ment of the observed with the results computed by equations (1) to (4) is good. A more detailed illustration of the calculation is shown in Fig. 1 in which the diffusion coefficient is plotted against the concentration in moles per liter. The curve at the top represents the complete calculation according to equations (1) to (4) while the bottom curve is the graph of equation (5). The solid graph in the center is the plot of equation (1) when $(\overline{\mathfrak{M}}/c)$ is constant and equal to its value when c equals zero. Under this condition equation (1) becomes

$$\mathfrak{D} = 7.437 \times 21.097 \times 10^{-7}\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (6)$$

The difference between the graph of this equation and the top curve in Fig. 1 represents the calculated effect of electrophoresis.

The dashed graph, drawn through the experimental results, exhibits a maximum deviation from theory of 0.4%. It appears that the two results at 0.0025 molar concentration are low. In any case, when the complicated nature of the calculation is considered, good concordance with the theory is obtained. Further, the results confirm the essential correctness of the electrophoretic terms.

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The Solubility of Aromatic Hydrocarbons in Water

BY E. F. G. HERINGTON

In a recent paper under the above title Bohon and Claussen[1] have described the determination of the solubility of various aromatic hydrocarbons including benzene, toluene, ethylbenzene, *m*- and *p*-xylene in water for the temperature range 0–40°. The partial molar heats of solution ($\Delta\bar{H}_{\text{sol}}$) were calculated by the aid of equation 1 where m is the molar solubility and R and T have their usual significance.

$$\Delta\bar{H}_{\text{sol}} = RT^2[\mathrm{d}(\ln m)/\mathrm{d}T] \quad (1)$$

The authors state that, "Since the process of solution of the hydrocarbon into water can be considered an isothermal equilibrium reaction, the free energy change is zero and the entropy of solution, $\Delta\bar{S}_{\text{sol}}$, is given by $\Delta\bar{S}_{\text{sol}} = \Delta\bar{H}_{\text{sol}}/T$." The large variation of the quantity $\Delta\bar{H}_{\text{sol}}$ with temperature and the values of $\Delta\bar{S}_{\text{sol}}$ found in this manner were examined in terms of the possible nature of the aqueous solutions.

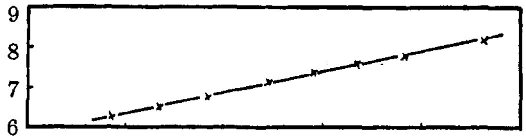
Since the solution of a hydrocarbon in water is in fact accompanied by a free energy change and since Bohon and Claussen's choice of the liquid hydrocarbon as a standard state is not a very convenient one for the discussion of the nature of the aqueous solutions because the liquid hydrocarbons themselves exhibit some structure,[2] the experimental data have been examined on a different basis. The treatment adopted follows that developed by Butler[3] and the thermodynamic quantities ΔF, ΔS and ΔH have been calculated from the experimental results by means of equations 2, 3 and 4 where p is the vapor pressure of the hydrocarbon in mm., and N is the mole fraction of the hydrocarbon in solution.

$$\Delta F = RT\ln(p/N) \quad (2)$$

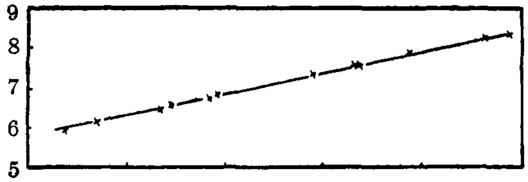
$$\Delta S = -[\mathrm{d}\Delta F/\mathrm{d}T] \quad (3)$$

$$\Delta H = \Delta F - T[\mathrm{d}\Delta F/\mathrm{d}T] \quad (4)$$

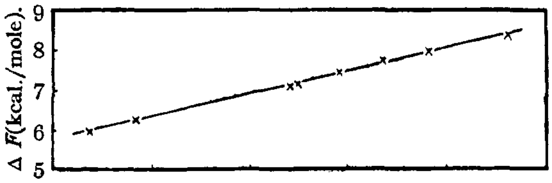
The quantity ΔF is the free energy of hydration[4] and is equal to the difference between the molar free energy of the hydrocarbon in the standard state referred to the infinitely dilute aqueous solution and at 1 mm. pressure in the vapor while ΔS and ΔH are the corresponding entropy and heat terms. Hildebrand[5] has recently re-emphasized the importance of adopting a constant pressure of the vapor as the standard state of the solute for the discussion of the structure of solutions. The vapor pressures of liquid benzene, toluene, ethylbenzene, *m*- and *p*-xylene were calculated from the Antoine equation using the accurate data for these compounds presented by the A.P.I.



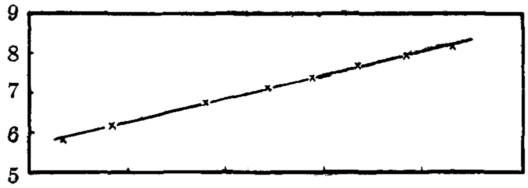
Benzene.



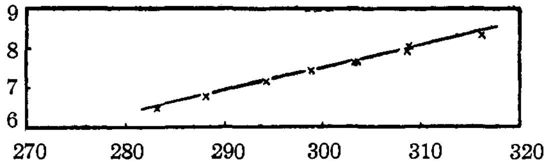
Toluene.



Ethylbenzene.



m-Xylene.



p-Xylene.

Fig. 1.—Free energy of hydration, ΔF, plotted against the temperature, T, in degrees absolute.

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[1] Bohon and Claussen, THIS JOURNAL, **73**, 1571 (1951).

[2] Herington, *Trans. Faraday Soc.*, **40**, 481 (1944).

[3] Butler, "Chemical Thermodynamics," 4th ed. (1 Vol.), The Macmillan Co., London, 1946, p. 389.

[4] ΔF is the Gibbs free energy change and is represented in Britain by the symbol ΔG.

[5] Hildebrand, *J. Phys. Colloid Chem.*, **53**, 973 (1949).

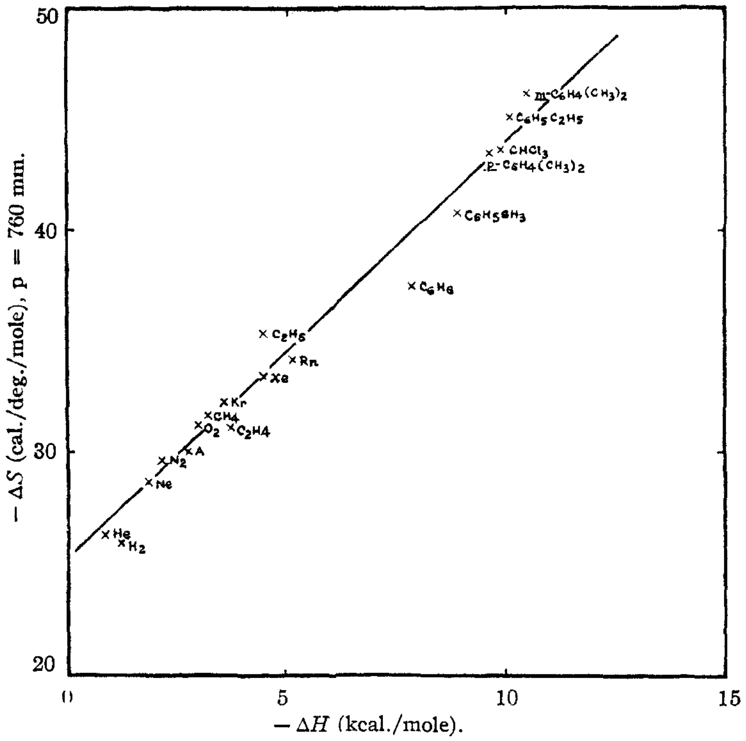

Fig. 2.— $-\Delta S$ plotted against $-\Delta H$ for a number of non-polar substances. All values refer to 25°.

project.[6] In some instances the vapor pressures so calculated involved an extrapolation of the observed data.

Figure 1 shows that the relationship between ΔF and ΔT can be represented by a straight line for each hydrocarbon and hence the values of ΔS and ΔH are almost temperature independent in the range 0 to 40°. This observation indicates that the variation of $\Delta \bar{H}_{\text{sol}}$ (equation 1) with temperature arises from the adoption of the liquid hydrocarbon as the standard state and is not to be ascribed to any property of the aqueous hydrocarbon solution. The values of $-\Delta H$ and $-\Delta S(p = 1$ mm.) given in Table I were obtained from the slopes of the lines shown in Fig. 1. Column 4 of this table lists the entropy changes when a standard state of $p = 760$ mm. is chosen for the hydrocarbon vapor.

Table I

Hydrocarbon	$-\Delta H$, kcal./mole	$-\Delta S(p = 1$ mm.), cal./deg./mole	$-\Delta S(p = 760$ mm.), cal./deg./mole
Benzene	7.83	50.7	37.5
Toluene	8.85	54.1	40.9
Ethylbenzene	10.03	58.4	45.2
m-Xylene	10.40	59.5	46.3
p-Xylene	9.60	56.9	43.7

In Fig. 2 the values of $-\Delta H$ are plotted against $-\Delta S(p = 760$ mm.) for the above compounds together with those for the rare gases and for hydrogen, nitrogen, oxygen, methane, ethane, ethylene and chloroform at 25° quoted by Frank and Evans.[7] The points for the aromatic hydrocarbons follow closely the straight line connecting the $-\Delta S$ and $-\Delta H$ values for the other non-polar substances, but there is however a marked difference between the reported temperature dependence of ΔS for the rare gases and that of the aromatic hydrocarbons. Frank and Evans[7] present a plot of $-\Delta S(p = 760$ mm.) against T for the rare gases in the temperature range 0–100° which shows that $-\Delta S$ may have a big temperature coefficient and that for a large atom such as radon in water the partial molar heat capacity exceeds 60 cal./deg./mole. The temperature coefficient of ΔS for these aromatic hydrocarbons is zero within experimental error (see Fig. 1) although these molecules are undoubtedly larger than the radon atom. If the high partial molar heat capacity which has been reported for radon in water is to be attributed to "iceberg" formation[7] then the results for the aromatic hydrocarbons discussed here show that these compounds do not form "icebergs."

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[6] A.P.I.–N.B.S. project 44, Table 5k.

[7] Frank and Evans, *J. Chem. Phys.*, **13**, 507 (1945).

Synthesis of 3,4-Difluorophenylarsonic Acid

By Arthur F. Helin and Calvin A. VanderWerf

As part of our program on the synthesis and testing of fluorine containing compounds of pharmacological interest, we have synthesized 3,4-difluorophenylarsonic acid, an analog of stovarsol. Several projected routes for the preparation of the critical intermediate, 3,4-difluoroaniline, were explored. In one of these p-fluoroaniline was nitrated in good yield to give 3-nitro-4-fluoroaniline, which, after acetylation, was hydrogenated catalytically to 3-amino-4-fluoroacetanilide. Attempted conversion of this product to 3,4-difluoracetanilide *via* the Schiemann reaction was, however, unsuccessful because of the rapid decomposition of the diazonium fluoborate to yield an intractable tar. This fact is in line with the general observation[1] that the presence of amino group lowers the yields obtained in the decomposition of diazonium fluoborates.

Preparation of 3,4-difluoronitrobenzene by means of the Schiemann reaction as applied to 2-fluoro-5-nitroaniline was likewise thwarted by the fact that the diazonium fluoborate decomposed explosively with extensive carbonization when warmed even slightly. The sweet-tasting 2-fluoro-5-nitroaniline used as an intermediate was obtained by selective reduction of the 2-nitro group in 2,4-

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[1] A. Roe in Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 206.