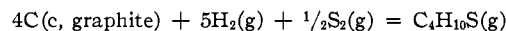


The following values of related properties were calculated as before: $\Delta Sf^\circ_{298.16} = -81.47$ cal. deg.⁻¹ mole⁻¹; $\Delta Ff^\circ_{298.16} = +1.32$ kcal. mole⁻¹; and $\log_{10} Kf = -0.97$.

Finally, the heat of formation of $\text{S}_2(\text{g})$ from rhombic sulfur¹⁸ was used to compute the standard heat of formation of

2-butanethiol vapor from $\text{S}_2(\text{g})$, $\Delta Hf^\circ_{298.16} = -38.39 \pm 0.19$ kcal.mole⁻¹, for the reaction



This value is listed in Table I.

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[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Volumetric and Thermodynamic Properties of Fluids. V. Two Component Solutions

BY KENNETH S. PITZER AND GLEN O. HULTGREN

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The acentric factor theory of volumetric behavior of pure fluids is applied to mixed gases. The pseudo-critical temperature and pressure and the acentric factor are evaluated for twelve binary systems each at several compositions. It is found that a linear equation in the mole fraction and the properties of the components is adequate for the acentric factor in all cases and for the pseudo-critical constants in some systems. In other systems small quadratic terms are required for the pseudo-critical temperature and pressure. The relationship of these quadratic terms to the intermolecular forces is considered. It is believed that useful predictions of fugacities as well as of volumetric data can be made on the basis of these results.

Corresponding states theory has been extensively used in the treatment of solutions. Particularly notable contributions were the introduction of the pseudo-critical concept by Kay¹ and of the method of conformal solutions by Longuet-Higgins.² Recent important work includes that of Prigogine and collaborators³ and of Scott.⁴ Salsburg⁵ and Prigogine⁶ have presented excellent reviews which give further references.

One limitation on all corresponding states theories of solutions is the fact that the pure components seldom follow the law of corresponding states strictly. Brown⁷ showed that the deviations of the CO-CH₄ system from solution theory of this type differed substantially depending on the choice of CO or CH₄ as the reference substance. In this paper we apply to solutions the extended theory based upon the acentric factor which has been applied to pure fluids in a recent series of papers.⁸

This removes the contradiction which is inherent in a corresponding states treatment of a solution of two components which do not themselves follow the principle of corresponding states. The acentric factor theory is not exact either, but it was found to reduce the magnitude of deviation in pure substances by about a factor of ten from that of simple corresponding states theory. At the present level of accuracy of solution studies, this residual uncertainty in treatment of pure substance properties is unimportant.

(1) W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

(2) H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A205**, 247 (1951).

(3) I. Prigogine, A. Bellemans and A. Englert-Chwoles, *J. Chem. Phys.*, **24**, 518 (1956), and earlier papers there cited.

(4) R. L. Scott, *ibid.*, **25**, 193 (1956).

(5) Z. W. Salsburg, *Ann. Rev. Phys. Chem.*, **8**, 55 (1957).

(6) I. Prigogine, "The Molecular Theory of Solutions," North-Holland Pub. Co., Amsterdam, 1957.

(7) W. B. Brown, *Phil. Trans. Roy. Soc. (London)*, **A250**, 175 (1957).

(8) Papers I-IV, respectively, K. S. Pitzer, *THIS JOURNAL*, **77**, 3427 (1955); K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Higgins and D. E. Petersen, *ibid.*, **77**, 3433 (1955); K. S. Pitzer and R. F. Curl, Jr., *ibid.*, **79**, 2369 (1957); R. F. Curl, Jr., and K. S. Pitzer, *Ind. Eng. Chem.*, **50**, 265 (1958).

In this investigation the volumetric properties of several solution systems in the single phase region are compared with the functions for pure substances. Best values of the pseudo-critical temperature and pressure and of the acentric factor are obtained as well as an estimate of the accuracy of agreement throughout the region of available data. Then the pseudo-critical constants and acentric factors for the solutions are compared with those for the pure components and methods of relating one with the other are discussed. Possible thermodynamic applications are illustrated by fugacity calculations.

Determination of Pseudo-critical Constants.—In the acentric factor theory the compressibility factor is given by the equation

$$(PV/RT) = z = z^{(0)} + \omega z^{(1)} \quad (1)$$

where $z^{(0)}$ and $z^{(1)}$ are functions of the reduced temperature T_r and the reduced pressure P_r which are tabulated in Paper II.⁸ The acentric factor ω is defined by the equation

$$\omega = -\log (P/P_c)_{\text{sat}} - 1.000 \text{ at } T_r = 0.700 \quad (2)$$

where $(P/P_c)_{\text{sat}}$ is the reduced vapor pressure at $T_r = 0.700$. It was explained in earlier papers that the acentric factor may be determined from vapor pressure data at any temperature well removed from the critical point.

In our present work, we seek to determine an acentric factor and pseudo-critical constants for a solution such that its volumetric behavior is given by eq. 1. Since solutions cannot be expected to conform exactly with even the acentric factor extension of the corresponding states theory for pure substances, there is necessarily some arbitrariness in the selection of pseudo-critical constants. The most characteristic and sensitive single phase region is that just above the critical point in both temperature and pressure. The two phase region is expanded for solutions, as compared to pure substances, consequently the range available for comparison of single phase properties begins somewhat above the point $T_r = 1$, $P_r = 1$. For

typical systems the isotherms from $T_r = 1.15$ to 1.4 were most useful. These isotherms have minima in the compressibility factor at reduced pressures between 2.3 and 3.3, and data over a pressure range of about a factor of two each way from the minimum were usually available.

The precise procedure comprised first the construction of a tracing paper graph of the compressibility factor z vs. $\log P$ for the region mentioned above. The values of the minima in z of the isotherms are then plotted vs. $\log T$ on a second graph. The slope of this second graph was found to be relatively sensitive to the acentric factor. These plots were made for the solution systems and in addition from the tables of Paper II⁸ for pure substance behavior. Comparison of graphs of the second type with translation along the $\log T$ axis served to determine both the acentric factor ω (from the fit in slope) and the pseudo-critical temperature (from the relative scales of $\log T$). Then comparison of graphs of the first type allowed determination of the pseudo-critical pressure (from the relative scales of $\log P$) and of the accuracy of fit away from the minima in the isotherms.

The resulting constants are presented in Table I. The deviation in z between the observed and theoretical values was less than 1% in most regions. Comparisons were made at temperatures and pressures well outside the region used in determining the pseudo-critical constants. In an extreme comparison of this type the second virial coefficient of 40% *n*-butane, 60% methane was predicted from the pseudo-critical constants fitted in the high pressure region and the empirical second virial coefficient equation of Paper III⁸ of this series. The calculated result differed from experiment by not over 6 cc./mole in the range 378–510°K. The resulting error compressibility factor at atmospheric pressure would be 0.02%.

The precision of determination of the pseudo-critical constants depends, of course, on the precision of agreement with the theoretical curves. The uncertainty in ω for the systems in Table I ranges from 0.02 to 0.1, while that in T_c or P_c ranges from 0.2 to 1%.

It is remarkable that pairs of components with such different volatility as methane and *n*-butane or nitrogen and ethane yield solutions which behave nearly like pure substances in the single phase region. These systems appear to be near the boundary, however, because the system methane-*n*-pentane deviates significantly. Experimental isotherms fitted near their minima in z fall about 2% below the theoretical curves at a pressure one-half or twice that of the minimum.

Composition Dependence of Pseudo-critical Constants.—The *prima facie* extension of Kay's postulates to the acentric factor system is the assumption that ω as well as T_c and P_c are linear functions of the mole fraction. Table II presents the tests of this assumption. The fourth, sixth and eighth columns contain the quantities which are zero if the critical temperature, the critical pressure and the acentric factor, respectively, are linear functions of the mole fraction. Three systems, propane-isopentane, propane-benzene and nitro-

TABLE I
PSEUDO-CRITICAL CONSTANTS OF SOLUTIONS
(Values for 50 Mole %)

System	Ref.	T_{cm} , °K.	P_{cm} , atm.	ω_m
CH ₄ -C ₂ H ₆	<i>a</i>	254	48.5	0.05
CH ₄ -C ₃ H ₈	<i>b</i>	287	37.9	.12
CH ₄ -iso-C ₄ H ₁₀	<i>c</i>	309	40.3	.10
CH ₄ - <i>n</i> -C ₄ H ₁₀	<i>d</i>	324	42.2	.17
C ₃ H ₈ -iso-C ₅ H ₁₂	<i>e</i>	415	37.3	.20
C ₃ H ₈ -C ₆ H ₆	<i>f</i>	464	45.2	.20
N ₂ -C ₂ H ₆	<i>g</i>	213	41.4	.05
CH ₄ -CO ₂	<i>h</i>	242	57.6	.15
CO ₂ -C ₂ H ₆	<i>i</i>	292	55.3	.10
CO ₂ -C ₃ H ₈	<i>j</i>	322	49.5	.14
CO ₂ - <i>n</i> -C ₄ H ₁₀	<i>k</i>	352	46.1	.20
CH ₄ -H ₂ S	<i>l</i>	269	63.2	.05

^a B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **31**, 1497 (1939); the 70°F. isotherms appear to be inaccurate; constants in Table I are based on higher temperature data. ^b H. H. Reamer, B. H. Sage and W. N. Lacey, *ibid.*, **42**, 534 (1950). ^c R. H. Olds, B. H. Sage and W. N. Lacey, *ibid.*, **34**, 1008 (1942). ^d H. H. Reamer, K. J. Kaapi, B. H. Sage and W. N. Lacey, *ibid.*, **39**, 206 (1947). ^e W. E. Vaughan and F. C. Collins, *ibid.*, **34**, 885 (1942). ^f J. W. Glanville, B. H. Sage and W. N. Lacey, *ibid.*, **42**, 508 (1950). ^g H. H. Reamer, F. T. Selleck, B. H. Sage and W. N. Lacey, *ibid.*, **44**, 198 (1952). ^h H. H. Reamer, R. H. Olds, B. H. Sage and W. N. Lacey, *ibid.*, **36**, 88 (1944). ⁱ H. H. Reamer, R. H. Olds, B. H. Sage and W. N. Lacey, *ibid.*, **37**, 688 (1945). ^j H. H. Reamer, B. H. Sage and W. N. Lacey, *ibid.*, **43**, 2515 (1951). ^k R. H. Olds, H. H. Reamer, B. H. Sage and W. N. Lacey, *ibid.*, **41**, 475 (1949). ^l H. H. Reamer, B. H. Sage and W. N. Lacey, *ibid.*, **43**, 976 (1951).

gen-ethane, appear to fit since none of their deviations exceed the limit of uncertainty. The remaining systems deviate by significant amounts and in a few cases by large amounts.

In cases where there is deviation from linear dependence on the mole fraction, a quadratic term suffices to yield agreement. Thus the following equations are obtained for the pseudo-critical constants of a solution of mole fraction x_1 and x_2

$$T_{cx} = x_1 T_{c1} + x_2 T_{c2} + 2x_1 x_2 (2T_{cm} - T_{c1} - T_{c2}) \quad (3)$$

$$P_{cx} = x_1 P_{c1} + x_2 P_{c2} + 2x_1 x_2 (2P_{cm} - P_{c1} - P_{c2}) \quad (4)$$

$$\omega_x = x_1 \omega_1 + x_2 \omega_2 + 2x_1 x_2 (2\omega_m - \omega_1 - \omega_2) \quad (5)$$

The T_c 's and P_c 's refer to the critical temperature and pressure throughout. The quantities with subscript 1 or 2 pertain to the pure components, those with subscript x to the mixture of composition x_1 , x_2 , while those with subscript m apply to the equimolar mixtures. The relationship of the quantities in parentheses to those in Table II is self-evident.

Two conclusions may be drawn from the results in Table II. First, the acentric factor of the solution is, within the limits of uncertainty, a linear function of the acentric factors of the components. Second, the deviation from linear dependence of the pseudo-critical temperature and pressure exceeds the limit of uncertainty in many cases but does not appear to follow any simple formula based on differences of properties of pure components. We shall return later to a discussion of these conclusions in terms of molecular properties.

Calculation of Fugacities.—The system defined by eqs. 1, 3, 4, 5 provides a basis for the calculation of various thermodynamic properties of solutions. The last term in eq. 5 is dropped in view of the re-

TABLE II
RELATIONSHIP OF PSEUDO-CRITICAL CONSTANTS OF 50 MOLE % SOLUTIONS TO PROPERTIES OF COMPONENTS

Comp. 1	System	Comp. 2	Critical T		Critical P		Acentric factor	
			$\frac{T_{c2}}{T_{c1}}$	$\left[\frac{2T_{cm}}{T_{c1} + T_{c2}} - 1 \right]$	$\frac{P_{c2}}{P_{c1}}$	$\left[\frac{2P_{cm}}{P_{c1} + P_{c2}} - 1 \right]$	$(\omega_2 - \omega_1)$	$\left[\omega_m - \frac{\omega_1 + \omega_2}{2} \right]$
CH ₄		C ₂ H ₆	1.60	0.02	1.07	0.02	0.09	-0.01
CH ₄		C ₃ H ₈	1.94	.02	0.92	.03	.14	+ .04
CH ₄		iso-C ₄ H ₁₀	2.14	.03	.79	-.01	.17	.00
CH ₄		n-C ₄ H ₁₀	2.23	.05	.82	+.01	.19	.06
C ₃ H ₈		iso-C ₅ H ₁₂	1.25	.00	.78	.00	.06	.02
C ₃ H ₈		C ₆ H ₆	1.52	.00	1.16	.00	.06	.02
N ₂		C ₂ H ₆	2.42	-.01	1.39	.00	.06	-.02
CH ₄		CO ₂	1.60	-.02	1.59	-.03	.21	+ .03
CO ₂		C ₂ H ₆	1.00	-.04	0.67	-.09	-.12	-.06
CO ₂		C ₃ H ₈	1.21	-.05	.58	-.14	-.07	-.05
CO ₂		n-C ₄ H ₁₀	1.40	-.03	.52	-.16	-.01	-.02
CH ₄		H ₂ S	1.96	-.05	1.94	-.06	.09	-.01

sults already discussed. The fugacity is probably of greatest interest because it determines both phase equilibria and chemical reaction equilibria. The derivation of fugacities from a pseudo-critical corresponding states system of equations has been given by Gamson and Watson.⁹ The method is straightforward and we shall merely give the resulting equations for two components.

$$\log \left(\frac{f_1}{x_1 P} \right) = \left[\log \left(\frac{f}{P} \right) \right]_x + x_2 Y \quad (6a)$$

$$\log \left(\frac{f_2}{x_2 P} \right) = \left[\log \left(\frac{f}{P} \right) \right]_x - x_1 Y \quad (6b)$$

Y =

$$\begin{aligned} & \left(\frac{H^* - H}{RT_c} \right)_x \frac{[T_{c2} - T_{c1} + 2(1 - 2x_2)(2T_{cm} - T_{c1} - T_{c2})]}{2.303 T} \\ & + \frac{(z_x - 1)[P_{c2} - P_{c1} + 2(1 - 2x_2)(2P_{cm} - P_{c1} - P_{c2})]}{2.303 P_c} \\ & - \left[\log \left(\frac{f}{P} \right) \right]^{(1)} (\omega_2 - \omega_1) \quad (6c) \end{aligned}$$

All of the quantities appearing in eq. 6 have been defined or tabulated before. The subscript x indicates that the quantity is to be calculated for the reduced temperature, pressure and the acentric factor of the solution of mole fraction x_1, x_2 . The compressibility factor functions were given in Paper II⁸ while the fugacity and enthalpy functions were given in Paper IV.⁸ In the low pressure region the equations of Paper III⁸ give values for all the functions.

In the two phase region the fugacity of each component must be the same for each phase. The calculated fugacities for four sets of experimental equilibrium compositions in the propane-isopentane system¹⁰ are presented in Table III as an example and test of this method.

The agreement for propane fugacity is good and that for isopentane is reasonably satisfactory in view of the fact that no experimental data in or near the two phase region were used in evaluating the pseudo-critical constants.

The extension of this method to other thermodynamic functions or to more than two components is quite straightforward. The principal limitation for predictive purpose is the need for the coef-

(9) B. W. Gamson and K. M. Watson, *Natl. Petroleum News*, **36**, R623 (1944); see also J. Jaffe, *Ind. Eng. Chem.*, **40**, 738 (1948).

(10) W. E. Vaughan and F. C. Collins, *ibid.*, **34**, 885 (1942).

TABLE III

FUGACITIES IN THE PROPANE-ISOPENTANE SYSTEM
(Component 1 is propane, 2 is isopentane; fugacities are in atm.)

T, °K.	P, atm.	x_1	Liquid f_1	f_2	x_1	Vapor f_1	f_2
348.2	15.0	0.509	10.6	2.0	0.822	10.6	1.8
373.2	20.0	.414	12.1	4.0	.713	12.2	3.7
373.2	39.0	.909	25.8	0.87	.951	25.9	0.74
398.2	37.0	.577	20.9	5.0	.735	21.6	4.7

ficients of the quadratic terms in eqs. 3 and 4 for the pseudo-critical temperature and pressure. We turn now to a discussion of this topic.

Discussion

Molecular solution theories^{5,6} commonly assume that the interaction energy between unlike molecules is given by the geometric mean of the interaction energies between like molecules. While the transfer of this postulate to a pseudo-critical constant theory is not simple, it would be expected to yield a solution critical temperature less than the arithmetic mean of those of the components. Table II, however, shows a zero or positive deviation for all of the hydrocarbon systems. Also for the systems with non-hydrocarbon components, the magnitude of the negative deviation has little or no correlation with the deviation of T_2/T_1 from unity. Tentatively, we conclude that difference in molecular size tends to yield a positive deviation in the pseudo-critical temperature. This is observed in the hydrocarbon systems where the principal intermolecular attractive force is the London force between C-H bonding electrons and is essentially the same regardless of the particular hydrocarbon molecules. The deviation in pseudo-critical temperature for the other systems in Table II is decreased and is usually negative because one component of the attractive force between unlike molecules is smaller than that for like molecules. For example permanent dipole-dipole interaction must contribute to the attractive force between two H₂S molecules but is absent in CH₄-H₂S force. Quadrupole forces probably are significant for interaction of CO₂ molecules but unimportant for the hydrocarbons. The more subtle differences in London forces which arise from differences in effective polarizability per electron or effective frequency of electronic motion also affect various

systems containing non-hydrocarbon components.

The pseudo-critical pressures of the hydrocarbon solutions deviate little from the arithmetic means of the values for the components. In the systems involving H₂S or CO₂, however, the deviations are substantial and always negative. The largest values arise when (T_2/T_1) and (P_2/P_1) deviate from unity in opposite directions, *i.e.*, when the molal volumes of the two components differ substantially.

The number of systems studied is not large enough to justify broad conclusions on an empirical basis. It would be desirable to have these quadratic term coefficients for additional systems. Nevertheless, consideration of the various factors affecting intermolecular forces should allow the experienced scientist to estimate values of ($2T_{cm} - T_{c1} - T_{c2}$) and ($2P_{cm} - P_{c1} - P_{c2}$) for systems similar

to those listed in Table II with sufficient accuracy for many purposes.

It should be noted that in this study the maximum ratio of critical temperatures of components is 2.4, that of critical pressures is 2.0 and the maximum ratio of critical volumes implied is about 3. We have reason to believe that the behavior of mixed gases may become more complex when the components differ from one another to a greater degree. Thus one should be cautious in extending the present methods outside the range defined above. Nevertheless the present method should yield useful predictions of considerable accuracy for a large variety of solution systems.

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[CONTRIBUTION FROM THE RALPH G. WRIGHT LABORATORY, SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Interaction of Stannic Chloride with Some Organic Bases in Benzene^{1,2}

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Thermometric titration results confirm the fact that stannic chloride forms AB₂-type addition products with tetrahydrofuran and pyridine in benzene. These results also indicate that with the bases, 1,4-dioxane and morpholine, stannic chloride forms AB-type products in addition to the AB₂-type. Heats of complex formation in dilute benzene solution were measured at 25° and the ΔH° values (kcal./mole) for the reactions A(soln.) + 2B(soln.) → A₂B(s) are: dioxane (-16.9 ± 0.7), morpholine (-47.1 ± 0.9) and pyridine (-39.5 ± 0.8). In the case of tetrahydrofuran, the complex was soluble and the ΔH° value obtained was -24.2 ± 0.2 . Other thermodynamic quantities were estimated for the pyridine and tetrahydrofuran reactions. Conductance curves for the tetrahydrofuran reaction indicate that ion pairs exist in solution, that the product which precipitates is ionic and that it redissolves in excess base to form a conducting solution.

Introduction

Although proton acid equilibria have been investigated extensively in organic solvents of low dielectric constant, very little work has been done with Lewis acids in these media. Information derived from such studies would bear relevance to the question of acid-base strength, which is important in the investigation of organic reaction mechanisms. This paper presents a study of the interaction of stannic chloride with the bases, 1,4-dioxane, morpholine, tetrahydrofuran and pyridine in the solvent benzene.

Although the reaction products formed in other solvents or in the absence of solvent already have been described in the literature,^{3,4} the stoichiometry was investigated in benzene by thermometric titration⁵ as well as by the analysis of the products. Enthalpy measurements and equilibrium constants were obtained by a calorimetric procedure.⁶

(1) Presented in part at the Symposium on Thermoanalytical Titrimetry, New York Meeting, American Chemical Society, September, 1957.

(2) This paper represents a part of the work submitted by Mr. Peter R. Segatto to the Graduate School, Rutgers, The State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, November, 1957.

(3) H. Rheinboldt and R. Boy, *J. prakt. Chem.*, **129**, 268 (1931); P. Pfeiffer, *Z. anorg. Chem.*, **71**, 97 (1911); A. R. Ingram and W. F. Luder, *THIS JOURNAL*, **64**, 2506 (1942); A. W. Laubengayer and W. C. Smith, *ibid.*, **76**, 5985 (1955).

(4) H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, *ibid.*, **70**, 3821 (1948).

(5) S. T. Zenchelsky, James Periale and J. C. Cobb, *Anal. Chem.*, **28**, 67 (1956).

(6) M. H. Dilke and D. D. Eley, *J. Chem. Soc.*, 2601 (1949).

Additional information was obtained from conductance measurements. It was expected that the equilibrium constants might provide a measure of the relative base strengths.

Experimental

Reagents.—Bakers Analyzed Reagent grade stannic chloride was used as received for most experiments, since further purification⁷ did not alter the experimental results.

U.S.P. grade thiophene-free benzene (isatin test) was refluxed over phosphorus pentoxide for at least 12 hr. and then distilled from fresh phosphorus pentoxide through a three-foot column packed with Raschig rings. A center cut with n_D^{25} 1.4971 was used. The reported value is n_D^{25} 1.4973.⁸ No difference in refraction was observed whether sodium or phosphorus pentoxide was used as drying agent.

Technical grade dioxane was purified by the method of Fieser⁹ and distilled from sodium. The center cut was used. It gave n_D^{25} 1.4196 as compared with n_D^{25} 1.4202¹⁰ reported.

Technical grade tetrahydrofuran was dried over phosphorus pentoxide, distilled, then refluxed with lithium aluminum hydride for 12 hr. and finally redistilled from fresh lithium aluminum hydride. The center cut gave n_D^{25} 1.4035. The literature value is n_D^{25} 1.4045.¹¹

Pyridine, technical grade, was refluxed over barium oxide for several days and distilled from fresh barium oxide. The center cut gave n_D^{25} 1.5059 as compared with n_D^{25} 1.5067.¹²

U.S.P. grade morpholine was purified by the method of

(7) J. H. Hildebrand and J. M. Carter, *THIS JOURNAL*, **54**, 3592 (1932).

(8) A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 129 (1946).

(9) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 369.

(10) P. R. Frey and E. C. Gilbert, *THIS JOURNAL*, **59**, 1344 (1937).

(11) F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, *ibid.*, **75**, 6044 (1953).

(12) C. R. Kinney, *Ind. Eng. Chem.*, **32**, 559 (1940).