$HOOC(CH_2)_nCOOH$ and shows the changes in $\Delta\bar{H}_2$ $[\Delta(\Delta\bar{H}_2)]$ with increasing chain length.

The values of $\Delta\bar{H}_2$ for formic acid are the most exothermic of the monocarboxylic acids, and within experimental error fit into the roughly colligative series of hydrogen peroxide, urea, and sucrose, up to $X_3 = 0.0309$. At higher mole fractions $\Delta\bar{H}_2$ becomes nonlinear. As the carbon chain lengthens $\Delta\bar{H}_2$ becomes less exothermic for acetic acid, with positive values for propionic and butyric acids. The overall changes from formic to butyric acids show the inability of the terminal carboxyl to overcome the unfavorable interaction between the growing hydrocarbon chain and the aqueous environment. There may be a leveling effect as $[\Delta(\Delta\bar{H}_2)]$ decreases from 70 to 45 cal/mol; however, the experimental error makes this trend uncertain.

Enthalpies of transfer to the three diacids are the most negative. Insertion of methylenes between the carboxyls in going from malonic to succinic and to glutaric acid represents a less drastic change than the extension of a carbon chain by one methylene in the monoacids. It is likely that this is the net result of carboxyl group solvation reducing the methylene–water interactions, with the carboxyls providing a shielding effect between the methylenes and their polar aqueous environment. It may be noted that the diacids are very important in enzyme inhibition since all three combine with the enzyme succinate dehydrogenase (*8*). Malonic and glutaric acids thus competitively inhibit the enzyme by blocking the active center, which apparently is not selective between the three acids, just as the transfer of NaCl is relatively nonspecific.

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Solubility of O_2 in 2-Propanone, 2-Butanone, 2-Pentanone, and 2-Hexanone

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Experimental data for the solubility of O_2 in CH_3COCH_3, $CH_3COC_2H_5$, $CH_3COC_3H_7$, and $CH_3COC_4H_9$ within the temperature range 298–344 K are reported. For T = 298.2 K the following values for Henry's constant were measured ($H_{O_2,1}^{(p_1^*)}$, bar/mole fraction): ketone C_3, 1190; C_4, 986; C_5, 904; C_6, 855. The data can be well correlated by using the semiempirical approach of Cysewski and Prausnitz. The prediction of Henry's constant of O_2 for higher ketones by the regular solution equation is tested and found applicable. A rapid technique for performing oxygen solubility measurements on a working sample is described and tested.

When making kinetic measurements for the autoxidation of hydrocarbons in the liquid phase, it is necessary to know the solubility of oxygen in the reaction mixture at elevated temperatures. There exist several experimental methods for determining gas solubility data (see, e.g., ref 1), but they are all rather cumbersome to use in this situation. A rather rapid working method, though not as precise as volumetric methods, consists of injecting a sample of small volume from a reaction mixture containing oxygen into a comparatively large volume of water with a fairly low, but known, concentration of oxygen. From the increase of the oxygen concentration the solubility of oxygen in the reaction mixture can be easily evaluated. This technique, as tested by comparison of oxygen solubility data for acetone with known data, is described herein. New solubility data for oxygen in 2-butanone, 2-pentanone, and 2-hexanone obtained by this technique within the temperature range from 298 to 344 K are reported.

To date there exists no theoretical approach for predicting solubility data of gases in industrially relevant solvents. A semiempirical approach for correlating the solubility of gases in polar solvents was given by Cysewski and Prausnitz (*2*). While one of the parameters of their model was physically interpreted by them and could therefore be well predicted, this was not tried for the second parameter. Further insight into this second parameter gained from new experimental results is an additional point treated in this contribution.

The polarity of ketones decreases with increasing chain length. So the prediction of Henry's constant of oxygen in ketones by the regular solution equation must yield more meaningful results for the higher ketones. This idea is being tested by comparing experimental and predicted solubility parameters for the different ketones.

Experimental Section

Apparatus. The apparatus (Figure 1) consisted of a 100-mL round-bottom flask (a) with SVL 15 and SVL 22 screw caps (b) and NS 14.5 and NS 29 ground joints (c). The upper cap was closed with a Teflon septum whereas in the lower one an oxygen electrode (Clark) with temperature compensation was built in. In the lower ground joint a glass capillary was fixed and on the upper one a storage flask (d) was mounted which could be separated from the round-bottom flask by closing stopcock NS 8 (e).

Preliminaries. Prior to the experiments the storage flask was filled up with bidistilled water with the stopcock closed. With the upper screw cap opened, the round-bottom flask was rinsed by N_2 via the capillary. After rinsing of the flask, the screw cap was closed and at the same moment the stopcock was partly opened so that the water was well gassed by N_2 without dropping into the round-bottom flask. After gassing of the water, the stopcock was closed for a short time and the capillary replaced

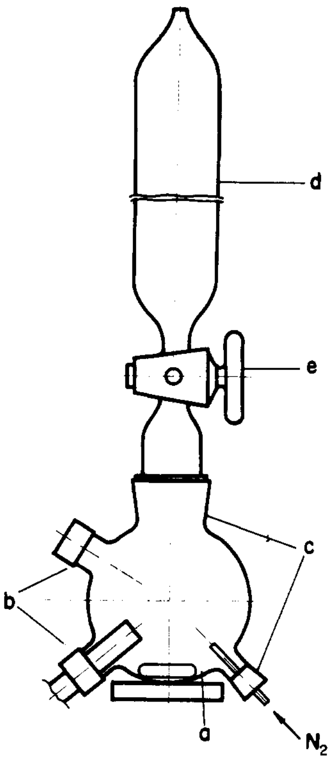

Figure 1. Apparatus.

by a ground-in stopper. Then the stopcock was opened wide and the water, now nearly free of oxygen, was allowed to enter the round-bottom flask up to the stopcock; after these preliminaries we carefully checked that no gas bubbles were inside the round-bottom flask up to the stopcock; the volume V_{fl} up to the stopcock was carefully measured each time after regenerating the oxygen electrode; the electrode was calibrated by water saturated with air.

Determination of Henry's Constant. After the magnetic stirrer was started, the stopcock was shut off and the stationary value of O_2 concentrations attended; with N_2 gassing, constant stationary values of O_2 concentrations $c_{O_2} < 0.1$ ppm in the water were obtained (purity of N_2 99.99%). With a 1-mL Hamilton precision syringe, samples with volume V_s were taken slowly from ketones saturated with oxygen at the prevailing temperatures (purity of O_2 99.996%, purity of ketones is p.a.). The samples were injected into the water through the Teflon septum, the stopcock being turned on for a moment; from the measured rise of the oxygen concentration from $c_{O_2,fl}{}^0$ to $c_{O_2,fl}{}^e$ the oxygen concentration of the sample $c_{O_2,s}$

$$c_{O_2,s} = \frac{V_{fl}c_{O_2,fl}{}^e - (V_{fl} - V_s)c_{O_2,fl}{}^0}{V_s} \qquad (1)$$

and the weight solubility c_w (index 1 solvent)

$$c_W = \frac{c_{O_2,s}}{M_{O_2}\rho_1}\frac{p_{O_2}}{(P - p_{vap})}\,\frac{\text{kmol O}_2}{\text{kg solvent}} \quad P_{O_2} = 1\text{ bar} \qquad (2)$$

were determined.

From c_w the mole fraction solubility $x_{O_2} = c_wM_1/(1 + c_wM_1)$ and Henry's constant $H_{O_2,1}{}^{(p_1^s)} = p_{O_2}/x_{O_2}$, at $p_{O_2} = 1$ bar and the saturation vapor pressure $p_1{}^s$, were calculated. For evaluation V_s was always neglected against V_{fl}, because $V_s/V_{fl} < 0.5\%$, V_s was taken at room temperature, and the values of ρ_1 and p_{vap} for the different ketones were taken from literature (API 44-TRC tables (*3*)). For determination of the error of the $H_{O_2,1}{}^{(p_1^s)}$ values the individual standard deviations of the measured quantities were estimated: V_s, 0.8%; V_{fl}, 0.5%; Δc_{O_2}, 2%; p_{vap} = 1%; ρ_1, neglected; these values resulted in a relative mean error of 2.4% for the $H_{O_2,1}{}^{(p_1^s)}$ values determined.

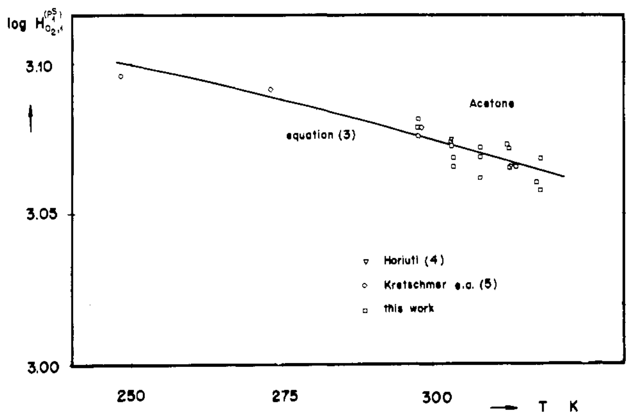

Figure 2. Comparison of experimental values of Henry's constant for oxygen in acetone for T = 238–318 K from this work with that from Horiuti (*4*) and Kretschmer et al. (*5*); regression line from the equation of Cysewski and Prausnitz (*2*).

Table I. Experimental Values of Henry's Constant for Oxygen in Acetone

T^a	$H_{O_2,1}{}^{(p_1^s)b}$	T^a	$H_{O_2,1}{}^{(p_1^s)b}$	T^a	$H_{O_2,1}{}^{(p_1^s)b}$
		This Work			
298.2	1190	303.2	1183	312.6	1185
297.4	1204	303.6	1173	312.8	1164
297.8	1207	303.6	1161	312.8	1184
297.8	1194	307.8	1171	313.5	1164
297.8	1203	308	1180	317.2	1146
303.2	1188	308	1143	318	1171
303.2	1186	308	1153	318	1144
		From Reference 5			
248	1249	273	1236	298	1199
		From Reference 4			
303.2	1187.8	313.2	1165		

[a] In K. [b] In bar/mole fraction.

Results and Discussion

Comparison of $H_{O_2,1}{}^{(p_1^s)}$ Values Determined for Acetone with Data from the Literature. Figure 2 compares the $H_{O_2,1}{}^{(p_1^s)}$ values determined for acetone with known data from Horiuti (*4*) and Kretschmer, Nowakowska, and Wiebe (*5*); all values are listed in Table I. The value of Henry's constant which was determined for O_2/acetone agrees well with the values found by Horiuti by the volumetric method. Furthermore, the dependences of the values from T are in agreement with those resulting from the data of Kretschmer, Nowakowska, and Wiebe and Horiuti. It is not possible to compare the experimental error of the values given here with that of Horiuti and Kretschmer, Nowakowska, and Wiebe because these authors have not published independently repeated measurements, but it is known from literature (*1*) that the values obtained by the volumetric method are precise in the range of ±1%. From this and the experimental error of the values obtained by the sample technique used here it can already be deduced that the experimental error of the method used here is greater, roughly a factor of 2 compared with the volumetric method. Further comments on this point will be given below.

Correlation of Henry's Constant. The values of $H_{O_2,1}{}^{(p_1^s)}$ obtained in the way described above for the solvents 2-butanone, 2-pentanone, and 2-hexanone are given in Table II and in Figures 3 and 4. As can be seen the experimental error never exceeds 2%; so we conclude that the value of 2.4% given above is the upper limit for the experimental error of the method. For correlating the values we have used the semiempirical approach

Table II. Experimental Values of Henry's Constant for Oxygen in 2-Butanone, 2-Pentanone, and 2-Hexanone

T^a	$H_{O_2,1}^{(p_1^s)b}$	T^a	$H_{O_2,1}^{(p_1^s)b}$	T^a	$H_{O_2,1}^{(p_1^s)b}$
		2-Butanone			
298.2	986	308.2	988	319.2	954
298.2	999	308.6	969	323.2	963
298.6	1000	308.9	965	323.4	924
298.6	990	313.2	979	323.6	950
302.7	964	313.7	960	327.8	963
303.7	963	314.2	969	332.2	936
307.9	974	318.4	947		
		2-Pentanone			
298.2	904	311.9	914	325.2	876
298.2	900	315.2	897	329.4	886
298.2	883	319.2	876	329.6	886
298.2	909	319.2	893	331.4	868
303.7	876	323.2	882	334.7	867
305.6	909	323.2	887	336.7	889
306.4	890	323.2	887	341.7	877
310.4	888				
		2-Hexanone			
298.2	855	318.2	863	336.2	906
298.5	860	318.2	893	336.6	881
298.7	850	318.2	883	337.0	912
307.7	847	326.1	889	337.2	871
307.7	865	327.0	864	341.2	893
308.4	849	328.0	895	343.7	896
309.0	850	335.7	897	343.7	874
316.5	881				

[a] In K. [b] In bar/mole fraction.

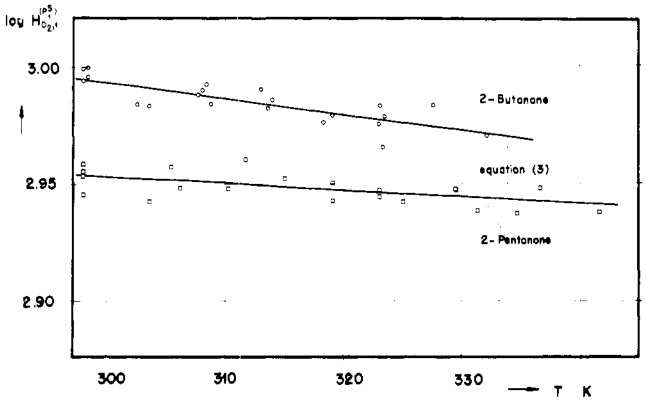

Figure 3. Experimental values of Henry's constant for oxygen in 2-butanone and 2-pentanone for T = 298–344 K; regression line from the equation of Cysewski and Prausnitz (*2*).

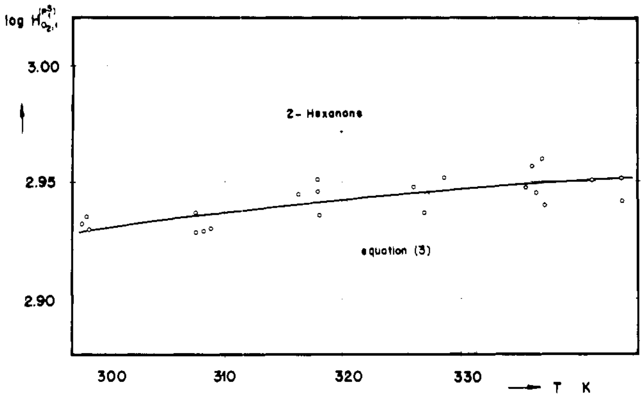

Figure 4. Experimental values of Henry's constant for oxygen in 2-hexanone for T = 298–344 K; regression line from the equation of Cysewski and Prausnitz (*2*).

Table III. Values of ν_{1O_2}* and T_{1O_2}* in Equation 3 from the Experimental Data in Tables I and II

	$10^3\nu_{1O_2}^*$, m³/kmol	$T_{1O_2}^*$, K
acetone	38.75 ± 0.06	211.6 ± 0.8
2-butanone	48.74 ± 0.14	231.1 ± 1.86
2-pentanone	58.38 ± 0.13	232.2 ± 1.47
2-hexanone	67.03 ± 0.21	225.2 ± 1.97

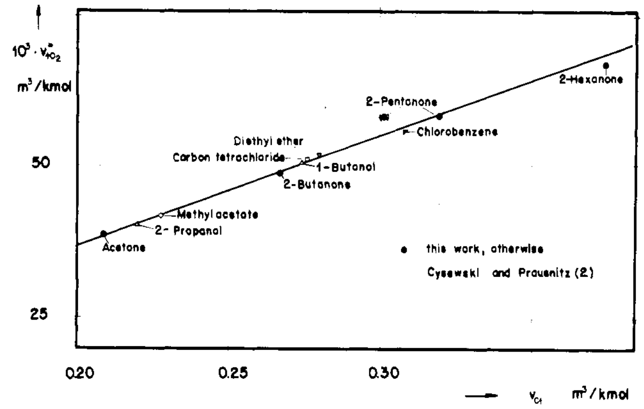

Figure 5. Comparison of the v_{1O_2}* values for acetone, 2-butanone, 2-pentanone, and 2-hexanone from this work with the values of Cysewski and Prausnitz (*2*) for water, alcohols, and other polar solvents.

chosen by Cysewski and Prausnitz (*2*). Briefly, this approach starts with an idea of Preston and Prausnitz (*6*) postulating that Henry's constant is the fugacity of a hypothetical pure liquid where all intermolecular forces are those acting between solute and solvent. This yields for $H_{O_2,1}^{(p_1^s)}$ with the only intermolecular potential Γ_{12} determining the equation of state

$$\ln \frac{H_{O_2,1}^{(p_1^s)} v_1}{RT} = \int_{v_1}^{\infty} \left(\frac{z-1}{v}\right) \mathrm{d}v + (z-1) = \frac{4(\tau/\tilde{v}) - 3(\tau/\tilde{v})^2}{(1-(\tau/\tilde{v}))^2} + \frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1-(\tau/\tilde{v}))^3} + \sum_{n=1}^{4} \sum_{m=1}^{M} A_{nm} \left(\frac{\tau/\tilde{v}}{0.74}\right)^m \left(\frac{1}{\tilde{T}}\right)^n (m+1) \quad (3)$$

if one uses a perturbation with hard spheres as a reference system and the hard-sphere equation given by Carnahan and Starling (*7*) where the values of A_{nm} and M can be found; for further details see Cysewski and Prausnitz (*2*) (eq 3 is identical with eq 10 given there—a misprint in this equation and in A_{33} has been eliminated). The parameters of the model are included in the reduced volume $\tilde{v} = v/v_{1O_2}$* and reduced temperature $\tilde{T} = T/T_{1O_2}$*, where the parameters v_{1O_2}* and T_{1O_2}* characterize the interaction of a single O_2 molecule with the matrix of ketone molecules. We have estimated these two parameters with the values of $H_{O_2,1}^{(p_1^s)}$ given in the Tables I and II by a nonlinear parameter estimation procedure (Table III). As we can see from the small estimated standard deviations of v_{1O_2}* and T_{1O_2}* and the analysis of residuals (see regression lines in Figures 2, 3, and 4) the model describes quite well the measured values of $H_{O_2,1}^{(p_1^s)}$. In a comparison with the values of $v_{1O_2}^*$ = 39.15 × 10^{-3} m³/kmol and $T_{1O_2}^*$ = 218.7 K already estimated for acetone by Cysewski and Prausnitz (*2*) it must be kept in mind that this was done by these authors using only the three values of Kretschmer, Nowakowska, and Wiebe (*5*) in the temperature range 248–298 K. As already mentioned by Preston and Prausnitz (*6*), the value of the parameter v_{1O_2}* is primarily determined by the size of the solvent molecules, so that v_{1O_2}* is strongly correlated with the critical volume v_{c1} of ketones and is nearly independent of the critical volume v_{cO_2} of oxygen. This fact is clearly demonstrated in Figure 5 where the values of v_{1O_2}* determined for the ketones (see above) are compared with the values for polar solvents already given by Cysewski and Prausnitz. The (redetermined) value of v_{1O_2}* for

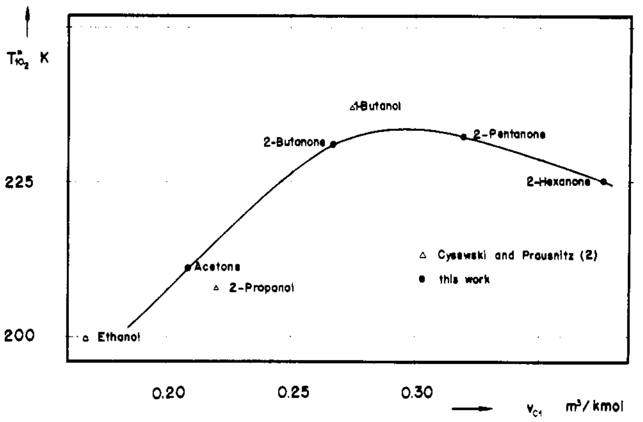

Figure 6. Comparison of the $T_{1O_2}^*$ values for acetone, 2-butanone, 2-pentanone, and 2-hexanone from this work with the values of Cysewski and Prausnitz (*2*) for alcohols.

acetone and the value of $v_{1O_2}^*$ for 2-butanone are well fitted by a regression line including the values of $v_{1O_2}^*$ for water, methanol, and ethanol (not shown in Figure 5). The value of 2-pentanone in parentheses is that for v_c = 0.301 m³/kmol usually found in literature (*3*). The second value of 2-pentanone at the regression line is that for v_c = 0.320 m³/kmol, predicted by the methods of Vetere and Lydersen (*8*). We cannot explain this great difference between the two values and assume that the value of v_c = 0.301 m³/kmol for 2-pentanone is reported too low in literature. The value of v_c for 2-hexanone was also estimated by the methods of Vetere and Lydersen with v_c = 0.376 m³/kmol because no value is reported in literature.

The correlation of $T_{1O_2}^*$ is not so simple (see Figure 6); we observe first an increase of $T_{1O_2}^*$ with increasing v_{c1}. There is some correspondence between the values of $T_{1O_2}^*$ for alcohols given by Cysewski and Prausnitz (*2*) and the values for the ketones resulting from this work. Using the picture of marbles (O_2 molecules) in the box filled with cigars (solvent molecules) given by these authors, we interpret $T_{1O_2}^*$ as a measure of the energy necessary to introduce a O_2 molecule into the matrix of solvent molecules. With increasing size of the solvent we observe an increase of energy which is necessary for the displacement of solvent molecules; for higher ketones this energy will reach a nearly constant value—the marbles have become sufficiently small compared with the long cigars; the increase in chain length of the ketones is accompanied by a decrease of polarity of the molecule which possibly causes the slow decrease in energy necessary to introduce a O_2 molecule in the matrix of ketone molecules. This explanation of the experimental results of $T_{1O_2}^*$ for ketones is speculative because of the few experimental results. Only further experiments done with higher alcohols (the situation must be similar) and still higher ketones will yield further insights.

Prediction of Henry's Constant for Higher Ketones by the Regular Solution Equation. Acetone is a polar aprotic solvent, but the polarity of the ketones decreases with increasing chain length. So it must be possible to predict solubility data for higher ketones by the regular solution equation (see, e.g., Prausnitz (*9*))

$$H_{O_2,1}^{(p_1^s)} = \frac{f_{\text{pure } O_2}^{L}}{f_{O_2}^{G}} \exp\left(\frac{\tilde{v}_{O_2}^{L}(\delta_1 - \delta_{O_2})^2 \phi_1^2}{RT} \right) \tag{4}$$

where δ_1 and δ_{O_2} are the solubility parameters of solvent and solute, $v_{O_2}^L$ is the molar "liquid" volume of O_2, and $f_{\text{pure } O_2}^L$ is the corresponding fugacity of the hypothetical liquid at 1 bar. Taking the volume fraction of the ketones $\phi_1 = 1$ and the gas fugacity $f_{O_2}^G = 1$ bar, the values of δ_1 were back-calculated from experimental values of $H_{O_2,1}^{(p_1^s)}$ at 298 K. With the mean values from Table I measured for 298 K, $\delta_{O_2} = 2.59 \times 10^2$ (kJ/m³)$^{1/2}$, $v_{O_2}^L = 33 \times 10^{-3}$ m³/kmol, and $f_{\text{pure } O_2}^L$ = 264 bar for this temperature (all values taken from Prausnitz (*9*)), the values of δ_1 obtained are shown in Table IV. The values of the cohesive energy density of $\delta_{1,c}$ are obtained from

$$\delta_{1,c} = \left(\frac{\Delta H_v - RT}{V_M} \right)^{1/2} \tag{5}$$

with the latent heat of vaporization ΔH_v for 298 K estimated from literature data (*10*) and (*3*) by using the Watson relation (Reynes and Thodos (*11*)) with an exponent n = 0.38. This relation yields values of ΔH_V and $\delta_{1,c}$ a little bit too low. But from the above remarks it can be deduced that the regular solution equation already predicts $H_{O_2,1}^{(p_1^s)}$ for 2-butanone and 2-hexanone quite well and that the precision of prediction increases with increasing C number. This result is in agreement with results from an extended regular solution equation for nonpolar gases dissolved in polar liquids given by Yen and McKetta (*12*); these authors also predict a decreasing deviation from the regular solution equation with increasing C number of the ketone. The prediction of the temperature dependence of $H_{O_2,1}^{(p_1^s)}$ for 2-hexanone resulting from equation (*4*) ($v_{O_2}^L(\delta_{C_6} - \delta_{O_2})^2$ = 2931 kJ/kmol is independent from temperature)

$$H_{O_2,C_6}^{(p_{C_6}^s)}\big|_T = 4.55 f_{\text{pure } O_2,T}^{L} \exp(1.185(298/T - 1)) \tag{6}$$

is almost zero and thus in fair agreement with the one measured, which is about +5%.

Table IV. Comparison of Values for the Solubility Parameter δ_1 Back-Calculated from Experimental Data with Equation 4, $\delta_{1,c}$ Calculated from Equation 5

	ketone			
	C_3	C_4	C_5	C_6
$H_{O_2,1}^{(p^S)}$, bar/mole fraction	1200	994	899	855
$10^{-2}\delta_1$, (kJ/m³)$^{1/2}$	5.96	5.74	5.61	5.55
$10^{-2}\delta_{1,c}$, (kJ/m³)$^{1/2}$	6.30	6.03	5.64	5.57[a]

[a] Value estimated with T_c = 582 K from Vetere.

Conclusions

Oxygen solubility data can be evaluated by injecting oxygen-saturated samples into water and measuring the rise of the oxygen concentration with an experimental error about ±2%. As tested with acetone this method seems to be suitable as a rapid working method for obtaining oxygen solubility data for hydrocarbons with lower precision.

The new experimental data of oxygen solubilities for 2-butanone, 2-pentanone, and 2-hexanone can be well fitted by the equation of Cysewski and Prausnitz, but the physical significance of the second parameter in their equation is still not clear. Since oxygen solubilities for higher ketones can be well predicted by the regular solution equation, it seems to be (at least in the moment) more reliable to use this equation in this case.

Glossary

A_{nm}	constant in eq 3 (values from Carnahan and Starling (*7*))
c	molar concentration, kmol/m³
f	fugacity, bar
H	Henry's constant of oxygen in solvent 1 evaluated at saturation pressure p_1^s, bar/mole fraction
M	molecular weight
p, P	pressure, bar
T	temperature, K
v	molar volume, m³/kmol
V	volume, m³

x	mole fraction
z	compressibility factor

Greek Letters

Γ	potential energy, kJ/mol
δ	solubility parameter, $(kJ/m^3)^{1/2}$
ρ	density, kg/m^3
τ	constant (0.74)

Superscripts

$\sim$	reduced property
$*$	reducing property
G	gas phase
L	liquid phase
s	saturated

Subscripts

1	solvent
c	critical
fl	flask
pr	probe
s	sample
vap	vapor

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Temperature Dependence of Excess Thermodynamic Properties of Ethanol + *n*-Heptane and 2-Propanol + *n*-Heptane Solutions

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Heat capacities of *n*-heptane, ethanol, 2-propanol, and their binary mixtures have been measured by adiabatic calorimetry with an uncertainty of about 0.2%: *n*-heptane (184–302 K), ethanol (160–306 K), 2-propanol (188–304 K), five mixtures of ethanol + *n*-heptane (195–305 K), and five mixtures of 2-propanol + *n*-heptane (188–305 K). These data were used to obtain the excess heat capacity, C_p^E, for the solutions. The molar excess thermodynamic functions H^E, G^E, and S^E were computed by using these C_p^E values, together with values of G^E and H^E at 303.15 K, reported by others. The variation of G^E with composition and temperature was correlated by using two forms of the Redlich–Kister equation, the Wilson equation, and the Wiehe–Bagley equation. The composition and temperature dependence of G^E and H^E of the above systems and the ethanol–methylcyclohexane system were used to test variations of the theory of associated solutions based on volume fraction and mole fraction statistics.

Introduction

The theory of solutions of nonelectrolytes has been the subject of discussion and research for many years. In the past few decades concentrated study has been made of solutions in which specific strong interactions occur, especially solutions of alcohols with an inert solvent in which hydrogen bonding effects are present.

One method of studying such solutions experimentally is to determine the excess thermodynamic properties, C_p^E, H^E, G^E, and S^E, of the solution as a function of temperature and composition. Two different theoretical approaches have proven useful in analyzing these excess property data. One approach, developed by Barker (*1*, *2*) and Tompa (*3*), is based on a quasi-lattice model of the liquid, in which each molecule occupies a certain number of sites of the lattice. A second approach (the theory of associated solutions) is based on a chemical model first proposed by Dolezalek (*4*) and since modified by others (*5*–*11*). The chemical theory ascribes the major effect of chemical interaction to the alcohol molecules which form polymeric species having varying stabilities.

In the present work C_p^E has been determined experimentally as a function of temperature and composition for the ethanol–*n*-heptane and 2-propanol–*n*-heptane systems. The resulting C_p^E data were used to compute the temperature and composition dependence of the excess thermodynamic properties H^E, G^E, and S^E. These latter calculations made use of the experimental data for G^E and H^E as a function of composition at 303.15 K of Van Ness et al. (*12*) for the ethanol–*n*-heptane system and of Van ness et al. (*13*) for the 2-propanol–*n*-heptane system. The present studies, together with those of Van Ness et al. (*11*–*13*) from room temperature to 75 °C, provide a very wide temperature range for the excess thermodynamic properties of these systems.

The variation of G^E with composition and temperature was correlated by using the Redlich–Kister equation (*14*), the Wilson equation (*15*), and the Wiehe–Bagley equation (*16*, *17*). The composition and temperature dependence of G^E and H^E were also used to test several variations of the theory of associated solutions based on volume fraction and mole fraction statistics (*11*).

Experimental Section

Heat Capacity Measurements. The heat capacity measurements were carried out in a precision adiabatic-shield

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