Heats and Entropies of Vaporization. The heats and entropies of vaporization at the normal boiling points (760 mm. of Hg) given in Table VI, were calculated from the three-constant vapor pressure equation by the thermodynamic relationship.

$$\Delta H^{\text{vap}} = T\Delta S^{\text{vap}} = RT^2[d\ln P/dT][1 + (B_2 - v_L)\, P/RT \tag{4}$$

In this equation the saturated vapor volume was estimated from the virial equation of state terminated at the second virial coefficient, B_2. The saturated liquid volume, v_L, was obtained from liquid densities compiled in (*12*). Values for B_2 were obtained from the literature for C_3F_8 (*2*), n-C_5F_{12} (*8*) and the various C_6F_{14} isomers (*19*). B_2 for 2-$CF_3C_4F_9$ and for 1,2-$(CF_3)_2$-cyclo-C_4F_6 were assumed to be the same as those for the normal isomers, n-C_5F_{12} and n-C_6F_{13}, respectively. B_2 for cyclo-C_5F_{10} was estimated by Pitzer's correlation (*11*) using critical constants estimated to be 422° K. and 25.6 atm.

The uncertainties listed in Table VI for ΔH^{vap} and ΔS^{vap} were estimated from the average deviations in the vapor pressure relationship used and the expected errors in the second virial coefficients. For C_3F_8 and n-C_5F_{12}, the new values of these properties agree with the earlier values at the limits of the estimated errors. For the remaining compounds in this table, the new values of ΔH^{vap} are lower by 100 to 200 cal. per mole than those reported previously. For cyclo-C_5F_{10} the new value is smaller than the earlier value by 600 cal. per mole.

Triple Points and Boiling Points. Table VI shows that the values for the triple-point temperature in this work are in general higher than those previously reported, while the normal boiling points are, within the experimental error, in essential agreement with earlier work for most of the compounds. The higher triple points particularly that for C_3F_8 which is 11.9° above the previously reported value, reflects the high purity of the samples used.

The estimated errors in the normal boiling points given in Table VI were obtained from the average deviations and the value of $d\ln P/dT$ at the boiling point for the three-constant Equation 1.

LITERATURE CITED

(1) Barber, E.J., Cady, G.H., *J. Phys. Chem.* **60**, 504 (1956).
(2) Brown, J.A., J. CHEM. ENG. DATA **8**, 106 (1963).
(3) Burger, L.L., Cady, G.H., *J. Am. Chem. Soc.* **73**, 4243 (1951).
(4) Connolly, J.F., Kandalic, G.A., *Phys. Fluids* **3**, 463 (1960).
(5) Dunlap, R.D., *J. Am. Chem. Soc.* **80**, 83 (1958).
(6) Fang, F., Joffe, J., J. CHEM. ENG. DATA **11**, 376 (1966).
(7) Frost, A.A., Kalkwarf, D.R., *J. Chem. Phys.* **21**, 264 (1953).
(8) Garner, M.D.G., McCoubrey, J.C., *Trans. Faraday Soc.* **55**, 1524 (1959).
(9) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor-Liquid Equilibrium," p. 239, Pergamon Press, 1954.
(10) The Matheson Co., Inc., "Matheson Gas Data Book," 1961.
(11) Pitzer, K.S., Curl, R.F., *J. Am. Chem. Soc.* **79**, 2369 (1957).
(12) Reed, T.M., "Fluorine Chemistry," Vol. **5**, Chapter 2, J. H. Simons, Ed., Academic Press, New York, 1963.
(13) Reed, T.M., *J. Chromatog.* **9**, 419 (1962).
(14) Reed, T.M., Walter, J.F., Cecil, R.R., Dresdner, R.D., *Ind. Eng. Chem.* **51**, 271 (1959).
(15) Rowlinson, J.S., Thacker, R., *Trans. Faraday Soc.* **53**, 1 (1957).
(16) Ruff, O., *Angew. Chem.* **46**, 739 (1933).
(17) Simons, J.H., Dunlap, R.D., *J. Chem. Phys.* **18**, 335 (1950).
(18) Stiles, V.E., Cady, G.H., *J. Am. Chem. Soc.* **74**, 3771 (1952).
(19) Taylor, Z.L., Ph.D. dissertation, University of Florida, Gainesville, Fla., 1965.

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Isothermal Vapor-Liquid Equilibrium Data for the System *n*-Heptane–*n*-Valeric Acid at 50°, 75°, and 100° C.

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Isothermal equilibrium vapor and liquid composition measurements have been made for the *n*-heptane–*n*-valeric acid system at 50°, 75°, and 100° C. Liquid phase activity coefficients for the *n*-heptane were calculated from the equilibrium data. The *n*-valeric acid activity coefficients could not be calculated directly from the composition data because the acid dimerizes in the vapor phase, but they were calculated from the *n*-heptane coefficients by integrating the Gibbs-Duhem equation. Composition–specific volume data were also obtained for this system at 25° C.

SOLUTIONS of carboxylic acids and paraffins exhibit a high degree of nonideality, not only in the liquid phase, but also in the vapor phase at low pressures. A review of the literature indicates that no vapor-liquid equilibrium data have been published for the *n*-heptane–*n*-valeric acid system. Isothermal equilibrium pressure and composition data have been obtained with the aid of a vapor recirculation still at 50°, 75°, and 100° C.

The nonideal vapor phase behavior of the system complicates the calculation of liquid phase activity coefficients from the vapor-liquid equilibrium data. If one is willing to forgo a thermodynamic consistency check of the experimental data, it is possible to calculate the liquid phase activity coefficients from equilibrium data and the Gibbs-Duhem equation. This method was used to calculate activity coefficients for the *n*-heptane and the *n*-valeric acid.

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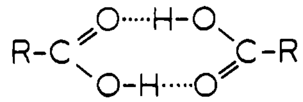
THEORY

Previous work (6) has recognized that carboxylic acids appear to exhibit nonideal vapor phase behavior at low pressures if the acid is considered to be unassociated. In reality, the apparent nonideal behavior is due to the acid being partially associated because of strong hydrogen bonding in the vapor phase. The vapor phase hydrogen bonding produces a carboxylic acid dimer of the structure:



The extent of dimerization depends on the temperature and pressure of the system. At pressures below atmospheric, higher polymers are not present in the vapor to any significant extent (6). Thus, a carboxylic acid–paraffin system is in reality, at least, a ternary system (acid monomer, acid dimer, and paraffin) and not a binary system. When this is accounted for, the vapor phase behavior at low pressures is ideal.

If a composition analysis of the three components in the vapor phase of an equilibrium vapor-liquid carboxylic acid-paraffin system is to be made—e.g., by infrared absorption—it must be made at the system equilibrium temperature and pressure. This is often difficult to do. It would be more convenient to express the phase composition in terms of the two species only (acid and paraffin) using such measurements as refractive index or density to establish the composition. If this is done, the thermodynamic analysis of the equilibrium data is more complex because of the apparent nonideal vapor behavior. *PVT* data or compressibility data for the vapor would be necessary to evaluate fugacity coefficients before liquid phase activity coefficients could be calculated. However, if one is willing to sacrifice an independent thermodynamic consistency check of the liquid phase activity coefficients, it is possible to calculate the activity coefficients from the binary analysis.

Consider a vapor composed of a paraffin, *p*, a carboxylic acid monomer, *a*, and a dimer of the acid, *d*. If all of the nonideality in the vapor phase is due to acid, then $\bar{Z}_p = 1.0$ and

$$Z = 1.0y_p + \bar{Z}_a y_a \qquad (1)$$

If $\bar{Z}_p = 1.0$, then $f_p = y_p P$ (7) and at equilibrium

$$\gamma_p = (y_p P / x_p P_p^0) \qquad (2)$$

If compressibility data are not available for the acid vapor, then the liquid phase activity coefficient, γ_a, can be calculated from γ_p by using the Gibbs-Duhem relationship:

$$x_p\, d \ln \gamma_p + x_a d \ln \gamma_a = 0 \qquad (3)$$

Noting that $x_a = 1 - x_p$ and rearranging Equation 3 gives:

$$\ln \gamma_a = \int_0^a d \ln \gamma_a = -\int_{\gamma_p^0}^{p} \frac{x_p}{1 - x_p} d \ln \gamma_p \qquad (4)$$

EXPERIMENTAL

Equipment and Materials. A modification of the vapor recirculating still described by Hipkin and Myers (3) was used in this investigation. The modified design (James T. Scanlon Co., Whittier, Calif.) is illustrated in Figure 1. The still (Model MES-100) is designed so that the contactor is self-lagged with its own vapor. This eliminates extra equipment otherwise needed to assure adiabatic operation and simplifies operation. The entire unit is vacuum-jacketed and silvered, with a 0.5-inch viewing window.

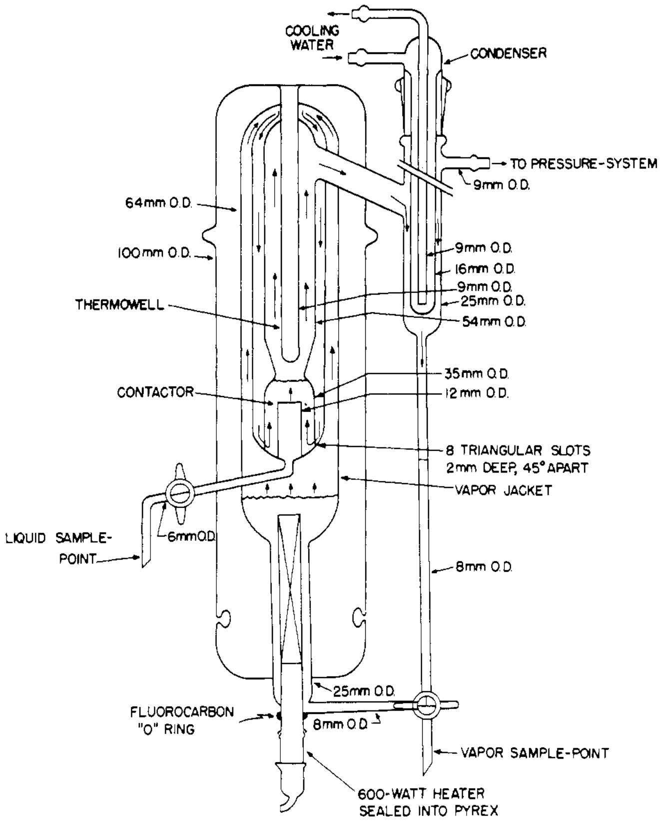


Figure 1. Modified vapor-liquid equilibrium still

Heat is supplied to the still vaporizer by means of a 600-watt borosilicate glass heater which is sealed in the still by means of a fluorocarbon "O" ring. The heater is thus readily removable. Heat input was controlled by connecting the heater to a powerstat.

All parts of the still, except the Teflon sampling valves and the "O" ring, are made of glass.

The desired still pressures were obtained and regulated by connecting the still to a vacuum pump through a Cartesian manostat (2). The pressure was measured with a mercury manometer and could be read to the nearest 0.1 mm.

Operating temperature was measured with a copper-constantan thermocouple and a Leeds and Northrup Type K-2 potentiometer capable of readings with a precision of 0.1% or better. The thermocouple was placed in the bottom of the thermowell shown in Figure 1. The cold junction was maintained at 0° C. in an ice-filled Dewar flask.

The thermocouple was calibrated at the transition point of sodium sulfate decahydrate (32.384° C.) and also against the boiling point of *n*-heptane at several pressures covering the operating range. The calibration was checked by using benzene. In the check, the millivolt reading corresponding to the desired temperature was set on the potentiometer, and the pressure was adjusted until equilibrium was attained. Thus the check was carried out by using the same technique that was to be used in obtaining the equilibrium data. The results indicate that the deviation was not greater than ±0.1° C.

The *n*-heptane and *n*-valeric acid used for this investigation were manufactured by Matheson, Coleman and Bell. The authors measured the densities of the materials and obtained values of 0.6793 and 0.9344 grams per cc., respectively. The *n*-valeric acid was stated to have a minimum purity of 99.0%. No analyses were made to check the suppliers specifications.

Procedure. Feed was introduced into the still by reducing the pressure in the system and allowing the atmospheric pressure to force the feed through the sampling valves. Normal operating capacity of the vaporizer is about 35 ml. and that of the contactor about 40 ml.

The liquid levels in the vaporizer and contactor readjust themselves, depending upon the concentrations, until equilibrium is reached. At this time, the vapor passing through the contactor is in equilibrium with the liquid in the contactor, and the levels remain constant.

Table I. Specific Volume and Composition Measurements for the *n*-Heptane–*n*-Valeric Acid System at 25° C.

Mole Fraction *n*-Heptane	Specific Volume, Cc./G.
0.000	1.070
0.0552	1.091
0.1011	1.110
0.1540	1.131
0.2075	1.154
0.2588	1.173
0.3034	1.190
0.3441	1.207
0.4059	1.232
0.4275	1.241
0.4499	1.250
0.4954	1.269
0.5008	1.271
0.5572	1.293
0.6198	1.318
0.6988	1.351
0.7827	1.384
0.9816	1.464
1.000	1.472

Table II. Isothermal Equilibrium Data and Liquid Phase Activity Coefficients for the System *n*-Heptane–*n*-Valeric Acid at 50°, 75°, and 100° C.

T, ° C.	P, Mm. of Hg	x_p	y_p	γ_p	γ_a^a
50	141.6^b	1.000	1.000	1.000	4.350
	126.0	0.767	0.987	1.144	2.030
	113.3	0.567	0.993	1.401	1.349
	105.6	0.497	0.988	1.483	1.236
	101.1	0.453	0.989	1.559	1.184
	90.3	0.365	0.988	1.726	1.111
	1.7^c	0	0	2.780	1.000
75	361.4^b	1.000	1.000	1.000	4.100
	329.6	0.778	0.991	1.162	2.179
	326.9	0.789	0.984	1.128	2.191
	323.3	0.758	0.984	1.162	2.028
	301.5	0.652	0.986	1.262	1.613
	297.3	0.600	0.987	1.354	1.467
	278.1	0.534	0.985	1.419	1.333
	262.7	0.464	0.983	1.540	1.225
	256.0	0.408	0.983	1.706	1.162
	217.2	0.308	0.977	1.908	1.080
	216.4	0.287	0.978	2.040	1.067
	166.2	0.201	0.959	2.197	1.032
	130.0	0.136	0.937	2.480	1.012
	126.4	0.126	0.952	2.642	1.009
	117.7	0.128	0.924	2.350	1.010
	7.7^c	0	0	2.940	1.000
100	794.5^b	1.000	1.000	1.000	3.960
	687.4	0.701	0.966	1.192	1.777
	665.0	0.657	0.980	1.248	1.633
	622.2	0.557	0.975	1.370	1.410
	579.0	0.483	0.966	1.458	1.288
	544.2	0.411	0.963	1.604	1.206
	455.7	0.291	0.952	1.876	1.099
	436.7	0.264	0.943	1.962	1.079
	365.2	0.183	0.936	2.350	1.037
	302.8	0.138	0.926	2.560	1.019
	200.6	0.077	0.860	2.820	1.004
	177.6	0.062	0.863	3.114	1.002
	27.8^c	0	0	3.470	1.000

[a] Calculated from Equation 4. [b] Literature values (*1*). [c] Literature values (*5*).

During each run, the still temperature was maintained by setting the proper millivolt reading on the potentiometer and adjusting the pressure to obtain the desired temperature.

The boilup rate was limited by the capacity of the condenser and by the entrainment in the still. At high valeric acid concentrations, the tendency for entrainment appeared to be high, so the boilup rate was reduced. Ordinarily, the rate was about 1 drop per second from the condenser and not less than about 1 drop every 2 seconds. This minimum rate furnished a volume of condensate equal to the vapor line holdup in about 3 minutes.

The time required to attain equilibrium was obtained from previous experience and preliminary testing. About 2 hours were required for each run.

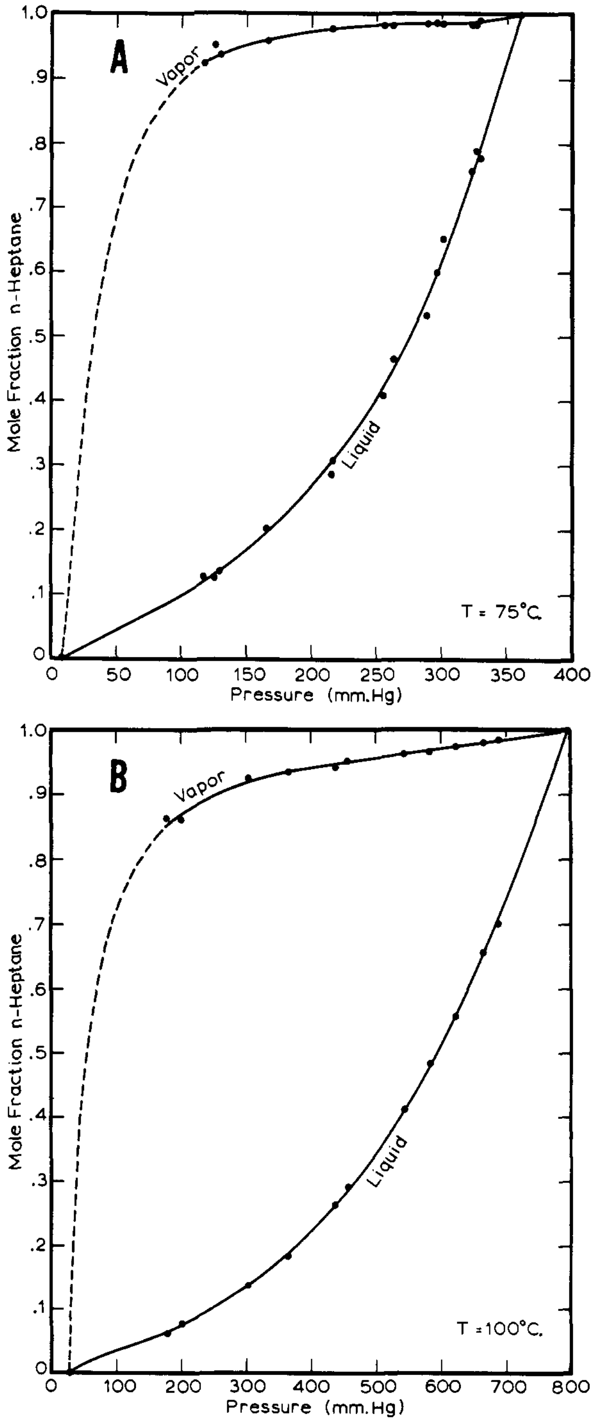


Figure 2. Pressure-composition relationship for the system *n*-heptane–*n*-valeric acid at *A* 75° and *B* 100° C.

Table III. Interpolated Equilibrium Values for the System n-Heptane–n-Valeric Acid at 75° and 100° C.

P, Mm. of Hg	x_p	y_p
	$T = 75°$ C.	
120	0.122	0.925
100	0.097	0.896
80	0.076	0.846
60	0.056	0.756
40	0.036	0.594
20	0.014	0.288
	$T = 100°$ C.	
180	0.064	0.853
160	0.056	0.831
140	0.048	0.804
120	0.041	0.771
100	0.034	0.719
80	0.027	0.650
60	0.020	0.535
40	0.010	0.300
30	0.002	0.081

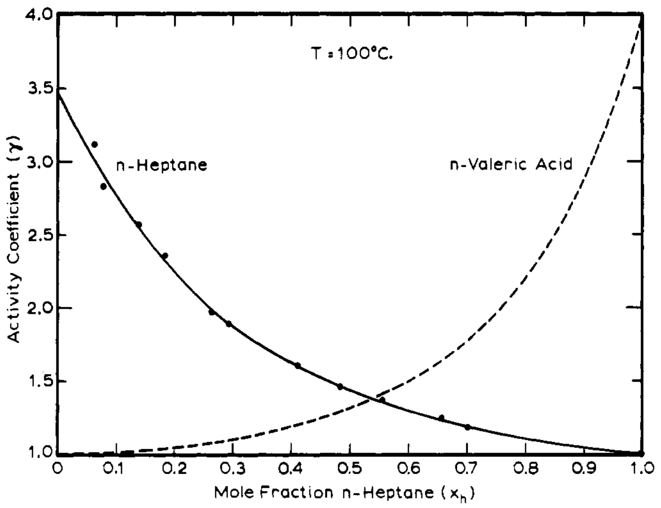


Figure 3. Liquid phase activity coefficients at 100° C.

Because heptane is much more volatile than valeric acid, precautions had to be taken to prevent loss of heptane during the sampling process. Since the still was operated at subatmospheric pressures, it was more desirable to increase the system pressure rapidly to atmospheric pressure just before taking samples. This rapid increase in pressure, made possible by the three-way valve in the vacuum line, immediately stopped the boiling in the still, thus preventing any further change in compositions. In addition, it reduced the danger of flashing off heptane when sampling at low pressures.

The liquid sample line was flushed with about 5 ml. of liquid and the vapor valve about 2 ml., as suggested by Hipkin and Myers (*3*), before samples were taken. The possibility of loss owing to evaporation was further reduced by keeping the sample flasks in ice during the sampling process.

Under ordinary operating conditions, the liquid level in the vapor condensate return line is higher than the level in the vaporizer, so the condensate is not contaminated by liquid from the vaporizer. Just prior to increasing the pressure in the system, it was necessary to close the three-way valve in the condensate arm in such a manner that it would prevent the condensate from being forced into the vaporizer. The condensate could then be withdrawn, while the vaporizer remained closed off to prevent contamination of the vapor sample.

Samples were analyzed with precision pycnometers of the type discussed by Lipkin *et al.* (*4*). The difference in densities of the pure components used in this investigation is 0.2551 gram per ml. making the probable experimental error encountered by this analysis method relatively small. Specific volume (reciprocal density) *vs.* composition data were then obtained (Table I) for samples of valeric acid and heptane compounded to known compositions. The results were plotted on an expanded coordinate system which enabled the experimental compositions to be read to ±0.1 mole %.

DISCUSSION OF RESULTS

Table II contains the experimental isothermal x, y, P equilibrium data obtained at 50°, 75° and 100° C. Figures 2,*A* and 2,*B* are plots of the 75° and 100° C. equilibrium data.

Because of excessive bumping in the equilibrium still vaporizer at high valeric acid concentrations and resultant entrainment of liquid into the contactor, the authors were unable to obtain experimental equilibrium data at the lower pressures. In order to draw a complete x, y, P diagram at 75° and 100° C., vaporization equilibrium constants (K-values) were calculated from the experimental data. Next, log K's were plotted against pressure, interpolated, and extrapolated to the vapor pressure of pure n-valeric acid. Dew point vapor compositions were then calculated using these K-values at pressures below the lower experimental limits. These vapor compositions are indicated as dashed lines on Figure 2. The calculated compositions in this range are contained in Table III.

Liquid phase activity coefficients for the n-heptane were calculated from the experimental data using Equation 2. Valeric acid activity coefficients were calculated from the n-heptane activity coefficients using Equation 4, where the integration was done graphically. Table II includes a tabulation of the activity coefficients at 50°, 75°, and 100° C. Figure 3 is a graph of liquid phase composition *vs.* the activity coefficients at 100° C.

NOMENCLATURE

f = fugacity
P = pressure
P^0 = vapor pressure
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
Z = compressibility factor for the gas mixture
$\bar{Z}$ = compressibility factor for a component in a gas mixture
γ = liquid phase activity coefficient
γ^0 = infinite dilution activity coefficient

Subscripts

a = acid monomer
p = paraffin

LITERATURE CITED

(1) American Petroleum Institute Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1953.
(2) Gilmont, R., *Ind. Eng. Chem., Anal. Ed.* **18**, 633 (1946).
(3) Hipkin, H., Myers, H.S., *Ind. Eng. Chem.* **46**, 2524 (1954).
(4) Lipkin, M.R., Davison, J.A., Harvey, W.T., Kurtz, S.S., Jr., *Ind. Eng. Chem., Anal. Ed.* **16**, 55 (1944).
(5) Perry, J.H., "Chemical Engineers Handbook," 3rd ed., p. 165, McGraw-Hill, New York, 1950.
(6) Pimentel, G.C., McClellan, A.L., "The Hydrogen Bond," p. 206 ff., H. Freeman and Co., San Francisco, 1960.
(7) Smith, J.M., Van Ness, H.C., "Introduction to Chemical Engineering Thermodynamics," 2nd ed., p. 381 ff., McGraw-Hill, New York, 1959.

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