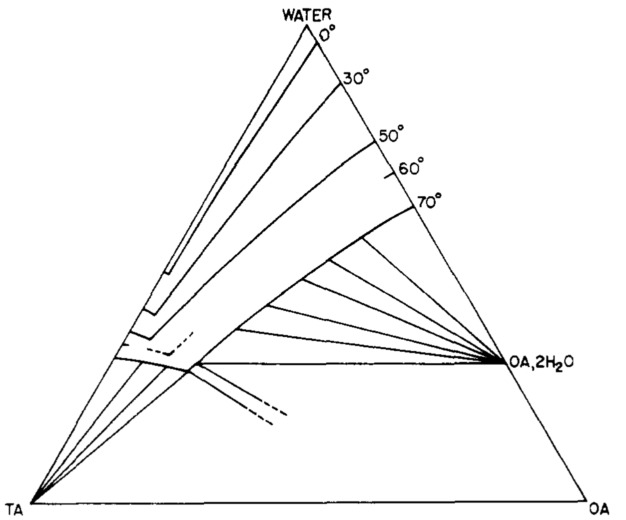

Figure 1. Solubilities at 0°, 30°, 50°, 60° (partially), and 70° C.

are shown in a consolidated form in Figure 1. Solubilities of pure compounds in water reported in the literature (*3*) were satisfactorily reproducible in the present investigations.

Discussion. The different isotherms show that the system exhibits a simple phase behavior involving neither solid solution nor double salt formation up to 60° C. The solid phases, determined by geometric extrapolation of tie-lines, show that they are pure substances up to 60° C.—hydrated in the case of oxalic acid. The 60° C. isotherm was partially established to delineate the temperature range where the change in phase behavior starts, though the true invariant point has not been determined. At 70° C., the phase behavior tends to change as evidenced by the composition of saturated solutions and the corresponding wet residues. Solid phases in this region could not be properly identified owing to the highly viscous nature of the adhering mother liquor.

The isothermal phase diagrams show that separation of the two acids is rendered practical by a judicious combination of cooling and evaporation of solutions, likely to be obtained in some cases. This is particularly true because of significant shifts of isothermal invariant compositions at increasing temperatures.

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Variation of Dielectric Constant with Temperature for Some Five- and Six-Carbon Ketones

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The dielectric constant values for seven five- and six-carbon cyclic and acyclic ketones, liquid in the −30° to +20° C. range, were determined in a noninductive-type cell. The measured values increased as the temperature decreased, as would be expected from theory. However, these changes in values did not correlate with other physical data.

THE CHANGE in dielectric constant with temperature of ketones has received only limited study. White and Bishop (*8*) included a few ketones in their determinations of the dielectric constant of the liquid and solid phase at the transition temperature. Cole (*1*) studied changes of density and dielectric constant with temperature in the liquid phase for a series of ketones.

The purpose here was to study the effect of changes in temperature and frequency on dielectric constant values for a group of five- and six-carbon cyclic and acyclic ketones.

MATERIALS AND EQUIPMENT

Compounds. The dielectric constants were determined from −30° to +20° C. and at five different frequencies from 3 to 25 mc. The selection of ketones was limited to those five- and six-carbon ketones that remained liquid over this temperature range.

Purification. Two physical constants, refractive index and boiling point, were used as a means of checking the purity of the compounds. The ketones and the other compounds that

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Table I. Physical Constants

Compound	Experimental: Boiling range, ° C.	Experimental: Refractive index$^{20° C.}$	Literature (*5*): Boiling point, ° C.	Literature (*5*): Refractive index
2,2,4-Trimethyl pentane	98.9- 99.4	1.3912	99.2	1.3916^{20}
Methyl ethyl ketone	79.0- 79.6	1.3784	79.6	1.3814^{15}
Acetone	56.0- 56.5	1.3584	56.2	1.3588^{20}
Methyl alcohol	64.6- 65.1	1.3292	64.96	1.3288^{20}
Diethyl ether	34.4- 34.8	1.3518	34.6	1.3526^{20}
Ethyl alcohol	78.4- 78.9	1.3615	78.5	1.3611^{20}
Methyl propyl ketone	101.6-102.2	1.3899	102	1.3895^{20}
Methyl isopropyl ketone	94.7- 95.5	1.3876	95	1.3879^{16}
Cyclopentanone	130.0-130.7	1.4370	130.65	1.4366^{20}
Methyl *n*-butyl ketone	126.8-127.4	1.3982	126	1.4015^{20}
Methyl isobutyl ketone	117.0-117.5	1.3962	116.85	1.3960^{20}
Methyl *tert*-butyl ketone	105.7-106.3	1.3962	106	1.3952^{20}
Cyclohexanone	155.1-155.7	1.4504	155.65	1.4502^{19}

Table II. Experimental and Literature Values Used to Evaluate Calibration

Compound		20° C.	0° C.	−20° C.	−30° C.
Ethyl ether	Exper.	4.332	4.763	5.251	5.485
	(*7*)	4.335	4.769	5.245	5.501
Ethanol	Exper.	25.05	28.34	31.22	33.28
	(*7*)	25.07	28.39	31.14	33.35

were used as standards were distilled through a fractionating column until the required purity was obtained. These data are listed in Table I. Water was removed by known methods (*4*).

Equipment. A noninductive-type cell was constructed which was similar in design to those described by Conner, Clarke, and Smyth (*2*), and by Critchfield (*3*). This unit included a built-in cooling jacket for temperature control and a Teflon screw-type plug or base as the insulator between the two electrodes. The inner metal parts were heavily plated with gold as an anticorrosion measure. This cell was used because no lead inductance corrections were necessary, and it was self shielding. At temperatures below +20° C., the Teflon plug was sealed with Dow Corning Silicon grease to prevent leakage. This leakage was due to the phase transition in Teflon at 18° C.

The General Radio, Type 821-A, twin-T impedance measuring circuit was used for all capacitance measurements. A Measurements Corp. standard signal generator served as the frequency input to the bridge, and a Hallicrafters SX-62 receiver was used as the detector.

The temperature control liquid was circulated from a large, heavily insulated, constant temperature bath through the cooling jacket of the cell by means of a small centrifugal pump and short connections of rubber tubing. The cell, pump, and leads were heavily insulated with cork tape. A calibrated multijunction copper-constantan thermocouple was used to determine the temperature of the experimental liquid in the cell.

EXPERIMENTAL

Application of Gauss's Law to the cell results in the equation

$$C = Ak' + D$$

where A and D are constants. Thus a plot of capacitance *vs.* dielectric constant should produce a straight line, and the cell is readily calibrated with known standards.

The cell was calibrated with 2,2,4-trimethylpentane, methyl ethyl ketone, acetone, and methyl alcohol at frequencies of 3, 6, 10, 15, and 25 mc. and at +20°, 0°, −20°, and −30° C., respectively. The dielectric constants of these liquids were known over the temperature range and also were known to show no frequence dispersion over the frequencies studied. The capacitance values plotted against the dielectric value obtained from the N.B.S. Circular 514 (*7*) yielded a straight line for each frequency at each temperature.

As a means of checking the accuracy of the calibration of the cell, the dielectric constant values were determined for ethyl ether and ethyl alcohol and compared with values obtained from the N.B.S. Circular 514 (*7*). These values are shown in Table II.

Table III. Determined Dielectric Constant Values[a]

Compound	20° C.	0° C.	−20° C.	−30° C.	
Cyclopentanone	13.80	14.76	15.78	16.26	
Methyl *n*-propyl ketone	15.38	16.78	18.35	19.26	
	15.45	16.86	18.40	19.23	(*7*)
	15.45	16.82	18.39		(*1*)
Methyl isopropyl ketone	16.57	17.85	19.24	19.91	
Cyclohexanone	16.10	17.28	18.53	19.09	
Methyl *n*-butyl ketone	14.56	16.43	18.61	19.78	
Methyl isobutyl	13.11	14.45	15.91	16.71	
	13.11	14.44	15.94	16.70	(*7*)
	13.11	14.50	15.91		(*1*)
Methyl *tert*-butyl ketone	12.73	14.56	16.61	17.79	

[a] The errors for the values listed in Table III, calculated from the limits of error information for the impedance measuring circuit and the precision of temperature control, are ±0.6% at 20° C. and ±1.5% at −30° C.

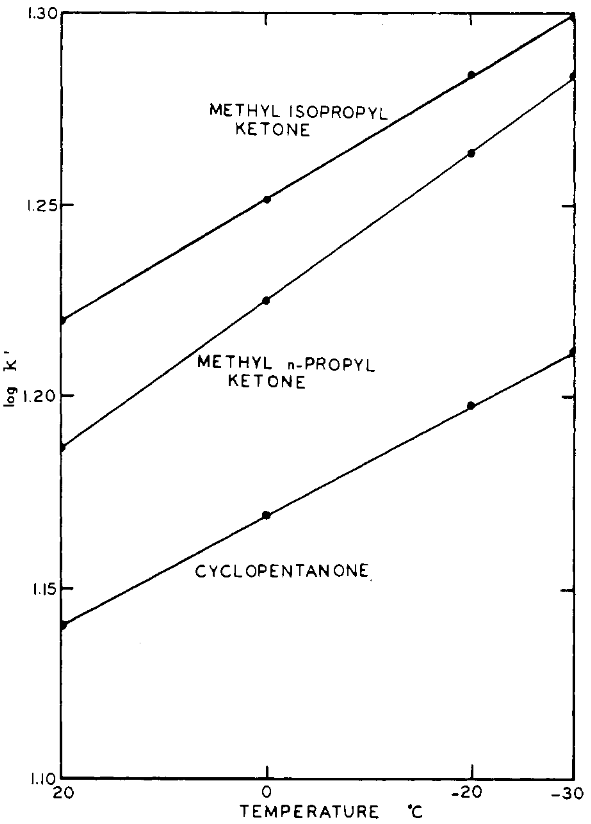

Figure 1. Slopes for five-carbon ketones

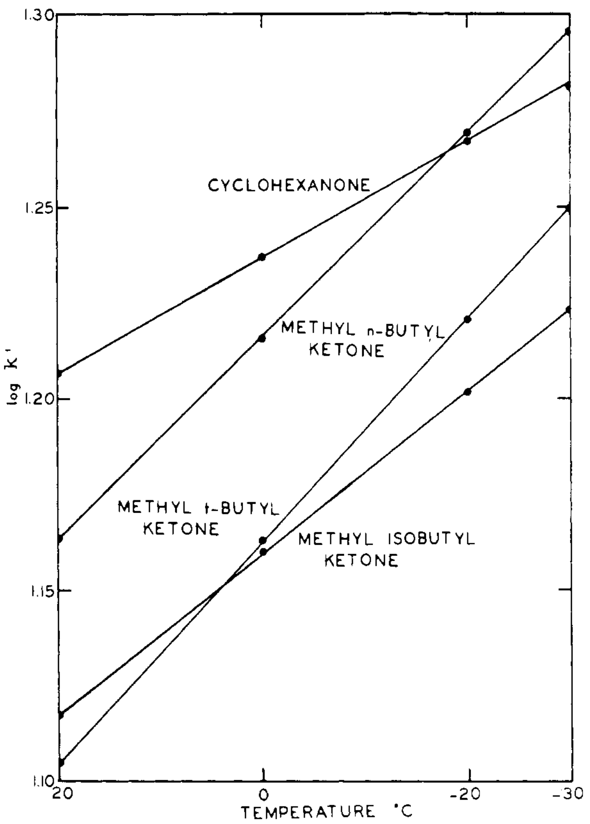

Figure 2. Slopes for six-carbon ketones

EXPERIMENTAL RESULTS AND DISCUSSION

The value for each of the seven ketones was constant for each of the five different frequencies. The static values are listed in Table III and plotted in Figures 1 and 2. Values for two of the ketones included in this study, methyl *n*-propyl ketone and methyl isobutyl ketone, were also found in the literature. The determined values agree with the literature values.

In Figures 1 and 2, the logarithms of the dielectric constant values were plotted against temperature. The decrease in temperature was accompanied by an increase in the dielectric constant values, a result which would be expected from theory.

The lines for methyl *n*-propyl ketone and methyl isobutyl ketone are nearly parallel and agree with the plotted data of Cole (*1*). The slope for methyl isobutyl ketone is slightly greater than that for methyl *n*-propyl ketone. The lines for cyclopentanone and cyclohexanone are also nearly parallel, with the slope for cyclopentanone being slightly less than the slope of the line for cyclohexanone. These slopes are considerably less than the slope for methyl *n*-propyl ketone. The line for methyl *tert*-butyl ketone was nearly parallel to the line for methyl *n*-butyl ketone. However, the slopes for these two ketones are much greater than that for the methyl *n*-propyl ketone and methyl isobutyl ketone.

Possibly, the slopes of the curves depend largely on the dipole moment of these compounds and the intermolecular reaction resulting from these moments. However, a survey of the more recent literature shows the dipole moment of ketones that have been determined to be about 2.72. This includes some of those used in this study. In addition, no correlation could be determined between the "red shift"—i.e., change in the absorption maxima to longer wavelenghts—or strain (*6*) at the carbonyl carbon—i.e., the R_1-C-R_2 angle, due to size or complexity of the R groups—and the slopes for the dielectric constant values for these compounds.

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