

TABLE IV
VALUES OF THE CONSECUTIVE COMPLEXITY CONSTANTS, β_1
AND β_2 FOR THE URANIUM(IV) SULFATE SYSTEM

$\beta_1 = \frac{k_1}{[H^+]}$	$\beta_2 = \frac{k_1 k_2}{[H^+]^2}$	$k_2/[H^+]$	k_1/k_2	Method	
131	1380	1320	10.5	12.5	Leden
128	1370	10.7	12.0		
130	1330	10.2	12.7		
128	1480	11.6	11.0		Bjerrum
126	1210	1160	9.6	13.1	Fronaesus
168	62.2	0.37	454		Betts and Leigh

For the $[H^+]$ dependent reactions the constants calculated refer to the expressions given below

$$\beta_1 = \frac{k_1}{[H^+]} = \frac{[USO_4^{++}]}{[U^{4+}][HSO_4^-]} \quad (38)$$

$$\frac{k_2}{[H^+]} = \frac{[U(SO_4)_2]}{[USO_4^{++}][HSO_4^-]} \quad (39)$$

The discrepancy between the constants calculated by the methods described in the present paper and those reported by Betts and Leigh arise in large part from the weighting of the data by these authors. Their values for the constants are based primarily on the extraction coefficients for the two highest bisulfate concentrations. If a $\log E'$ versus $\log [HSO_4^-]$ plot is made it is found that the curve using their constants passes through only these two experimental points and deviates from all their other points in such manner that at a given bisulfate concentration the calculated E' is less than that experimentally determined. It is obvious that the inherent uncertainty introduced in any attempt to describe the whole of a smoothed curve using parameters derived from one small region is greater than the probable error that can *a priori* be assigned to any given experimental point.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Calculation of Vapor Pressure Curves from Data at One Temperature. A Study of the Hildebrand Rule¹

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All liquids obeying the Hildebrand rule will fall on the same curve of $\log (P_{mm}/T)$ versus $\log (T/\theta)$. $\log \theta$ is a constant obtained from any one pair of P and T values. A standard table is presented by means of which the entire vapor pressure curve of any liquid obeying the Hildebrand rule may be calculated from data at a single temperature. Departures from the Hildebrand rule are presented as a function of vapor volume in the case of some hydrocarbons. It is found that for straight chained paraffin hydrocarbons the excess entropy of vaporization at constant vapor volume is a linear function of the number of carbon atoms from 4 to 12 carbon atoms.

Hildebrand's rule³ that the molal entropy of vaporization is the same for all normal liquids when measured at the temperatures at which their vapors have equal molal volumes was shown by Hildebrand to lead to the conclusion that for all normal liquids the plots of $\log P$ versus $\log T$ could

be superimposed by sliding them along a line of unit slope. He also showed that a general vapor pressure equation could be written for all such liquids with a single constant to be determined from a single pair of P and T values. Hildebrand⁴ showed the degree of agreement reached by taking slopes of $\log P$ versus $\log T$ plots for a number of substances at a value of $\log nR/V = 0.1$ corresponding to a vapor volume of 49.5 liters per mole.

The rule can be given a more stringent test by a slight revision in the method of treatment. Since from the perfect gas law $P/T = nR/V$, different liquids at the same value of P/T have the same vapor volume per mole. Also $(d \log P)/(d \log T) = \Delta S_v/R$ for the low pressure region, and so by subtracting $(d \log T)/(d \log T) = \Delta S_v/R - 1$. Thus all liquids which obey Hildebrand's rule will have the same slope for the same value of $\log (P/T)$. It will be noted in Fig. 1 that all plots of $\log (P/T)$ against $\log T$ for the normal liquids shown can be made to coincide by subtracting $\log \theta$ from each value of $\log T$, where $\log \theta$ is a constant for each substance to be determined from any one pair of P and T values. It will be observed that all the liquids of Fig. 1 have vapor pressures of one atmosphere or less at the value $\log (P/T) = 0.1$ used by Hildebrand.

In order to test the Hildebrand rule and to

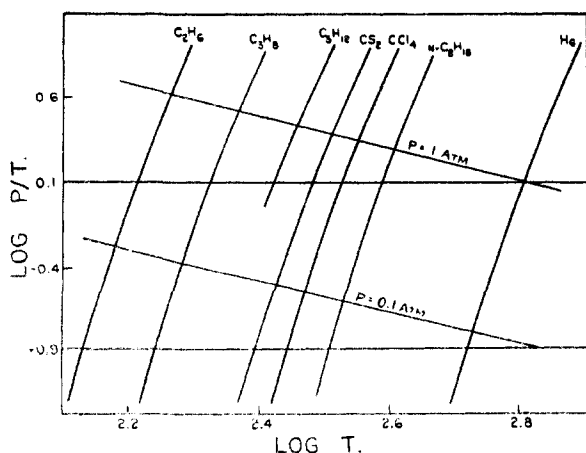


Fig. 1.

(1) Presented before the Division of Physical and Inorganic Chemistry, 121st Meeting of the American Chemical Society, Buffalo, N. Y., March 26, 1952.

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(3) J. H. Hildebrand, *THIS JOURNAL*, **37**, 970 (1915); **40**, 45 (1918).

(4) J. H. Hildebrand, *J. Chem. Phys.*, **7**, 233 (1939).

TABLE I
 Log (P_{mm}/T) for 0.001 Increments in log (T/θ)

log (T/θ)	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009
2.65	-1.80882	-1.79355	-1.77833	-1.76315	-1.74800	-1.73289	-1.71782	-1.70279	-1.68780	-1.67285
2.66	-1.65793	-1.64305	-1.62821	-1.61341	-1.59865	-1.58392	-1.56923	-1.55458	-1.53997	-1.52540
2.67	-1.51086	-1.49636	-1.48189	-1.46746	-1.45307	-1.43873	-1.42442	-1.41014	-1.39590	-1.38170
2.68	-1.36753	-1.35340	-1.33931	-1.32525	-1.31123	-1.29724	-1.28329	-1.26938	-1.25550	-1.24166
2.69	-1.22785	-1.21408	-1.20035	-1.18665	-1.17299	-1.15936	-1.14577	-1.13221	-1.11869	-1.10520
2.70	-1.09175	-1.07833	-1.06495	-1.05160	-1.03829	-1.02501	-1.01176	-0.99855	-0.98538	-0.97224
2.71	-0.95913	-0.94606	-0.93302	-0.92001	-0.90704	-0.89410	-0.88120	-0.86833	-0.85549	-0.84269
2.72	-0.82992	-0.81718	-0.80448	-0.79181	-0.77917	-0.76656	-0.75399	-0.74145	-0.72895	-0.71648
2.73	-0.70404	-0.69163	-0.67926	-0.66691	-0.65460	-0.64233	-0.63008	-0.61786	-0.60568	-0.59353
2.74	-0.58141	-0.56932	-0.55726	-0.54524	-0.53324	-0.52128	-0.50935	-0.49745	-0.48558	-0.47375
2.75	-0.46195	-0.45017	-0.43842	-0.42671	-0.41503	-0.40338	-0.39176	-0.38017	-0.36861	-0.35708
2.76	-0.34558	-0.33411	-0.32267	-0.31126	-0.29988	-0.28853	-0.27721	-0.26593	-0.25467	-0.24344
2.77	-0.23224	-0.22107	-0.20993	-0.19882	-0.18773	-0.17668	-0.16566	-0.15466	-0.14370	-0.13276
2.78	-0.12186	-0.11098	-0.10013	-0.08930	-0.07851	-0.06775	-0.05701	-0.04630	-0.03563	-0.02498
2.79	-0.01436	-0.00376	0.00680	0.01734	0.02785	0.03833	0.04878	0.05921	0.06961	0.07998
2.80	0.09032	0.10064	0.11093	0.12119	0.13142	0.14163	0.15181	0.16196	0.17209	0.18219
2.81	0.19226	0.20230	0.21232	0.22231	0.23228	0.24222	0.25213	0.26202	0.27188	0.28171
2.82	0.29152	0.30130	0.31105	0.32078	0.33048	0.34016	0.34981	0.35943	0.36903	0.37861
2.83	0.38816	0.39768	0.40717	0.41664	0.42609	0.43551	0.44490	0.45427	0.46362	0.47294
2.84	0.48224	0.49150	0.50075	0.50997	0.51916	0.52833	0.53748	0.54661	0.55571	0.56478

establish an easy non-graphical method of applying the rule, mercury was selected as a standard reference substance. Mercury is a monatomic liquid and vapor, and departs but little from the ideal gas at low pressures. To calculate the standard table of log (P/T) versus log (T/θ), the value zero was assigned to log θ for mercury and the precise equation for the vapor pressure of liquid mercury due to Epstein and Powers,⁵ was converted to the form

$$\log_{10} (P_{mm}/T) = 11.253082 - 3337.8142/T - 2.153093 \log_{10} T + 2.98647 \times 10^{-4} T - 8.84088 \times 10^{-8} T^2 - 8.84868 \times 10^{-12} T^3 + 3.13504 \times 10^{-14} T^4 \quad (1)$$

These values are listed in Table I.

The numerical example given in Table II illustrates the use of Table I in calculating the vapor pressure of any liquid obeying the Hildebrand Rule provided that its value is known at any one temperature. A plot of deviations of observed

points near one atmosphere to the normal boiling point where no other data exist.

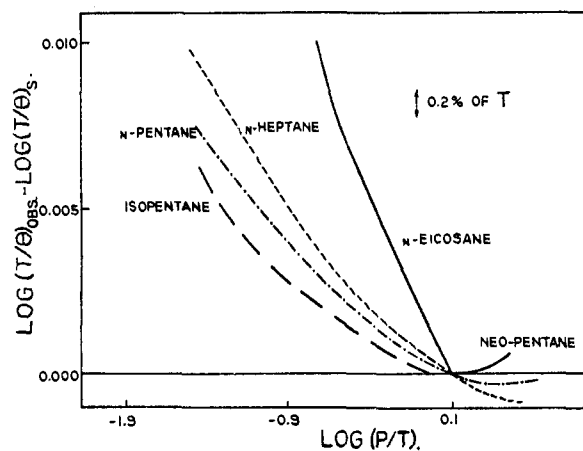


Fig. 2.

Plots such as shown in Fig. 2 make convenient deviation plots for smoothing experimental data on vapor pressures. From the slope of such plots it is possible to calculate the difference between the entropy of vaporization of the substance and that of mercury at the same vapor volume with much greater precision than is possible from a direct plot of log P versus log T . However, since the data on hydrocarbons was available⁶ as Antoine equations of the form

$$\log P = A - B/(T + C') \quad (2)$$

it was more convenient to calculate the entropies of vaporization at selected values of log (P/T) where gas imperfections were not important by means of the relation

$$\Delta S_v = 2.3026BRT/(T + C')^2 \quad (3)$$

Table III presents the excess entropy of vaporization compared to mercury at the same vapor volume. The values in parentheses are those obtained by Hildebrand in reference 4 from plots of log P versus log T . As shown in Fig. 3, these excess

values of log (T/θ) from those calculated using Table I is presented in Fig. 2. The departures are dependent upon chain length and extent of branching. It will be noted that the degree of agreement shown in Table II between calculated and observed pressures is much closer than would have been the case if the comparisons had been made at lower pressures, due to the tendency of all the deviation curves to have smaller slopes at higher values of log (P/T). This smaller slope appears to be due to the effect of gas imperfections at the higher pressures. Because of it Table I can be used with considerable confidence to correct observed boiling

(5) L. F. Epstein and M. Powers. Nuclear Science Abstracts No. 6117 (AECU-1640) Nov. 15, 1951.

(6) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of the Properties of Hydrocarbons, Tables 1-k, 2-k, 20-k.

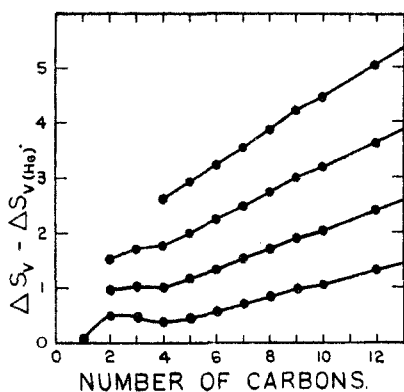


Fig. 3.

entropies are a linear function of the number of carbon atoms from 4 to 12 carbon atoms.

The increase in excess entropy of vaporization with increasing molal volume of vapor (which corresponds to decreasing temperature) is evidence for the freezing in of degrees of freedom in the liquid state as the molecules are crowded more

TABLE III
($\Delta S_v - \Delta S_{v(\text{He})}$) for normal hydrocarbons (Cal. Mole⁻¹ Deg.⁻¹)

	$\log_{10}(P_{\text{mm}}/T)$			
	0.1	-0.4	-0.9	-1.4
Methane	0.06			
Ethane	.49	0.95	1.51	
Propane	.46	1.02	1.69	
Butane	.36	1.00	1.76	2.60
Pentane	.43 (0.6)	1.15	1.99	2.92
Hexane	.54 (1.4)	1.32	2.23	3.24
Heptane	.67 (1.4)	1.51	2.48	3.55
Octane	.81 (1.1)	1.69	2.73	3.87
Nonane	.95	1.90	3.00	4.22
Decane	1.04	2.03	3.18	4.45
Dodecane	1.31	2.40	3.66	5.04
$\Delta S_{v(\text{He})}$	22.46	25.11	27.70	30.28

closely together in the contracting liquid. Halford⁷ suggested that hindered rotation could be the cause of such departures, but investigated this only for the case of $\log(P/T) = 0.1$.

(7) R. S. Halford, *J. Chem. Phys.*, **8**, 496 (1940).

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NOTES

Preparation of Glycerol Evenly Labeled with C¹⁴

BY S. ABRAHAM

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Various methods for the preparation of glycerol singly labeled with C¹⁴ have already been reported.²⁻⁴ Although certain of these procedures could be adapted to the preparation of this compound with all of its carbons uniformly labeled with C¹⁴, I should like to report here an alternate method utilizing uniformly labeled glucose⁵ as starting material.⁶

Evenly labeled glucose with a specific activity of 3×10^5 c.p.m. per mg.⁷ was prepared photosynthetically.⁵ It was converted in 84% yield to the methyl glucopyranoside with methanol and hydrochloric acid.⁸ No attempt was made to isolate the isomers of methylglucopyranoside.

The methyl glucoside was treated with sodium periodate

(1) Aided by a grant from the American Cancer Society as recommended by the Committee on Growth of the National Research Council.

(2) A. P. Doerschuk, *THIS JOURNAL*, **73**, 821 (1951).

(3) H. Schlenk and B. W. DeHaas, *ibid.*, **73**, 2921 (1951).

(4) M. L. Karnovsky and L. I. Gidez, *Federation Proc.*, **10**, 205 (1951).

(5) E. W. Putman, W. Z. Hassid, G. Krotkov and H. A. Barker, *J. Biol. Chem.*, **173**, 785 (1948).

(6) For complete details order Document 3658 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

(7) All compounds were oxidized, and assayed as BaCO₃ with an end-window counter.

(8) E. Fischer, *Ber.*, **28**, 1145 (1895).

at 2° for 24 hours. The reaction was quantitative as determined by titration of the resulting formic acid. The solution was treated with barium chloride, and the resulting precipitate was filtered and washed. The filtrate was concentrated⁹ under reduced pressure at a temperature below 60°.

The dialdehyde remaining in solution was then hydrogenated with Raney nickel at 2,700 p.s.i. and 140° for 18 hours. The dialdehyde in the filtered solution was hydrolyzed with H₂SO₄. Addition of 2,4-dinitrophenylhydrazine solution precipitated the glycolaldehyde as its hydrazone. Excess 2,4-dinitrophenylhydrazine was removed by the addition of formaldehyde.

The solution containing the radioactive glycerol was neutralized with solid BaCO₃. The filtrate was clarified with charcoal and concentrated *in vacuo*, at 40°, to a thick, viscous mass. Extraction with boiling, anhydrous acetone (C.P.) and final evaporation of the acetone at room temperature yielded the C¹⁴-glycerol. The over-all yield based on glucose was 64%.¹⁰ The refractive index of this glycerol was 1.4398 at 25°. This represents 77.6% glycerol in water.¹¹ The specific activity of the resulting glycerol was 3×10^5 c.p.m. per mg. BaCO₃.

Two-dimensional paper chromatography using phenol: water and butanol:acetic acid:water¹² revealed only one radioactive spot, and this spot was identical with the color spot obtained with inactive glycerol, using a solution of lead tetraacetate in benzene as the color spray.

Two similar experiments with inactive glucose yielded glycerol (65%) which was identified in the following manner: (a) by its refractive index, as given above, (b) by the preparation of the crystalline glycerol tribenzoate, and (c) two-dimensional paper chromatography.

(9) The formic acid distilled assayed at 3×10^5 c.p.m. per mg.

(10) Corrected for 78% glycerol in water as judged by refractive index.

(11) "International Critical Tables," Vol. 7, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 68.

(12) S. M. Partridge, "Partition Chromatography," Vol. 3, Biochemical Society Symposia, Cambridge, 1950, p. 52.