The difference between the experimental composition and the composition calculated by means of Raoult's law ($\gamma_1 = \gamma_2 = 1$) is recorded for each data point in Table II. These differences are generally smaller than the estimated limit of experimental error in the composition (±0.005 mole fraction).

CONCLUSION

For the vapor-liquid equilibria at 1 atm. and within the experimental error stated previously, the benzene-alkylbenzene systems benzene-toluene, benzene-ethylbenzene, and benzene–*n*-propylbenzene obey Raoult's law.

NOMENCLATURE

A = a constant, Equation 6
B_{ij} = second virial coefficient for i–j interactions
C_i = a dimensionless correction for vapor phase imperfections
g^e = excess Gibbs free energy
h^e = excess enthalpy
P_i° = vapor pressure of pure i
P = pressure
R = gas constant
t = temperature, ° C.
T = temperature, ° K.
v_i^L = molar volume of pure liquid i
x_i = mole fraction of i in liquid phase
y_i = mole fraction of i in gas phase
α = relative volatility = $(x_1 y_2 / y_1 x_2)$
γ_i = activity coefficient of i in liquid phase

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Correlation of Some Thermodynamic Properties of Nitriles

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Available thermodynamic data for nitriles are partitioned and correlated to yield contributions to S° and ΔH_f° from several different types of groups in nitriles. These groups are formed to take account of possible perturbations of portions of the molecule by neighboring groups. Testing of these partitioned contributions for self-consistency, which is done wherever possible, shows that the correlations are satisfactory.

QUANTUM chemical theories must ultimately be tested against experimental information, or, as in the case of semi-empirical theories, they may require calibration with empirical data. In addition, it may be possible to formulate quantum chemical techniques analogous to the group contribution methods of thermodynamics. To date few if any attempts have been made to employ thermodynamic results for any of these purposes. In connection with work from this laboratory on the quantum chemistry of nitrogen compounds (*7-9, 11*), and in particular on the nature of the CN bond (*10*), accurate thermodynamic data on nitriles were required. The paucity of such information soon became apparent from an examination of the literature. Hence, the only convenient alternative was to resort to calculation of the required values by one of the many additivity methods. One of the best of such techniques is the "second-order" method of Benson and Buss (*1*), but unfortunately, only one of the group contributions listed by them contains a nitrile group. Therefore, the available values of the thermodynamic properties of nitriles were used to attempt to complete the group contribution terms given for nitriles by Benson.

METHOD

The best available data which was employed in this work is listed in Table I. In the case of most of the compounds, the results given are the only data available for the gas phase. In some cases, such as that of malononitrile and succinonitrile, older data are available and are referred to in the references. In all cases, the most recent data have been taken as the best available, since the previous results are usually much older, sometimes having been obtained in the nineteenth century. Reliability of data is not always directly related to its age, of course, as can be seen by noting the comparisons made with some of the older data (*3*). Hence, wherever necessary, comparisons of experimental methods were made. This paper will deal with the gas phase at 298.16° K. only.

The method of Benson and Buss was then applied to each of the nitriles in succession. However, to do this, an appropriate partitioning of the nitriles into new groups, some which had not been considered by Benson, was required. The first group contribution which appeared to be appropriate for consideration was that of C_t—$(N_t)(C)$, which, in Benson's notation, is that for the carbon atom of the nitrile group, where the nitrile group carbon is attached to a single bonded carbon atom. C_t and N_t refer to triple bonded carbon and nitrogen atoms, respectively. Then acetonitrile is composed of one C_t—$(N_t)(C)$ group and one C—$(H)_3(C_t)$ group, the contributions of which must be summed.

A symmetry correction of $-R \ln 3 = -2.2$ is then applied to the entropy term for acetonitrile. The term y, which

Table I. Observed Data for Nitriles in the Gaseous State at 298.16 °K.

Compound	C_p°, Cal. Mole^{-1} Deg.$^{-1}$	S°, Cal. Mole^{-1} Deg.$^{-1}$	ΔH_f°, Kcal. Mole^{-1}	Ref.
Cyanogen			73.6	(*15*)
Acrylonitrile			43.7	(*6*)
Tricyanoethylene (Tri-CNE)			123.9	(*2*)
Tetracyanoethylene (TCNE)			168.5	(*2*)
7,7,8,8-tetracyano-quinodimethan (TCNQ)			184.0	(*2*)
Succinonitrile		79.04	54.42	(*12, 17*)
Glutaronitrile		88.1		(*4*)
Acetonitrile	12.51	58.20	21.0	(*5, 14*)
Dimethylmalononitrile		83.42		(*13*)
Trimethylacetonitrile		76.63		(*16*)
Malononitrile			63.5	(*3*)
Fumaronitrile			81.3	(*3*)

is the contribution of the group $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ to the entropy s°, is then 29.99. The process may then be repeated for the other nitriles in which the $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ appears. Table II shows the results of this calculation.

Apparently, the results given in Table II show that, at least for the molecules shown, the amount contributed to the entropy by the group $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ is constant to a high accuracy. Hence, the selection of this group as a primary one appears to be supported.

Examination of the contribution of the group $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ to the heat of formation, ΔH_f°, for each of the compounds given in Table II would be of interest. Unfortunately, however, values of the heat of formation are not available for all these compounds, and only succinonitrile, acetonitrile, and malononitrile may be considered for purposes of evaluating contributions of $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ to the heat of formation.

The decomposition of these compounds into groups may be accomplished in the following way. Succinonitrile is composed of two $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ groups and two $\mathrm{C}\text{—}(\mathrm{H}_2)(\mathrm{C})(\mathrm{C}_t)$ groups. Hence, one may write

$$[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})] + [\mathrm{C}\text{—}(\mathrm{H}_2)(\mathrm{C})(\mathrm{C}_t)] = 27.21 \qquad (1)$$

and consider this as the group D. Acetonitrile may then be decomposed into

$$D + [\mathrm{C}\text{—}(\mathrm{H}_3)(\mathrm{C}_t)] - [\mathrm{C}\text{—}(\mathrm{H}_2)(\mathrm{C})(\mathrm{C}_t)] = 21.0 \qquad (2)$$

The latter group will be referred to as E and is one already listed by Benson as contributing −5.2 kcal. mole^{-1} to the heat of formation. Hence, from acetonitrile, the contribution of group D to the heat of formation is 26.2 kcal. mole^{-1}, to be compared with 27.21 kcal. mole^{-1} as obtained from succinonitrile. Because the succinonitrile data is presumably more accurate, the latter value was employed in subsequent calculations. Malononitrile may then be decomposed as

$$2D + [\mathrm{C}\text{—}(\mathrm{H}_2)(\mathrm{C}_t)_2] - 2[\mathrm{C}\text{—}(\mathrm{H}_2)(\mathrm{C})(\mathrm{C}_t)] = 63.5 \qquad (3)$$

where the latter group is labeled as M. M apparently contributes 9.08 kcal. mole^{-1} to the heat of formation. Unfortunately, Benson does not list the group M in his data.

Table II. Contribution of the Group $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$ to the Entropy in Various Nitriles

Nitrile	ΔS°, Cal. Mole^{-1} Deg.$^{-1}$, from $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C})$
Acetonitrile	29.99
Succinonitrile	30.15
Glutaronitrile	29.92
Dimethylmalononitrile	29.95
Trimethylmalononitrile	30.00
Average	30.00

Those nitriles of Table I which contain a double-bonded carbon atom may be employed to determine a group contribution to ΔH_f° for the group $\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)$ where C_d refers to a double-bonded carbon atom. This is illustrated by an examination of TCNE and Tri-CNE. The former contains four of the basic groups $[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)]$ and two of the basic groups $[\mathrm{C}_d\text{—}(\mathrm{C}_t)_2(\mathrm{C}_d)]$. Hence, there appear to be two unknowns in the equation for ΔH_f° for TCNE. On the other hand, Tri-CNE contains three of $[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)]$, one of $[\mathrm{C}_d\text{—}(\mathrm{C}_t)_2(\mathrm{C}_d)]$, and one of $[\mathrm{C}_d\text{—}(\mathrm{H})(\mathrm{C}_t)(\mathrm{C}_d)]$, a total of three unknowns. The two algebraic equations derived for TCNE and Tri-CNE are, of course, insufficient to allow for solution. However, the problem may be solved by forming the group

$$2[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)] + [\mathrm{C}_d\text{—}(\mathrm{C}_t)_2(\mathrm{C}_d)]$$

By inspection, TCNE is composed entirely of only two of the above groups. Hence, the contribution of this group to ΔH_f° is exactly half the value of ΔH_f° for TCNE after the cis correction of Benson has been subtracted. The contribution of $2[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)] + [\mathrm{C}_d\text{—}(\mathrm{C}_t)_2(\mathrm{C}_d)]$ to ΔH_f° is therefore 83.75 kcal. per mole.

In the same way, Tri-CNE is composed of one of the groups $2[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)] + [\mathrm{C}_d\text{—}(\mathrm{C}_t)_2(\mathrm{C}_d)]$ and one of a new group $[\mathrm{C}_t\text{—}(\mathrm{N}_t)(\mathrm{C}_d)] + [\mathrm{C}_d\text{—}(\mathrm{H})(\mathrm{C}_t)(\mathrm{C}_d)]$ plus one cis correction. If these two groups are labeled A and B, respectively, then

$$A + B + 0.50 = 123.9 \qquad (4)$$

Consequently the contribution of group B to ΔH_f° is 39.65 kcal. per mole.

This correlation may be tested on fumaronitrile which consists of two groups B plus correction of −0.50 kcal. mole^{-1} for a trans isomer. The estimated value of ΔH_f° for fumaronitrile is 78.8 kcal. mole^{-1}, to be compared with the observed value of 81.3 kcal. per mole. Similarly, the estimated value for acrylonitrile is 45.90 kcal. mole^{-1}, compared with an observed value of 43.7 kcal. per mole.

It thus appears preferable to consider the four compounds Tri-CNE, TCNE, fumaronitrile, and acrylonitrile together, and in so doing to obtain an average value for the contribu-

Table III. Comparison of Calculated and Observed Values of ΔH_f° for Some Nitriles

	ΔH_f°, Calcd.	ΔH_f°, Obsd.
Acrylonitrile	45.6	43.7
Tri-CNE	123.6	123.9
TCNE	168.5	168.5
Fumaronitrile	78.2	81.3

Table IV. Groups and Their Contributions to Thermodynamic Properties in Nitriles

	Contribution	
Group	S°, Cal. Mole^{-1} Deg.$^{-1}$	ΔH_f°, Kcal. Mole^{-1}
$C_t—(N_t)(C)$	30.00	...
$[C_t—(N_t)(C)] + [C—(H_2)(C)(C_t)]$	...	27.21
$[C—(H_2)(C_t)_2] - 2[C—(H_2)(C)(C_t)]$	...	9.08
$2[C_t—(N_t)(C_d)] + [C_d—(C_t)_2(C_d)]$	...	83.75
$[C_t—(N_t)(C_d)] + [C_d—(H)(C_t)(C_d)]$	...	39.33

tion of group *B* to ΔH_f°, which was 39.33 kcal. per mole. The results of using this value are shown in Table III.

The values given for the calculated and observed values of ΔH_f° for TCNE are the same. This agreement results, of course, from the fact that the contribution of group *A* was determined from the observed value of ΔH_f° for TCNE, which is composed entirely of two of these *A* groups. The correlation is not as satisfactory as that given in Table II, but nevertheless, the estimated values agree to 3% or better with the observed values. That the correlation is less satisfactory in Table III than in Table II may be attributed to various possible causes. Since there is no reason to suspect that ΔH_f° values will be inherently less reliable than s° values, it does not seem reasonable to suggest this as a major factor. However, all compounds in Table III have been decomposed into one or more groups, to each of which is assigned a contribution to ΔH_f°. In addition, all groups contain at least two of the type of group found in Table II. Hence, it may well be that the numbers assigned to the group contributions are in error by a factor of two or more when compared with the simpler groups of Table II. However, the most intriguing possible explanation of the difference in correlation errors relates to a difference in the nature of the molecules of Table II and those of Table III. The molecules of Table II are largely composed of bonds with which localized electrons are usually associated, while a substantial amount of delocalization of electrons can reasonably be attributed to the molecules of Table III. It is not unreasonable to suggest that such delocalization over the entire molecular framework may render partitioning less accurate than in the case of localized bonds.

CONCLUSION

A satisfactory correlation of heats of formation and absolute entropies of nitriles was obtained by employing the groups and values listed in Table IV.

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Sulfur–Naphthalene–*n*-Octadecane System

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Phase equilibria in a ternary system consisting of molten sulfur, naphthalene, and *n*-octadecane were investigated at 113° C. Experimental data were obtained by infrared absorption measurements. The phase diagram indicates that, contrary to recent literature, molten sulfur is quite selective when considered as a solvent with respect to the other two components. The direction of the tie lines indicates that naphthalene can be preferentially extracted by molten sulfur from a mixture of the two hydrocarbons.

THIS study was undertaken in an effort to establish whether molten sulfur can exhibit any selectivity toward one hydrocarbon over another one in a ternary system. A recent paper (*2*), reporting phase diagrams of 15 ternary systems of elemental sulfur, concludes that in every case tried, all tie lines pointed directly toward the sulfur corner, indicating that in all of these systems, molten sulfur is characterized by a complete lack of solvent selectivity. The present investigation deals with a ternary system of sulfur, naphthalene, and *n*-octadecane—that is, a system which, although not identical, is very similar to that represented by phase diagram 11 in reference (*2*). Although the general shapes of the solubility curves are quite alike in both cases, the directions of the tie lines are not. This gives rise to the new conclusions concerning the selectivity of molten sulfur presented in this paper.