technique. In cooling the calorimeter to the lowest temperature, 11.7°K., the three-stage vacuum pump described by Giauque and Johnston² was used. All runs were timed by a stop watch calibrated before and after measurements with watches at the University Observatory. The values obtained for the specific heat and the molal heat capacity are given in Table I in calories per degree K. The high value at 274.75°K. may be explained by the assumption of less than 0.1% of water occluded inside the crystals. The mean deviation of the values excluding the lowest and the ice points is $\pm 0.3\%$.

TABLE I

HEAT CAPACITY PER GRAM AND PER MOLE OF POTASSIUM PERCHLORATE					
Temp., °K.	C_p per gram	C_p per mole	Temp., °K.	C_p per gram	C_p per mole
12.53	0.00523	0.725	122.27	0.1238	17.15
16.39	.00763	1.058	132.15	.1273	17.64
19.49	.01217	1.686	142.22	.1311	18.17
21.85	.01622	2.247	153.21	.1355	18.77
23.98	.01981	2.745	163.78	.1402	19.43
27.02	.02567	3.557	175.05	.1445	20.02
33.39	.03882	5.379	186.90	.1479	20.49
37.01	.04606	6.382	192.38	.1502	20.81
45.18	.06038	8.366	202.90	.1544	21.39
54.79	.07434	10.30	213.09	.1589	22.01
58.95	.07939	11.00	224.60	.1631	22.60
62.99	.08384	11.62	230.85	.1632	22.61
66.58	.08726	12.09	237.33	.1663	23.04
71.74	.09244	12.81	243.95	.1670	23.14
73.37	.0978	13.55	250.30	.1700	23.56
80.63	.1004	13.91	256.32	.1719	23.86
89.53	.1063	14.73	262.58	.1756	24.33
90.37	.1066	14.77	268.90	.1888	26.16
94.40	.1089	15.08	274.75	.1982	27.46
99.87	.1118	15.49	280.46	.1875	25.98
105.29	.1141	15.80	286.33	.1869	25.90
110.16	.1172	16.23	291.49	.1864	25.82
117.13	.1210	16.76	298.07	.1901	26.34

² Giauque and Johnston, *THIS JOURNAL*, 51, 2300 (1929).

Entropy of Potassium Perchlorate.—Figure 1 gives the plot of C_p against $\log T$, from which the entropy may be obtained graphically as the integral $S = \int_0^T C_p d \ln T$. The extrapolation at low temperatures was carried out by fitting the lower points to a Debye function. In this region the curve is rapidly approaching the T^3 law. The value which we found from the integration is $S_{298.1} = 36.1 \pm 0.3$ cal./deg.

Heat of Solution.—The measurements of the heat of solution were made in a calorimeter which consisted of a vacuum-walled flask of about a liter capacity fitted with a stirrer and resistance thermometer. The resistance thermometer contained about 300 ohms of number 40 copper wire and served also as the heating coil for the determination of the heat

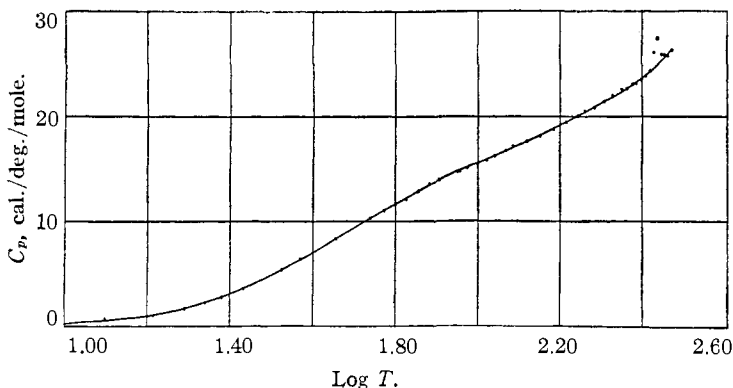


Fig. 1.—Molal heat capacity of potassium perchlorate.

capacity of the calorimeter. A small tube in the neck of the flask contained a definite weight of the solid potassium perchlorate, which could be dumped into the water by an outside control. The whole apparatus was submerged in a 25° thermostat constant to 0.01°. The value obtained for the heat of solution of one mole of potassium perchlorate in 1800 moles of water at 298.1°K. was $12,115 \pm 50$ cal.

Entropy of Perchlorate Ion.—We may now calculate the entropy change for the process: solid potassium perchlorate to give a hypothetical one molal solution of its ions, from the relations

$$\Delta S^\circ = \frac{\Delta H - \Delta F^\circ}{T} \quad \text{and} \quad \Delta F^\circ = -RT \ln (\gamma m)^2$$

This requires in addition to the heat of solution ΔH a knowledge of the solubility, m , and the activity coefficient, γ . The former has been carefully determined by a number of investigators;³ their results, agreeing

³ (a) Noyes, Boggs, Farrell and Stewart, *THIS JOURNAL*, **33**, 1650 (1911); (b) Noyes and Sammet, *Z. physik. Chem.*, **43**, 534 (1903); (c) Rothmund, *Z. physik. Chem.*, **69**, 538 (1909).

to within 0.3%, give $m = 0.148$ mole per liter at 298.1°K. The activity coefficient in the saturated solution is not readily determined experimentally, as the ordinary freezing-point method encounters as a difficulty the small solubility of the salt at low temperatures. From the conductivity measurements of Noyes and Sammet,^{3b} the value α_λ for the saturated solution at 298.1°K. is 0.78, and since this value agrees closely with the value for potassium nitrate, we feel justified in assuming the activity coefficient as given by Lewis and Randall⁴ for the latter salt, namely 0.70 ± 0.05 . This then gives

$$\Delta F_{298.1}^\circ = -1364.9 \log (0.148 \times 0.70)^2 = +2690 \pm 100 \text{ cal.}$$

and

$$\Delta S_{298.1}^\circ = \frac{12,115 - 2690}{298.1} = +31.6 \text{ entropy units}$$

Using our value for the entropy of the solid, 36.1, we obtain for the sum of the entropies of potassium and perchlorate ions, 67.7. Latimer and Buffington gave 22.0 for the entropy of potassium ion as the average of two methods. This now becomes 21.5 when we use the recent value of Lange⁵ for the heat of solution of potassium chloride which entered into one of the calculations. Hence we obtain for the entropy of perchlorate ion in the hypothetical one molal solution at 298.1°K, $S_{298.1}^\circ = 46.2$.

Free Energy of Perchlorate Ion.—Berthelot⁶ found as the average of two methods for the reaction,



Combining this with our experimental heat of solution of potassium perchlorate and with Lange's value for the heat of solution at infinite dilution of potassium chloride, +4157 calories, we obtain



Then from the value of the entropy of perchlorate ion obtained above, the entropy of chloride ion,^{1b} 15.6, and the entropy of oxygen,² 49.03, we obtain for the same reaction, $\Delta S_{298.1}^\circ = 67.5$. Hence

$$\begin{aligned} \text{ClO}_4^- = \text{Cl}^- + 2\text{O}_2 \quad \Delta F_{298.1}^\circ &= -358 - 298.1 \times 67.5 \\ &= -20,480 \text{ cal.} \end{aligned}$$

We can also calculate, as a check, the free energy of this reaction by another path which does not involve the ionic entropies. Thus using the entropy of potassium chloride,⁷ 19.7, together with that for potassium perchlorate and oxygen, we obtain

$$\begin{aligned} \text{KClO}_4 = \text{KCl} + 2\text{O}_2 \quad \Delta F_{298.1}^\circ &= +7600 - 298.1 \times 81.7 \\ &= -16,755 \text{ cal.} \end{aligned}$$

⁴ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

⁵ Lange, *Z. Elektrochem.*, **35**, 29 (1929).

⁶ Berthelot, *Ann. chim. phys.*, [5] **27**, 226 (1882).

⁷ Lewis and Gibson, *THIS JOURNAL*, **39**, 2554 (1917).

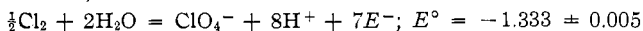
Combining this value with the free energy of solution of potassium perchlorate, +2688, and of potassium chloride,⁸ -936, gives



Using -20,430, the average of the two methods, and the Lewis and Randall⁴ value for the free energy of chloride ion, -31,367, we obtain for the free energy of perchlorate ion, $F_{298.1}^\circ = -10,937$ cal.

The error in this value is determined very largely by the accuracy of the heat of decomposition of potassium perchlorate measured by Berthelot. Although this is difficult to estimate, we judge it is within ± 500 cal.

For many purposes it is more convenient to express the free energy of perchlorate ion in terms of the reduction potential referred to the $\text{H}_2\text{-H}^+$ couple as zero. Using the Lewis and Randall⁴ value for the free energy of water, we find



Summary

The specific heat-temperature curve and the heat of solution of potassium perchlorate have been determined. These values have been used in the calculation of the entropy and free energy of perchlorate ion.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XII. THE DETERMINATION OF TELLUROUS ACID

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Introduction

An excellent survey of the volumetric methods proposed for tellurium up to the year 1926 has been given by Lenher.¹ The electrometric titration of tellurate with titanous chloride either in a hydrochloric or a sulfuric acid solution has been described recently.² The volumetric method based upon the oxidation of tellurous acid by dichromate, proposed first by Brauner³ and modified by Moser and Miksch,⁴ Lenher and Wakefield,⁵ and Schrenk and Browning,⁶ appears to be the most satisfactory and is applicable in the presence of selenious acid. The oxidation, if carried out at room temperature in hydrochloric acid solution,⁵ is rather slow and

⁸ Rodebush, *ibid.*, **40**, 1204 (1918).

¹ Lenher, *Proc. Am. Phil. Soc.*, **65**, 33 (1926).

² Tomiček, *Bull. soc. chim.*, **41**, 1389 (1927).

³ Brauner, *Monatsh.*, **11**, 526 (1890).

⁴ Moser and Miksch, *ibid.*, **44**, 349 (1923).

⁵ Lenher and Wakefield, *THIS JOURNAL*, **45**, 1423 (1923).

⁶ Schrenk and Browning, *ibid.*, **48**, 139 (1926).