TABLE II

TYPE AND LOCATION OF SAMPLES FROM WHICH CHLORINE ISOTOPIC ANALYSES WERE MADE

Sample	Location	Cl, %	Ratio Cl^{35}/Cl^{37} Standard[e]	Sample[e]
Nepheline–Sodalite Syenite	Red Hill, New Hampshire	0.32	3.109	3.101
Phonolite[a]	Devil's Tower, South Dakota	.44	3.107	3.105
Hornblende Gabbro[b]	Shelby, North Carolina	.15	3.143	3.150
Obsidian[a]	Obsidian Cliff, Wyoming	.01	3.142	3.150
Scapolite[b]	Bolton, Massachusetts	.16	3.111	3.117
Sodalite[b]	Bancroft, Ontario	6.8	3.131	3.127
Hackmenite[b]	Dungannon Top, Ontario	.09	3.136	3.142
Sodium chloride[c]	Atlantic Ocean, Eastern Long Island		3.146	3.142
Sodium chloride	Great Salt Lake, Utah		3.126	3.130
Halite[b]	New Gulf Salt Dome, Texas		3.125	3.123

[a] Collected by G. Friedlander, Brookhaven National Laboratory. [b] Ward's Natural Science Establishment, Rochester, N. Y. [c] Collected by J. Dominy and J. Galvin, Brookhaven National Laboratory. [d] Courtesy of J. L. Kulp, Lamont Observatory, Columbia University. [e] Average deviation ±0.006.

ten scans over the region M/e 47–52 were made each time. If the two determinations of the standard were in agreement, the set was considered satisfactory. This procedure minimized the effects of instrumental variations and systematic errors. As a further precaution against memory effects the liquid N_2 was removed from the main cold trap before each run to allow condensed CH_3Cl to be pumped away. In addition, the sample inlet system was flushed several times prior to making a run.

The mass spectral pattern of CH_3Cl in the region M/e 47–52 is shown in Table I. Minor contributions such as $C^{13}HCl^{37}$ are not shown. The mass 50 peak had to be corrected for the contribution of the $C^{12}HCl^{37}$ ion. The correction was made (assuming the patterns of the two isotopic methyl chlorides were the same) from the $C^{12}HCl^{35}/C^{12}H_3Cl^{35}$ ratio. This ratio was determined from the 48/50 peak height ratio after suitable corrections for the small C^{13} contributions. The total corrections amounted to approximately one per cent. and were practically constant over a period of several months, indicating excellent pattern stability.

In Table II the origins of the samples are shown. In each case chlorine was present as chloride ion, in amounts varying from less than 0.01% in the case of Obsidian to 6.8% in the case of Sodalite. There were no observable differences in the Cl^{35}/Cl^{37} ratio in any of the ten samples examined. The precision of the measurements was such that a variation in the ratio Cl^{35}/Cl^{37} greater than 0.2% would have been observed. In each case the samples were analyzed at least twice, and in most cases more than one sample preparation was made. The ratios listed are average values of each determination of a particular sample. The lack of variation in these samples is not too surprising as the chlorine was present as chloride ion, and has not been known to have undergone an oxidation–reduction cycle. In the case of certain South American nitrate deposits, where small amounts of perchlorates are present one might expect variations on the order of a per cent. as a result of repeated oxidation–reduction processes taking place. To date no samples of this type have been analyzed. For the purpose of comparison all the results were averaged, giving a value of the Cl^{35}/Cl^{37} ratio of 3.13. As the instrument used was not calibrated with samples of known abundance a reasonable uncertainty in the absolute value of the Cl^{35}/Cl^{37} ratio is 1% or 3.13 ± 0.03. In Table III the results are compared with previous determinations, the most probable value being a combination of the precise atomic weight determinations of Harkins and Stone and the atomic mass determinations of Nier.[11]

TABLE III

A COMPARISON OF RESULTS OF ABUNDANCE DETERMINATIONS OF Cl ISOTOPES

	Year	Cl^{35}/Cl^{37}
Aston	1919	3.0–3.1
Kallman and Lazereff	1933	3.24
Nier	1936	3.07 ± 0.03
Harkins and Stone	1926	3.096
Nier's atomic masses	1951	
This research	1954	3.13 ± 0.03

Acknowledgment.—The authors wish to acknowledge the valuable assistance of Frederick Silkworth in performing the chemical separations.

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[11] T. L. Collins, A. O. Nier and W. H. Johnson, *Phys. Rev.*, **84**, 717 (1951).

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A Method for Determining the Distribution Constant for a Substance between the Gas Phase and a Condensed Phase[1,2]

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The need for accurate values of the thermodynamic properties for the solution of gaseous olefins in water[4] has led us to develop a method of determining vapor distribution constants. We employ a saturation method[5] and measure the pressure drop on solution of the vapor in a constant volume system. The apparatus employed is a simple modification of the one we have used to determine rates of reactions involving either a volatile reactant or product.[6] The precision of the method (*ca.* 1%) compares quite favorably with that of a number of reported quantitative procedures, but it is not as highly precise as some.[7]

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[1] Taken in part from the Ph.D. Thesis of E. Lee Purlee, The Pennsylvania State University, June, 1954.

[2] The work reported herein was carried out on Project NR055–295 between the Office of Naval Research and the Pennsylvania State University.

[3] Allied Chemical and Dye Corp. Fellow for 1953–1954.

[4] *Cf.*, for example E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, THIS JOURNAL, **77**, 837 (1955).

[5] *Cf.*, review of experimental methods, A. E. Markham and K. A. Kobe, *Chem. Revs.*, **28**, 519 (1941).

[6] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron, L. P. Hammett, THIS JOURNAL, **73**, 3992 (1951); (b) R. W. Taft, Jr., J. B. Levy, D. Aaron, L. P. Hammett, *ibid.*, **74**, 4735 (1952); (c) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952); (d) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, *ibid.*, **75**, 3955 (1953); (e) Ref. 4; (f) unpublished data of E. L. Purlee, P. Riesz, C. A. DeFazio, and R. W. Taft, Jr.

[7] For example, we have not achieved the degree of precision (one to two parts per thousand) obtained by T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **57**, 1708 (1935), and A. E. Markham and K. A. Kobe, *ibid.*, **63**, 449 (1941), in determining the solubility of carbon dioxide in water. On the other hand, our precision is somewhat better than that reported by W. F. Claussen and M. F. Polglase, *ibid.*, **74**, 4817 (1952), for the solubility of alkanes in water.

The distribution constants and their temperature coefficients for alkanes and alkyl halides between the gas phase and aqueous solution have been determined by the present method. The results of most of these measurements will be reported at a later time. The distribution constants for gaseous olefins have also been measured using aqueous nitric, perchloric and sulfuric acids as the condensed phase. Much of this work is reported here.

Experimental

Volatile Non-reactive Liquids.—The distribution constant, *h*, was obtained using the same type of apparatus illustrated in Fig. 1 of ref. 6a. A 200-ml. flask (of the same general design) was substituted for the 50-ml. reaction flask (f). Tube (G) to which was added the volatile liquid was sealed directly to the system, *i.e.*, ground glass joint (J) was eliminated. A second precision, two-way stopcock (T′) was introduced at (O). The condensed phase and the volatile liquid were introduced as described in procedure B of reference 6a and ref. 6e.

The system was then completely immersed in a thermostat. A vacuum line was maintained to the system using small diameter pressure tubing which was connected by a precision joint to the system *via* (T′). When temperature equilibrium was established the volatile liquid was vaporized into the system *via* (S). With (S) closed, the manometer was tapped gently to prevent clinging of the mercury and the pressure reading recorded. During this operation the apparatus was rigidly mounted in order to prevent any measurable solution of gas in the condensed phase. Shaking of the flask (as previously described) was then started and pressure readings were recorded every half-minute or minute until equilibrium was established. Two to four minutes were generally required for obtaining equilibrium pressures, depending upon the temperature and the nature of the solute.

After one determination was completed, the system up to (S) was evacuated *via* (T′). (S) was opened and the volatile substance withdrawn with the apparatus at rest. (S) was then closed and the shaking started. Residual gas was again withdrawn without shaking. This process was repeated until the equilibrium pressure of the solvent was maintained with the solubility flask in motion. The distribution constant measurement was then repeated.

The precision measures reported are generally based on the results of four to ten experiments performed with a given solvent at each temperature. In several cases, experiments were repeated using fresh condensed phase, different solubility flasks (varying in volume from 209–217 ml.), and different ratios of volume of vapor to liquid volume (liquid volume varied from 80 to 125 ml.). Initial pressures of the solute were varied from 10 to 33 cm. Shaking rates have been varied from 200–350 r.p.m. None of the above factors measurably affected the distribution constants obtained.

Non-reactive Gas.—The method used was same as that given above with the apparatus modified to accommodate the introduction of the gas directly from a commercial storage cylinder. The three-way stopcock (S) was replaced by a precision two-way stopcock (S′), fitted with a ground-glass precision joint which connected the system *via* small-diameter pressure tubing to a three-way stopcock (located outside the thermostat). This stopcock led to the vacuum system and the gas storage cylinder. After the system was immersed in the thermostat, the three-way stopcock was opened so the line leading from (S′) to the storage cylinder was evacuated to 0.1 mm. The stopcock was then adjusted to cut out the vacuum line, and maintain an open system between the cylinder and (S′). With (S′) opened, the gaseous solute was introduced into the system *via* a needle valve at the cylinder. A few minutes (varied without effect on the results) were allowed to ensure temperature equilibrium between the gas and liquid phases before the initial pressure was taken and shaking started. The more soluble vapors were observed to slowly "creep in" solution on relatively long standing over the liquid phase, but the amount appeared to be negligible for short time intervals.

Reactive Solutes.—In aqueous acid solution, the rates of hydration of the olefins studied are not negligible. When the hydration rate is relatively slow, it has been possible to obtain distribution constants as above by applying an extrapolation procedure. Pressure readings were taken for about ten minutes. Values taken during the last five or six minutes gave the initial hydration rate. The hypothetical "equilibrium" pressure of olefin above solution before reaction occurs was calculated by the relationship

$$P^e = P^\circ - [P + \rho(t - t')] \qquad (1)$$

where

P^e = hypothetical "equilibrium" pressure before reaction
P° = initial partial pressure of solute
ρ = rate of reaction of solute in cm./min.
P = partial pressure of solute at time, t
t' = hypothetical time at which olefin began to react at rate, ρ

The time, t', was estimated in the following manner: log P was plotted *vs.* time. This plot gave a curve which became linear after dynamic equilibrium between vapor and liquid phase was attained (generally two to three minutes were required). The linear portion of the curve was extrapolated toward zero time (the time when shaking was started). A second line approximately tangent to the curved portion and passing through zero time was then drawn. The point of intersection between these two lines was taken as a measure of t'.

The limiting conditions for the application of this method appear to be 25° for isobutene and 30° for trimethylethylene in one molar acid. Shaking rates of 300–350 were employed in all of these measurements.

Definition and Calculation of Distribution Ratio.—The distribution constant, *h*, is defined by the equation

$$h = C^e/P^e \qquad (2)$$

where C^e is the equilibrium concentration of dissolved solute in moles liter^{-1} and P^e is the equilibrium partial pressure of solute over the solution in atm.

The distribution constant, *h*, is calculated from the expression

$$h = (r/RT)\left(\frac{P^\circ - P^e}{P^e}\right) \qquad (3)$$

where

r = the ratio of vapor vol. to liquid vol. in the solubility apparatus
R = the gas constant in l. atm. deg.$^{-1}$ mole^{-1}
T = absolute temperature
P° = initial partial pressure of solute in atm.

Solvent Loss.—During the removal of solute between individual experiments, this is not negligible in all cases and necessary corrections were applied.[1]

Check for Pre-solution.—We were concerned by the possibility that a measurable amount of gas might go into solution by the time the initial pressure reading could be obtained, or that adsorption of gas by stopcock grease affected the reliability of measurements (outside of the precision reported) by our method. To test these sources of error, we prepared a modified apparatus and carried out experiments with several types of solutes of varying distribution constants. A calibrated flask (F″) of about 100-ml. volume was inserted *via* a T-section at (L) and a precision two-way stopcock was inserted at (C″). With C″ closed the volatile solute was introduced into (F″) giving a convenient manometer reading. With the apparatus rigidly mounted as previously described, C″ was opened and a second pressure reading made. The agreement between the second pressure reading and that calculated from the first reading indicated that the suspected sources of error do not measurably affect the distribution ratios obtained by the present method.

Materials.—The carbon dioxide, methane, ethylene and methyl chloride were obtained from the Matheson Co. The carbon dioxide is given as 99.8%, methane as 99.0%, ethylene as 99.5%, and methyl chloride as 99.5%.

The isobutene used was Phillips research grade (99.44 mole %) product. Trimethylene was obtained from a center cut (b.p. 38.46–38.51° (760 mm.); $n^{20}\mathrm{D}$ 1.3875) from the fractionation of a sample of Phillips research grade (99.59 mole %) product.

Results

Listed in Table I are distribution constants, *h*,

TABLE I

DISTRIBUTION CONSTANTS, *h*, FOR SEVERAL SOLUTES BETWEEN WATER AND THE VAPOR PHASE IN UNITS OF 10^3 MOLES l.$^{-1}$ ATM.$^{-1}$

Substance	Temp., °C.	*h*	P.e.	(ΔH_v) soln., kcal./mole	*h* (lit.)	$(\Delta H_v)_{soln.}$ (lit.), kcal./mole
Carbon dioxide	25.00	33.2	0.2		33.75 ± 0.03[8]	
Methane	25.00	1.342	.007		1.342[9]; 1.43[10]; 1.34[11]	
Ethylene	20.00	5.17	.05		5.5[9]	
	25.00	4.66	.02	$4.05 \pm .27$	4.8[9]; 4.62[12]	3.92 ± 0.26[9]
	30.00	4.11	.05		4.4[9]	
Isobutene	0.01	15.36	.07			
	25.00	5.18	.01	*cf.* ref. 14		
Trimethylethylene	0.01	18.40	.10	*cf.* ref. 14		
	30.00	4.89	.03			
Methyl chloride	20.00	118.1	.9	6.95 ± 0.14	128. ± ?[13]	6.31 ± ?[13]
	30.00	79.7	.1		88. ± ?	

between the vapor state and the saturated aqueous solution determined by the method reported here. The results given are for those solutes and temperatures for which direct comparison can be made with previously reported values.

The general accord of the distribution constants obtained in the present work with those reported previously appears to indicate that the former are about as accurate as their precision measures. We have noticed no tendency of solutions to supersaturate (*cf.* Experimental on variation of shaking rate) as has sometimes been reported.[15]

TABLE II

DISTRIBUTION CONSTANTS, *h*, FOR TRIMETHYLETHYLENE AND ISOBUTENE BETWEEN THE VAPOR PHASE AND AQUEOUS ACID SOLUTIONS IN UNITS OF 10^3 MOLES L.$^{-1}$ ATM.$^{-1}$

Acid	Concn., *M*	Temp., °C.	*h*	P.e.
		Trimethylethylene		
HNO_3	0.0973	0.00	18.40	0.10
	0.973		18.63	.08
	2.995		18.37	.09
HNO_3	0.0973	30.00	4.88	.03
	0.500		5.25	.04
	0.973		5.66	.06
$HClO_4$	0.507	30.00	5.22	.03
	1.013		5.83	.05
H_2SO_4	0.0487	30.00	4.25	.04
	1.014		3.68	.04
		Isobutene		
HNO_3	0.0324	0.00	15.36	0.07
	0.0973		15.09	.07
	0.973		14.62	.04
	2.011		13.59	.07
	2.995		13.09	.06
HNO_3	0.500	25.00	5.38	.04
	0.973		5.75	.04

Table II reports the distribution constants which have been obtained for trimethylethylene and isobutene in sulfuric, perchloric and nitric acid solutions at several temperatures. These distribution constants follow the well-known Setschenow equation[16]

$$\log\left(\frac{h^\circ}{h}\right) = KC \qquad (4)$$

where h is the distribution constant in an electrolyte solution of concentration, C, and h° is that in water. K is a constant characteristic of non-electrolyte, electrolyte and temperature. This equation may also be written as

$$\log f = KC \qquad (5)$$

where f is molar activity coefficient of the non-electrolyte in the electrolyte solution with a pure water solution of the non-electrolyte as the reference state.[17]

Table III summarizes the Setschenow parameters obtained from the data of Table II and illustrates the precision of fit of the data to eq. 4.

TABLE III

SETSCHENOW PARAMETERS OBTAINED FROM THE DATA OF TABLE II

Acid	Temp., °C.	*K*	P.e.
	Trimethylethylene		
HNO_3	0.00	0.000	0.002
	30.00	−0.074	.003
$HClO_4$	30.00	−0.075	.008
H_2SO_4	30.00	+0.122	.001
	Isobutene		
HNO_3	0.00	+0.024	.001
	10.00	0.000[a]	.003
	25.00	−0.052[b]	.004

[a] *Cf.* Ph.D. Thesis of E. L. Purlee, Pennsylvania State University, June, 1954, p. 38. [b] A value of −0.090 was estimated earlier by indirect means by Taft, ref. 6c.

The dependence of the Setschenow parameters on electrolyte type is in the expected direction.[16] The change from "salting-out" or no effect at 0° to "salting-in" at 25 or 30° exhibited by isobutene

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(8) (a) J. L. R. Morgan and H. R. Pyne, *J. Phys. Chem.*, **34**, 1578 (1930); (b) T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **57**, 1708 (1935); A. E. Markham and K. A. Kobe, *ibid.*, **63**, 449 (1941).

(9) L. W. Winkler, as given in "I.C.T.," vol. 3, p. 260.

(10) W. F. Claussen and M. F. Polglase, THIS JOURNAL, **74**, 4817 (1952).

(11) Extrapolated from data of A. Eucken and G. Hertzberg. *Z. physik. Chem.*, **195**, 1 (1950).

(12) A. Grollman, *J. Biol. Chem.*, **82**, 317 (1929).

(13) Calculated from a formula given in "I.C.T.," vol. 3, p. 261, based upon early measurements by Plank.

(14) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, THIS JOURNAL, **77**, 837 (1955).

(15) *Cf.* discussion by Markham and Kobe, ref. 5, p. 530.

(16) *Cf.* F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

(17) Ref. 16, p. 123.

and trimethylethylene in nitric acid solutions is striking and apparently unusual.[18]

[18] Ref. 16, p. 151.

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Thermodynamic Properties for the System Isobutene–*t*-Butyl Alcohol[1]

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In order to compare the rates, equilibria and their thermodynamic properties for the hydration of 4- and 5-membered ring olefins with those of isobutene, we have measured[2] over the temperature interval 50–70° the equilibrium constant, K_p, for reaction (1)

$$\text{isobutene(g)} + H_2O(l) = t\text{-butyl alcohol(aq)} \quad (1)$$

The aqueous phase is 0.0973 molar in perchloric acid and one-tenth to two-tenths molar in *t*-butyl alcohol. The apparatus and procedures are those which have previously been used to study rates of olefin hydration and carbinol dehydration.[3,4]

Equilibrium has been attained starting from the carbinol. We have also obtained directly the dehydration rate and its temperature coefficient. These in combination with earlier results on the hydration rate and its temperature coefficient[3] serve as a check on the measurements.

Standard thermodynamic properties have been derived for the hydration reaction by combining present and earlier data. In a similar manner the free energy and enthalpy of formation of liquid *t*-butyl alcohol at 25° have been obtained.

Experimental

A sample of *t*-butyl alcohol was fractionated over calcium hydride. A center cut, m.p. 25.0°, was retained for the present work.

The apparatus and procedure used were essentially those reported earlier.[4] Experiments were carried out in 0.0973 *M* perchloric acid. At 60 and 70° preliminary work indicated that 0.973 *M* nitric acid (the solvent used in a number of previous experiments[4]) led to decomposition of the carbinol.

Solutions either one-tenth or two-tenths molar in *t*-butyl alcohol were made up in the acid solution, a measured volume of the solution added to the apparatus, and the system degassed as described in procedure B reference 4b. At room temperature and below (at which the solutions were kept during the above operation) the rate of dehydration at this acidity is so small that no measurable loss of olefin occurs. The closed and evacuated systems were completely submerged in a thermostat at the desired temperature and rapid shaking was begun within 2 or 3 minutes.

Pressure readings were taken at one-minute intervals. The time at which the system reached thermal equilibrium with the thermostat was that at which the time derivative of pressure became constant (about four minutes were generally required). The vapor pressure of the acidified carbinol solution was obtained from the initial pressure reading obtained at the desired temperature. At 60 and 70° this pressure was obtained by extrapolation of the initial dehydration rate to the time shaking was begun. This extrapolation procedure introduced no errors out-side of those involved in the reading of pressure (±0.03 cm.), for the dehydration rates were relatively slow (the smallest half-life of the total pressure increase was about one hour).

Duplicate experiments were carried out at each temperature and the average equilibrium constant is reported. At 60 and 70° the dehydration rates, S, were observed directly over at least 50% of the reaction ($S = -d \ln (P^e - P)/dt$. The results are summarized in Table I. The equilibrium constant, K_p, is given by C^e_a/P^e_o, where C^e_a is the equilibrium carbinol concentration in moles l.$^{-1}$ and P^e_o is equilibrium partial pressure of olefin in atm.

Table I

Summary of Experimental Data

Temp., °C.	50.07	50.07	60.05	60.05	69.95	69.95
$10^{3r}/RT$	73.1	95.9	70.9	119.5	68.8	116.0
C^e_a, M	0.2014	0.2006	0.1986	0.1951	0.0970	0.0940
P^e_o, cm.	2.77	2.74	5.86	5.67	5.58	5.29
K_p	5.53	5.56	2.58	2.61	1.322	1.351
$10^5 S$	....	....	5.42	3.16	12.57	7.97

Results

The equilibrium constants, K_p, are tabulated in Table II along with their probable errors.

Table II

Equilibrium Constant, K_p, for the Hydration of Gaseous Isobutene to Dilute Aqueous Tertiary Butyl Alcohol in Units of Moles l.$^{-1}$-atm.$^{-1}$

Temp., °C.	50.07	60.05	69.95
K_p	5.54	2.59	1.336
P.e.	0.02	0.02	0.014

A plot of K_p against $1/T$ is linear within the precision of measurement. Thus the value of K_p at 60.05° computed on the basis of this linearity is 2.65 ± 0.04 compared with the experimental value of 2.59 ± 0.02. Accordingly, the best values of the enthalpy and entropy changes accompanying reaction 1 are obtained by the Van't Hoff equation from the slope of the $1/T$ plot as defined by the points for the extreme temperatures. In this manner the enthalpy change, ΔH_p, is found to be -15.76 ± 0.12 kcal. mole^{-1}, and the entropy change. ΔS_p, is -45.3 ± 0.3 cal. deg.$^{-1}$ mole^{-1} for the interval 50–70°.

The rates of dehydration of *t*-butyl alcohol at unit concentration, k_{-1}, by 0.0973 *M* perchloric acid at 60 and 70 have been calculated from the rate data of Table I by equation 4 of reference 4a using distribution constants of isobutene between gas and liquid phases obtained by extrapolation of the data of Purlee, Taft and DeFazio.[3,5] The

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[1] The work herein reported was carried out on Project NR055-295 between the Office of Naval Research and the Pennsylvania State University.

[2] *Cf.* P. Riesz and R. W. Taft, Jr., This Journal, **77**, in press (1955).

[3] *Cf.* E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955), and previous references cited there.

[4] (a) R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952); (b) J. B. Levy, R. W. Taft, Jr., D. Aaron, L. P. Hammett, *ibid.*, **73**, 3792 (1951).

[5] The value of the distribution constant makes little contribution under these conditions to the value of k_{-1} calculated. Thus complete neglect of the distribution constant would in the worst case decrease the value of k_{-1} by 3%. Any error introduced in the extrapolation will therefore not affect the value of k_{-1} obtained.