TABLE III. VISCOSITY OF AMMONIA IN THE LIQUID PHASE

Pressure, Lb./Sq. Inch Absolute	40° F.	70° F.	100° F.	130° F.	160° F.	190° F.	220° F.
	(73.32)[a]	(128.8)	(211.9)	(330.3)	(492.8)	(708.9)	(989.5)
Bubble point	1880[b]	1592	1306	1028	748	488	[240][c]
200	1884	1595	.....	.....	....	.....	.....
400	1892	1603	1316	1030	....	.....	.....
600	1898	1611	1324	1038	754	.....	.....
800	1905	1618	1332	1044	762	492	.....
1000	1911	1624	1338	1051	772	503	[243][c]
1500	1924	1641	1362	1070	795	527	[274][c]
2000	1940	1656	1367	1088	822	551	304
2500	1954	1670	1380	1108	846	576	330
3000	1972	1684	1395	1127	870	600	355
3500	1987	1697	1410	1145	890	625	362
4000	3004	1712	1427	1163	910	650	390
5000	....	....	1460	1201	654	700	429
6000	....	....	....	....	1000	750	468

[a] Figures in parentheses represent bubble point pressures expressed in pounds per square inch.

[b] Viscosity expressed in micropoises.

[c] Figures in brackets involve added uncertainties.

(*14*) were used to establish the specific weight of ammonia at the states in question. The effect of temperature upon the viscosity of ammonia is relatively small in comparison to that for many liquids and is shown in Figure 8. In Figure 9 the measurements of Pinevich (*16*), Shatenshtein *et al.* (*26*), and Stakelbeck (*27*) at bubble point have been compared with the present measurements. It was possible to investigate the behavior of ammonia at temperatures above that of the critical state for pressures high enough to yield roll times of approximately 10 seconds. For short roll times the flow may be turbulent as indicated in Figure 6 and the accuracy of measurement is markedly decreased. In Table III is recorded the viscosity of ammonia in the liquid phase as a function of pressure and temperature. These data were smoothed from the experimental information submitted in Figures 7 and 8

ACKNOWLEDGMENT

These measurements were carried out with financial support from the Office of Naval Research. The assistance of R. F. Meldau in preparing the data in a form suitable for publication is acknowledged. W. N. Lacey reviewed the manuscript in detail.

NOMENCLATURE

A = dimensional coefficient of Equation 1
B = dimensional coefficient
η = absolute viscosity, micropoises
θ = roll time of ball, seconds
σ = standard deviation, Figure 5
σ_B = specific weight of ball, pounds per cubic foot
σ_f = specific weight of fluid, pounds per cubic foot

LITERATURE CITED

(1) Bridgeman, O. C., *J. Am. Chem. Soc.*, **49**, 1174–83 (1927).
(2) Fitzgerald, F. F., *J. Phys. Chem.*, **16**, 621–61 (1912).
(3) Flowers, A. E., *Proc. Am. Soc. Testing Materials*, **14**, II, 565–616 (1914).
(4) Henney, K., "Electron Tubes in Industry," p. 134, New York, McGraw-Hill Book Co., 1937.
(5) Hersey, M. D., *J. Washington Acad. Sci.*, **6**, 525, 628 (1916).
(6) Hersey, M. D., and Shore, H., *Mech. Eng.*, **50**, 221–32 (1928).
(7) Höppler, F., World Petroleum Congr. I, London, 1933, *Proc.*, Refining, Chemical, and Testing Section, **2**, 503–7 (1934).
(8) Hubbard, R. M., and Brown, G. G., IND. ENG. CHEM., ANAL. ED., **15**, 212–18 (1943).
(9) Kellström, G., *Phil. Mag.*, 7th Ser., **23**, 313–38 (1937).
(10) Kendall, B. H., and Sage, B. H., *Petroleum (London)*, **14**, 184–6 (1951).
(11) Keyes, F. G., *J. Am. Chem. Soc.*, **53**, 965–7 (1931).
(12) Kingsbury, A., Hersey, M. D., Duff, A. W., Dickenson, H. C., and Flowers, A. E., *Mech. Eng.*, **45**, 315 (1923).
(13) Nasini, A. G., and Pastonesi, G., *Gazz. Chim. Ital.*, **63**, 821–32 (1933).
(14) Natl. Bur. Standards (U. S.), *Circ.* **142** (1945).
(15) Phillips, P., *Proc. Roy. Soc. (London)*, **A87**, 48–61 (1912).
(16) Pinevich, G., *Kholadil Tekh.*, **20**, 30–7 (1948).
(17) Plank, C. J., and Hunt, H., *J. Am. Chem. Soc.*, **61**, 3590–1 (1939).
(18) Rankine, A. O., and Smith, C. J., *Phil. Mag.*, **42**, 601–14 (1921).
(19) Reamer, H. H., and Sage, B. H., IND. ENG. CHEM., **44**, 185–7 (1952).
(20) Rossini, F. D., "Selected Properties of the Lighter Hydrocarbons," New York, API, 1947.
(21) Sage, B. H., IND. ENG. CHEM., ANAL. ED., **5**, 261–3 (1933).
(22) Sage, B. H., and Lacey, W. N., IND. ENG. CHEM., **30**, 829–34 (1938).
(23) Sage, B. H., and Lacey, W. N., *Trans. Am. Inst. Mech. Engrs.*, **127**, 118–34 (1938).
(24) *Ibid.*, **174**, 102–20 (1948).
(25) Sage, B. H., Sherborne, J. E., and Lacey, W. N., IND. ENG. CHEM., **27**, 954–6 (1935).
(26) Shatenshtein, A. I., Izrailevich, E. A., and Ladyshnikova, N. I., *Zhur. Fiz. Khim.*, **23**, 497–9 (1949).
(27) Stakelbeck, H., *Z. Kälte-Ind.*, **40**, 33–40 (1933).
(28) Wobser, R., and Müller, F., *Kolloid-Beihefte*, **52**, 165–276 (1941).

RECEIVED for review April 29, 1952. ACCEPTED July 17, 1952.

Equilibria of Several Reactions of Aromatic Amines

G. N. VRIENS AND A. G. HILL
Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

IN THE study of the variables of a chemical process, with the object of improving the yield or conversion, the most important basic consideration is the distinction between those effects due to an equilibrium and those due to a rate process. Since this distinction is not always easy to make without an extended experimental investigation, it is of great practical interest to be able to calculate both the rate of a reaction and its equilibrium conversion from fundamental information. In the former case, progress has been slow; however, the determination and correlation of thermodynamic properties have proceeded to the point where it is now possible to predict reaction equilibria with considerable assurance. In this paper, previous calculations (*19*) have been revised and extended to include the thermodynamic properties of aniline, the *N*-methylanilines, the *N*-ethylanilines, and diphenylamine. The values obtained are summarized in Table I. The equilibrium conversions based on these data are then compared with experimental results for a number of reactions involving these compounds.

TABLE I. THERMODYNAMIC PROPERTIES OF AROMATIC AMINES AT 298° K.

	Aniline	MA[a]	DMA[b]	EA[c]	DEA[d]	DPA[e]
$\Delta H_c(l)$, kcal./mole	−810.5	−973.5	−1136.3	−1129.1	−1449.0	−1535.9
$\Delta H_f^0(l)$, kcal./mole	7.1	7.7	8.2	0.9	−3.9	31.5
$\Delta H_f^0(g)$, kcal./mole	19.7	20.4	20.1	13.4	9.6	48.2
ΔH_v, kcal./mole	12.6	12.7	11.9	12.5	13.5	16.7
Vapor pressure, mm.	0.70	0.47	0.75	0.40	0.20	0.0027
$S_f^0(l)$, e.u./mole	45.8	53.6	61.2	57.2	63.5	67.5
$S_f^0(g)$, e.u./mole	74.1	81.6	87.5	84.1	92.4	97.5
$\Delta S_f^0(l)$, e.u./mole	−94.5	−119.3	−144.3	−148.3	−207.1	−143.4
$\Delta S_f^0(g)$, e.u./mole	−66.2	−91.3	−118.0	−121.4	−178.2	−113.4
$\Delta F_f^0(l)$, kcal./mole	35.3	43.3	51.2	45.1	57.8	74.2
$\Delta F_f^0(g)$, kcal./mole	39.4	47.6	55.3	49.6	62.7	82.0

[a] *N*-Methylaniline.
[b] *N,N*-Dimethylaniline.
[c] *N*-Ethylaniline.
[d] *N,N*-Diethylaniline.
[e] Diphenylamine.

CALCULATED VALUES

HEATS OF FORMATION. Heats of combustion of monomethylaniline, dimethylaniline, and diethylaniline were taken from the compilation by Kharasch (*10*) and corrected to 25° C. His calculated values were deemed to be more accurate than the early experimental data, also given in his report, since more recent determinations of the heats of combustion of aniline (*2*) and monoethylaniline (*9*) have substantiated the calculated figures of Kharasch for those compounds. A comparison of the calculated and experimental heats of combustion is given in Table II. It may be seen that although more recent experimental results confirm the calculated values in the case of aniline and ethyl aniline, the reverse is true for diphenylamine. Apparently Kharasch's value for the bond energy of the second nitrogen–aromatic carbon bond is much less accurate than his values for the first nitrogen–aromatic carbon bond and for the nitrogen–aliphatic carbon bond.

TABLE II. COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF COMBUSTION

Compound	Calculated ΔH_c (*10*)[a]	Early Exptl. ΔH_c (*10*)	Recent Exptl. ΔH_c
		Kcal./mole	
Aniline	−810.7	−812.2	−810.5 (*2*)
N-Methylaniline	−973.5	−973.5	....
N,N-Dimethylaniline	−1136.3	−1142.7	....
N-Ethylaniline	−1129.8	−1121.5	−1129.1 (*9*)
N,N-Diethylaniline	−1449.0	−1451.6	....
Diphenylamine	−1543.2	−1537.2[b]	−1535.9[b] (*2*)

[a] Corrected to 298° K.
[b] Corrected to liquid state.

In the case of monoethylaniline, a sample was purified by: fractionation of a material of 98% purity, acetylation, crystallization of the acetyl derivative from petroleum ether to constant freezing point, hydrolysis, and vacuum distillation. The product assayed 99.5% and contained no aniline. Physical constants were as follows: refractive index, $n_D^{20} = 1.5542$, specific gravity at 25° C. = 0.9587. The heat of combustion of this sample was determined by H. M. Huffman to be 1129.1 kcal. per mole with a probable error of less than 1.0 kcal.

The heat of combustion of solid diphenylamine, 1531.9 kcal. per mole (*2*), was corrected to the liquid state by making use of the heat of fusion at the melting point and assuming a difference between the specific heats of the solid and liquid of 10 calories per mole degree, thus giving a value of 4.0 kcal. per mole for the heat of fusion of this compound at 298° K. The heats of formation of these various compounds in the liquid state were then determined from the heats of combustion using the National Bureau of Standards' values (*11*) for the heats of formation of carbon dioxide and water.

In order to obtain the heat of formation in the gaseous state, it was necessary to have available the heat of vaporization of each compound at 298° K. For this purpose vapor pressure data for aniline (*6*), the alkylanilines (*12*), and diphenylamine (*18*) were extrapolated down to room temperature by means of an equation of the following form,

$$\ln p = \frac{A}{T - 43} + B \tag{1}$$

The heat of vaporization may then be obtained from the following relationship,

$$\Delta H_v = RT^2 \frac{d\ln p}{dT} = \frac{-ART^2}{(T - 43)^2} \tag{2}$$

The values calculated for the vapor pressure equation constants of these amines are given in Table III and the heats of vaporization and vapor pressures, in Table I.

TABLE III. CONSTANTS IN VAPOR PRESSURE EQUATION

Compound	$A \times 10^{-3}$	B
Aniline	−4.66	17.91
N-Methylaniline	−4.69	17.63
N,N-Dimethylaniline	−4.40	16.96
N-Ethylaniline	−4.60	17.13
N,N-Diethylaniline	−4.97	17.87
Diphenylamine	−6.15	18.18

ENTROPIES OF FORMATION. The molar entropy of liquid aniline has been determined by Parks and Huffman (*13*) to be 45.8 ± 0.7 e.u. From this value, along with the heat of vaporization and vapor pressure obtained from Equations 1 and 2, the entropy in the perfect gas state at 1 atmosphere may be calculated to be 74.1 e.u. per mole. Since no entropy data for the alkylanilines were available, an approximate method had to be used to estimate this information. Aston *et al.* (*3–5*) have measured accurately the entropies of methylamine, dimethylamine, and trimethylamine in the perfect gas state at 1 atmosphere and found them to be 57.73, 65.24, and 68.91 e.u. (by extrapolation), respectively. If it is assumed that the changes in entropy on substituting the second and third methyl groups in the methylamines are the same as those on substituting the first and second methyl groups in the methylanilines, then the difference between the entropies of aniline and methylaniline and those of methylaniline and dimethylaniline in the perfect gas state at 1 atmosphere might be estimated to be 7.5 and 3.7 e.u., respectively. However, the rigid trimethylamine molecule has a symmetry number of 3, whereas that of the other molecules involved is 1. Hence, its entropy is lower than would otherwise be expected by the quantity R ln 3, or 2.2 e.u. Therefore, it is believed that 5.9 e.u. is a better value for the change in entropy on substituting a second methyl group in methylaniline, and this figure was used in estimating the entropies given in Table I. This procedure represents an application of the principle of group contributions (*1*), the accuracy of which depends on the number of steps and the quality of the data. Since the experimental values used are of a high order of accuracy and only one step was required, the results are believed to be correct to within 1 e.u.

A further approximation was necessary in order to obtain the entropies of the ethylanilines. Perry (*16*) gives the heat and free energy of formation of gaseous ethylamine as −12.24 and 10.01 kcal., respectively, from which the absolute entropy may be calculated as 60.18 e.u. Thus, the entropy change on substituting a methyl group for a hydrogen attached to the carbon of methylamine is 2.45 e.u. This quantity was added to the entropy of methylaniline to obtain the value for ethylaniline and was doubled and added to the entropy of dimethylaniline to get the figure given for the entropy of diethylaniline. Since the original source of the ethylamine data is not given in the reference cited, its accuracy cannot be judged and the correctness of the entropies calculated for the ethylanilines cannot be estimated. The liquid phase entropies of the alkylanilines were calculated from the perfect gas values using the vapor pressures and heats of vaporization given in Table I.

In order to obtain the entropy of diphenylamine, use was made of a different type of approximation. The entropy of solid aniline at 298° K. was first calculated by extrapolation of the specific heat data of Parks and Huffman (*13*), giving a figure of 35.1 ± 0.7 e.u. Since the entropy of solid triphenylamine is given as 73.0 e.u. (*15*), that of solid diphenylamine may be estimated at 54.1 e.u. by splitting the difference between solid aniline and triphenylamine. This type of assumption may be observed to be valid within experimental error in the case of the di-, tri-, and tetraphenylmethanes (*14*). In view of the accuracy of the aniline and triphenylamine values, it is believed that the entropy of diphenylamine is correct to within 1 e.u. The liquid and vapor state entropies of diphenylamine were calculated from the solid state value using the heats of fusion and vaporization and vapor pressure previously discussed. The National Bureau of Standards' values (*11*) for the entropies of the elements were used in calculating the entropies of formation of the compounds in Table I.

The methods of approximation employed in these calculations were chosen so as to make the best use of the available experimentally determined information. Any other methods would of necessity have been more empirical in nature and, hence, not to be preferred.

Table IV. Standard Energy Changes of Several Reactions of Aromatic Amines at 298° K.

Reaction	1[a]	2[b]	3[c]	4[d]	5[e]
$\Delta H^0(l)$, kcal.	−10.7	−10.8	−8.2	−6.8	...
$\Delta H^0(g)$, kcal.	−9.0	−10.0	−7.9	−5.4	−2.2
$\Delta S^0(l)$, e.u.	−5.8	−6.0	−10.3	−15.4	...
$\Delta S^0(g)$, e.u.	−4.2	−5.8	−12.3	−14.0	−4.7
$\Delta F^0(l)$, kcal.	−8.9	−9.0	−5.1	−2.2	...
$\Delta F^0(g)$, kcal.	−7.7	−8.2	−4.1	−1.2	−0.8

[a] $C_6H_5NH_2 + CH_3OH \longrightarrow C_6H_5NHCH_3 + H_2O$.
[b] $C_6H_5NHCH_3 + CH_3OH \longrightarrow C_6H_5N(CH_3)_2 + H_2O$.
[c] $C_6H_5NH_2 + C_2H_5OH \longrightarrow C_6H_5NHC_2H_5 + H_2O$.
[d] $C_6H_5NHC_2H_5 + C_2H_5OH \longrightarrow C_6H_5N(C_2H_5)_2 + H_2O$.
[e] $2C_6H_5NH_2 \longrightarrow (C_6H_5)_2NH + NH_3$.

Table V. Liquid Phase Ethylation of Aniline

Alcohol/aniline ratio	2.5	3.0	3.5
Composition of amine portion of product, mole %			
Aniline	2.7	0.9	0.8
Ethylaniline	34.2	28.7	24.1
Diethylaniline	48.1	60.2	70.5
High boilers	15.0	10.2	4.6
Equilibrium constants, K_c			
Ethylation of aniline	23	42	30
Ethylation of ethylaniline	2.5	2.7	2.9

Predicted Equilibria. The free energies of formation of the six aromatic amines at 298° K. were calculated from the heats and entropies of formation given in Table I and are also listed in Table I. Although these values are given as calculated to 0.1 kcal., they are probably only accurate to within 2 kcal. in most cases. The reactions of interest involving these compounds are the methylation of aniline and methylaniline with methanol, the ethylation of aniline and ethylaniline with ethyl alcohol, and the preparation of diphenylamine by the deamination of aniline. These reactions are tabulated in Table IV along with the standard enthalpy, entropy, and free energy changes at 298° K. for both the liquid and gas phases. The thermodynamic properties used for methanol, ethyl alcohol, water, and ammonia were taken from the selected values of the National Bureau of Standards (*11*).

Since the temperatures of interest in these reactions are considerably above 298° K., it was necessary to estimate the variation of these thermodynamic properties with temperature. The available specific heat data for both liquids and gases were examined, and the conclusion was reached that the difference in specific heat between the products and the reactants in each of these equations was zero, within the error of the data or of the best approximations when experimental results were not available. This conclusion is not unexpected when it is realized that in each case there is an equal number of molecules, with similar type bonds, on each side of the equation. Hence, the standard enthalpy and entropy changes of the reactions are essentially independent of temperature and the equilibrium constants may be represented by the equation.

$$\ln K_T = \frac{-\Delta H^0_{298}}{RT} + \frac{\Delta S^0_{298}}{R} \qquad (3)$$

According to Equation 3, then, the equilibrium constant for any of these reactions at any temperature may be calculated directly from the enthalpy and entropy values given in Table IV. Qualitatively speaking, it may be predicted from the standard free energy changes of Table IV that the methylation of aniline and methylaniline would be highly favored thermodynamically, that the ethylation of aniline would be somewhat less favorable, and that the remaining two reactions, the ethylation of ethylaniline and the preparation of diphenylamine, would be definitely limited by equilibrium considerations. The great difference in the thermodynamic completeness of the methylation of aniline as contrasted with its ethylation may largely be traced to the considerable difference in the entropy of methanol and ethyl alcohol (8 to 10 e.u.) as compared with the small difference found between the entropies of methyl- and ethylamine and ascribed to the alkylanilines.

EXPERIMENTAL EQUILIBRIA

Methylation of Methylaniline. The equilibrium constant for the methylation of methylaniline in the liquid phase at 200° C. may be calculated to be about 5000 from the data of Table IV. An experimental study of the liquid phase reaction by Shreve *et al.* (*17*) showed conversions of over 99% to be readily attainable. The equilibrium constant was too high to be measured accurately but was reported to be about 200. It may have been considerably higher than this figure if the impurity in the product were not entirely methylaniline as was assumed.

A study of the vapor phase preparation of dimethylaniline at higher temperatures by Hill *et al.* (*7*) indicated that conversions of over 92% to tertiary amine were possible. Since the remaining primary and secondary amines were shown to be largely ring-alkylated materials, rather than methylaniline, the equilibrium of reaction in the vapor phase is also found to be very favorable, in accordance with the predicted result.

Ethylation of Aniline and Ethylaniline. Calculations made from the data of Table IV indicate that the liquid phase ethylations of aniline and of ethylaniline at 200° C. have equilibrium constants of about 35 and 0.6, respectively. The results of a study of this reaction using varying ratios of alcohol to aniline, under conditions such that the reactions were essentially carried to completion, are shown in Table V. The reaction products were analyzed by fractional distillation. The quantities of water and alcohol present at the end of the reaction were calculated from the initial alcohol/aniline ratio and the composition of the amine product, assuming that the high boiling ring-alklyated amines contained 2 ethyl groups per molecule. The wide variance of the equilibrium constant for the ethylation of aniline is undoubtedly due to the difficulty in determining accurately small quantities of aniline. It is apparent that the ethylation of aniline is much more favorable thermodynamically than that of ethyl-

Table VI. Preparation of Diphenylamine

Feed Rate, Grams/Hour/100 Ml Catalyst	Conversion, % of Aniline Converted to DPA
16.0	19.4
8.8	29.1
4.4	33.5
4.4	57.4[a]
20.0	85.7[b]

[a] At beginning of run.
[b] Starting with diphenylamine and ammonia in mole ratio of 2 to 3.

Table VII. Comparison of Calculated and Experimental Equilibria

Reaction	Phase	Temp., ° C.	Calcd. K_T	Exptl. K_c
Methylation of methylaniline	Liquid	200	5000	>200
Ethylation of aniline	Liquid	200	35	30
Ethylation of ethylaniline	Liquid	200	0.6	2.7
Deamination of aniline to diphenylamine	Gas	450	0.44	0.5

aniline, in agreement with the predictions based on the thermodynamic properties.

In their experiments on the vapor phase ethylation of aniline, Hill *et al.* (*7*) also found the conversion to tertiary amine to be very much limited.

Preparation of Diphenylamine. The equilibrium conversion of aniline to diphenylamine at 450° C. may be calculated as 57% of theory from the data of Table IV. An experimental investigation of this reaction over an alumina catalyst at 450° C. has confirmed its reversible nature by the approach of the equilibrium position from both directions. The data, shown in Table VI, indicate an equilibrium conversion in the neighborhood of 60%. It is believed that the value of 57%, obtained during the first hour of a 40-hour run with the lowest space velocity, is very close to the equilibrium figure. Since the feed rate in the experiment starting with diphenylamine and ammonia was comparatively high, it seems certain that only a partial approach to equilibrium was attained in this run. The object of this experiment was merely to establish that an equilibrium existed, not to determine its exact position. In the case of this reaction, the agreement of theory and experiment is practically quantitative.

In a recent paper and correction (*8*) Hoelscher and Chamberlain reported a study of the vapor phase condensation of aniline to diphenylamine. Their thermodynamic calculations, made by a highly empirical method, at first indicated a favorable equilibrium but later were corrected to give a result very similar to that reported here. However, this agreement is somewhat fortuitous since their heats and entropies of reaction differ greatly from those of Table IV. It is felt that the values listed in Tables I and IV are accurate since they are based to the maximum extent on recent experimental data rather than on highly empirical methods of approximation.

COMPARISON OF PREDICTED AND EXPERIMENTAL EQUILIBRIA

A comparative summary of the predicted and experimental equilibria of the reactions which have been discussed is given in Table VII. In general, the agreement of prediction and experiment is surprisingly good and indicates that the thermodynamic properties of Table I are well within the stated error of ±2 kcal. This follows from the fact that a 2-kcal. change in the free energy will cause a several-fold change in the equilibrium constant.

In the case of the liquid phase reactions, it is to be expected that the activity coefficients of the components may differ significantly from unity and, hence, the thermodynamic equilibrium constant, based on activities, will differ from that based on concentrations. In the complete absence of data on activity coefficients under such conditions of temperature and pressure, it may best be assumed that the activity coefficients of the several amines are equal and those of the lower alcohols and water are similar, in which case they will tend to cancel out. In any event, deviations between calculated and experimental values from this cause will likely be much smaller than those caused by errors in the thermodynamic properties.

NOMENCLATURE

A, B = constants in vapor pressure equation
$\Delta F^0_f(g)$ = free energy of formation in the standard gas state (unit fugacity)
$\Delta F^0_f(l)$ = free energy of formation in the standard liquid state
$\Delta F^0(g)$ = standard free energy change of reaction referred to the gas state
$\Delta F^0(l)$ = standard free energy change of reaction referred to the liquid state
$\Delta H_c(l)$ = heat of combustion in the liquid state
$\Delta H^0_f(g)$ = heat of formation in the standard gas state
$\Delta H^0_f(l)$ = heat of formation in the standard liquid state
$\Delta H^0(g)$ = standard enthalpy change of reaction referred to the gas state
$\Delta H^0(l)$ = standard enthalpy change of reaction referred to the liquid state
ΔH_v = heat of vaporization
K_c = equilibrium constant in concentration units
K_T = thermodynamic equilibrium constant of reaction at temperature T
p = vapor pressure, in millimeters of mercury
R = Universal gas constant
$\Delta S^0_f(g)$ = entropy of formation in the standard gas state
$\Delta S^0_f(l)$ = entropy of formation in the standard liquid state
$S^0(g)$ = absolute entropy in the standard gas state
$\Delta S^0(g)$ = standard entropy change of reaction referred to the gas state
$S^0(l)$ = absolute entropy in the standard liquid state
$\Delta S^0(l)$ = standard entropy change of reaction referred to the liquid state
T = absolute temperature, in ° *K*.

LITERATURE CITED

(1) Andersen, J. W., Beyer, G. H., and Watson, K. M., *Natl. Petroleum News*, **36**, R476 (1944).
(2) Anderson, C. M., and Gilbert, E. C., *J. Am. Chem. Soc.*, **64**, 2369 (1942).
(3) Aston, J. G., Eidinoff, M. L., and Forster, W. S., *Ibid.*, **61**, 1539 (1939).
(4) Aston, J. G., Sagenkahn, M. L., Szasz, G. J., Moessen, G. W., and Zuhr, H. F., *Ibid.*, **66**, 1171 (1944).
(5) Aston, J. G., Siller, C. W., and Messerly, G. H., *Ibid.*, **59**, 1743 (1937).
(6) Garrick, F. J., *Trans. Faraday Soc.*, **23**, 560 (1927).
(7) Hill, A. G., Shipp, J. H., and Hill, A. J., Ind. Eng. Chem., **43**, 1579 (1951).
(8) Hoelscher, H. E., and Chamberlain, D. F., *Ibid.*, **42**, 1558 (1950); **43**, 1828 (1951).
(9) Huffman, H. M., private communication, 1941.
(10) Kharasch, M. S., *Bur. Standards J. Research*, **2**, 359 (1929).
(11) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., U. S. Department of Commerce, 1947–48.
(12) Nelson, O. A., and Wales, J., *J. Am. Chem. Soc.*, **47**, 867 (1925).
(13) Parks, G. S., and Huffman, H. M., "The Free Energies of Some Organic Compounds," p. 35, New York, Chemical Catalog Co., 1932.
(14) *Ibid.*, p. 90.
(15) *Ibid.*, p. 188.
(16) Perry, J. H., "Chemical Engineers' Handbook," p. 238, New York, McGraw-Hill Book Co., 1950.
(17) Shreve, R. N., Vriens, G. N., and Vogel, D. A., Ind. Eng. Chem., **42**, 791 (1950).
(18) Stull, D. R., *Ibid.*, **39**, 517 (1947).
(19) Vriens, G. N., Ph.D. thesis in chemical engineering, Purdue University, 1949.

Received for review September 13, 1951. Accepted August 6, 1952. Presented as part of the 16th Unit Process Symposium before the Division of Industrial and Engineering Chemistry at the 120th Meeting of the American Chemical Society, New York, N. Y.