The filtrate resulting from the ammonium carbonate group may then be treated as follows.

MODIFIED PROCEDURE FOR THE ALKALI GROUP

Acidify the filtrate from Group IV with dilute sulfuric acid and evaporate carefully to dryness in a porcelain dish, finally heating to expel ammonium salts. After cooling treat the residue with 2 cc. of cold distilled water and stir for several minutes to bring the sulfates into solution. Finally filter through a small filter. Divide the filtrate into two equal parts.

Part I.—Test for potassium in the usual way with sodium cobaltinitrite, confirming by means of the flame test.

Part II.—Add 10–20 cc. of cobalt–uranyl acetate reagent, stopper the test-tube and shake thoroughly for two to three minutes. Allow the mixture to stand for at least five minutes. The formation of a yellow precipitate indicates the presence of sodium.

NOTES ON THE PROCEDURE

1. In case large amounts of these alkalies are present the sulfate residue will not all go into solution. This is no disadvantage since the usual tests will be obtained.
2. Care must be taken to use not more than 1 cc. of solution for the sodium test.
3. The amount and speed of formation of the triple acetate precipitate in the test for sodium afford a valuable indication of the probable amount present.

Summary

1. There has been described a new qualitative reagent for sodium composed of a solution of uranyl and cobalt acetates in normal acetic acid.

2. The application of this reagent in the qualitative scheme for the common metals has been indicated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. V. A REVISION OF THE ENTROPIES AND FREE ENERGIES OF NINETEEN ORGANIC COMPOUNDS

BY GEORGE S. PARKS, KENNETH K. KELLEY AND HUGH M. HUFFMAN

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In four preceding papers[1] the entropies and free energies of eighteen organic compounds have been calculated from heat capacity data by means of the third law of thermodynamics. In these calculations the entropy increase for each compound between zero absolute and 90°K. was obtained by use of the "n formula" of Lewis and Gibson,[2] as in most cases the heat capacity data did not go much below the latter temperature. This formula was recognized as being only a rough first approximation but its simplicity and ease of application justified its use for comparative purposes.

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[1] Parks, THIS JOURNAL, **47**, 338 (1925); Parks and Kelley, *ibid.*, **47**, 2094 (1925); Parks and Anderson, *ibid.*, **48**, 1506 (1926); Parks and Huffman, *ibid.*, **48**, 2788 (1926).

[2] Lewis and Gibson, *ibid.*, **39**, 2565 (1917).

However, recent measurements down to liquid hydrogen temperatures, made on a number of these substances by one of us (K. K. K.) at the University of California, have demonstrated that in the case of organic compounds the "n formula" gives results for the entropies at 90°K. which are 20 to 30% too high. Since our entropy and free energy calculations were primarily for comparative purposes, this fact does not invalidate the important conclusions drawn in the preceding papers. However, the desirability of now putting the results on an absolute basis has rendered necessary a revision of our earlier values.

In the case of at least twelve organic compounds heat capacity data for the crystalline state are at present available down to or below 20°K. With the aid of these data we have developed a simple, accurate method for estimating the entropy increases for organic substances between 0 and 90°K. The molecular heat capacity curves for the twelve compounds[3] fall naturally into two classes—one for aliphatic and one for cyclic compounds. In each class the various experimental curves are essentially similar in character and we have been able to construct a type or standard curve. For any particular substance in either class the molal heat capacity at each temperature is given quite accurately by the equation

$$C_p \text{ (per mole)} = (A + BT)C_p^\circ \qquad (1)$$

where A and B are characteristic constants for each substance and C_p° refers to the heat capacity on the standard curve at the temperature T. It then follows that

$$S_{90} = AS_{90}^\circ + B\int_0^{90} C_p^\circ \, dT \qquad (2)$$

where S_{90} is the molal entropy of the substance at 90°K. and S_{90}° is that for the standard. To evaluate A and B it is merely necessary to know C_p for the substance at two different temperatures, 90 and 120°K. for instance, whereupon two independent equations, similar to (1) and involving these constants as unknowns, may be set up and solved. Applying this method to the twelve compounds referred to, we have calculated the respective values of S_{90} and have compared these with the corresponding experimental ones. The average difference is 0.3 E. U., or about 2.6%, and is probably not much greater than the average error in the experimental values.

By means of this extrapolation method we have revised the entropies of the eighteen aliphatic compounds studied in the four preceding papers.

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[3] We are here using the data of Lange, *Z. physik. Chem.*, **110**, 350 (1924), for quinone and hydroquinol, the results of Simon, *Ann. Physik*, **68**, 258 (1922), for glucose, and those of Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923), and of Simon and Lange, *Z. Physik*, **38**, 227 (1926), for glycerol. The data for the remaining eight compounds (methyl alcohol, ethyl alcohol, *n*-hexyl alcohol, *iso*propyl alcohol, acetone, toluene, *m*-xylene and cyclohexanol) were obtained by the second author in recent work at the University of California.

The new values are given in Table I. For purposes of completeness we have also included formic acid, which was studied by Gibson, Latimer and Parks[4] in a still earlier investigation. In Col. 2 appear the entropy increments from 0 to 90°K., calculated by Equation 2. The third column then contains the entropy increments from 90 to 298°K., as calculated previously from the heat capacity data.

TABLE I

THE REVISED MOLAL ENTROPIES OF NINETEEN ORGANIC COMPOUNDS

Substance	Entropy increment 0–90°K.	90–298°K.	S_{298}
Methyl alcohol	8.2	22.82	31.0
Ethyl alcohol	9.3	29.13	38.4
n-Propyl alcohol	10.4	35.69	46.1
*Iso*propyl alcohol	10.2	32.91	43.1
n-Butyl alcohol	11.9	42.56	54.5
Tert.-butyl alcohol	10.8	34.47	45.3
Ethylene glycol	8.5	31.39	39.9
Glycerol	9.9	39.82	49.7
Erythritol	10.6	29.25	39.8
Mannitol	15.3	41.68	57.0
Dulcitol	14.4	41.64	56.0
Formic acid	7.1	23.59	30.7
Acetic acid	10.2	27.98	38.2
Butyric acid	12.8	41.30	54.1
Palmitic acid	35.0	78.66	113.7
Oxalic acid	9.2	19.50	28.7
Ethyl ether	14.0	46.45	60.4
Acetone	12.9	34.93	47.8
Glucose	13.2	37.54	50.5

The entropies at 298°K. appear in the last column of thet able; they are probably accurate to within 1 or 2% in all cases. As compared with the results previously published, the present values represent corrections varying from 1.7 E. U. in the case of oxalic acid to 16.2 E. U. for palmitic acid. However, the general principle that the entropy of an organic compound changes in a definite, additive manner with changes in its constitution still holds true. Thus in the normal alcohol series the average entropy increase per CH_2 increment is 7.8 E. U. in going from methyl to *n*-butyl alcohol. Likewise in the fatty acid series the change from formic acid to liquid palmitic acid at 25° is accompanied by an entropy increase of 120.4 or an average of 8.0 E. U. per CH_2 group.

Employing these revised entropy values, we have also recalculated the free energies of formation of the nineteen compounds by means of the thermodynamic equation $\Delta F = \Delta H - T\Delta S$. The essential data appear in Table II. For obtaining the figures (Col. 3) for the ΔH_{298} of formation

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[4] Gibson, Latimer and Parks, THIS JOURNAL, **42**, 1540 (1920).

of these organic substances, we have used the heats of combustion[5] given in the preceding column in conjunction with the values 68,320 cal.[6] and 94,270 cal.[7] for the heats of combustion at 25° of hydrogen and graphitic carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respective entropies of carbon, hydrogen and oxygen were taken as 1.3,[8] 14.8[9] and 24.5[10] E. U. per gram atom. The resulting

TABLE II

THERMAL DATA AT 298° K.

The 15° calorie is used throughout and all weights have been reduced to a vacuum basis

Substance	Ht. of comb. at const. press., cal.	ΔH_{298}, cal.	ΔS_{298}, entropy units	ΔF_{298}, cal.
Methyl alcohol	170,600	−60,300	−54.0	−44,200
Ethyl alcohol	327,200	−66,300	−77.5	−43,200
n-Propyl alcohol	482,800	−73,300	−100.7	−43,300
*Iso*propyl alcohol	477,100	−79,000	−103.7	−48,100
n-Butyl alcohol	638,700	−80,000	−123.2	−43,200
Tert.-butyl alcohol	629,100	−89,600	−132.4	−50,100
Ethylene glycol	281,800	−111,700	−100.5	−81,800
Glycerol	397,000	−159,300	−146.1	−115,700
Erythritol	503,700	−215,000	−211.4	−152,000
Mannitol	727,000	−317,000	−305.0	−226,100
Dulcitol	726,000	−318,000	−306.0	−226,800
Formic acid	62,700	−99,900	−49.2	−85,200
Acetic acid	208,100	−117,000	−72.6	−95,400
n-Butyric acid	520,000	−130,400	−118.5	−95,100
Palmitic acid	2,379,000	−222,000	−429.0	−94,000
Oxalic acid	60,100	−196,800	−101.5	−166,500
Ethyl ether	651,400	−67,300	−117.3	−32,300
Acetone	430,500	−57,300	−69.4	−36,600
Glucose	673,000	−303,000	−281.9	−219,000

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[5] For the four alcohols, methyl, ethyl, *n*-propyl and *n*-butyl, we have utilized substantially the results of Richards and Davis as recently revised by Swietoslawski and Bobinska, THIS JOURNAL, **49**, 2478 (1927). For *iso*propyl alcohol and acetone we have used the values calculated by Kelley, THIS JOURNAL, **51**, 1149 (1929). In the case of the remaining compounds we have employed the data which will appear in "The International Critical Tables" (private communication from Dr. M. S. Kharasch). In all instances the heats of combustion have been calculated to 25° for our present purpose.

[6] The value selected for "The International Critical Tables" is 68,380 cal. at 18° (private communication from Dr. F. R. Bichowsky); this is equivalent to 68,320 cal. at 25°.

[7] Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

[8] Lewis and Gibson, THIS JOURNAL, **39**, 2581 (1917).

[9] Giauque and Wiebe, *ibid.*, **50**, 121 (1928).

[10] Giauque and Johnston, personal communication.

free energies appear in the last column of the table. The differences between these results and those which were given in the preceding papers vary from 100 cal. in the cases of mannitol and glucose to 5000 cal. for palmitic acid. The accuracy of these revised values is now almost entirely limited by the accuracy of the heats of combustion involved.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE KINETICS OF THE OXIDATION OF IODIDE ION BY ACID DICHROMATE SOLUTIONS IN PRESENCE OF A NEUTRAL SALT

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Introduction

Many ionic reactions show kinetic anomalies in the sense that the order of reaction does not come out an integral number. Brönsted[2] has made the suggestion that if sufficient neutral salt be added to fix the activity coefficients of the ions, such reactions can be rendered normal.

The oxidation of iodide ion by means of potassium dichromate in acid solution is a reaction of this type.

DeLury[3] and also Kernot and Pietrofesa[4] concluded from their work that the reaction was first order with respect to $Cr_2O_7^{--}$ ion, nearly second order with respect to H^+ ion and between first and second with respect to I^- ion. In the preliminary work of this investigation the data confirmed the results of the above-named workers, but the order of reaction with respect to I^- ion was found to be more nearly second than first. Thus the reaction considered as a whole appeared to be approximately a fifth order one.

The purpose of this work is to test Brönsted's prediction regarding the effect of neutral salt on the kinetics of the reaction and, if possible, to obtain experimental evidence bearing on the activity rate theory of reaction mechanism.

Outline of Experimental Work

A preliminary investigation was made over a wide range of salt concentration. The salt used was sodium chloride and the source of H^+ ion was perchloric acid. Sixteen reaction mixtures were made up with the concen-

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[1] Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Minnesota, June, 1928.

[2] Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, **1927**, p. 13.

[3] DeLury, *J. Phys. Chem.*, **7**, 239 (1903).

[4] Kernot and Pietrofesa, *Rend. accad. sci. fis. mat. Napoli*, **IIIA**, 275 (1911).