$$z = ae^{+(k_3a/m)e^{-mt}}\Big[(1 - e^{-mt}) - \frac{k_3a}{m}(1 - e^{-2mt}) + \frac{k_3^2a^2}{2m^2}(1 - e^{-3mt}) - \frac{k_3^3a^3}{6m^3}(1 - e^{-4mt}) + \ldots - \frac{k_1}{m+n}(1 - e^{-(m+n)t}) + \frac{k_3a}{2m+n}\left(1 + \frac{k_1}{m}\right)(1 - e^{-(2m+n)t}) - \frac{k_3^2a^2}{m(3m+n)}\left(1 + \frac{k_1}{2m}\right)(1 - e^{-(3m+n)t}) + \ldots\Big]$$

where $m = k_1 + k_3b$ and $n = k_2b$. The specific chemical rate is given by $k_1 + k_3b$. k_2 has been evaluated from the experiment on the exchange of the chlorine on the nitrogen of the chloroamine.

The fraction of chloride ion in solution which is radioactive is given by $[b-(w + z)]/b$. This obviously depends upon the values chosen for k_1 and k_3. If we choose $k_1 = 0.0136$ and $k_3b = 0.0180$ we get curve 4 in Fig. 3 which agrees well with the experimental data. The values of the rate constants chosen above correspond to 43% of the acetylchloroaminobenzene rearranging *intramolecularly* and 57% disappearing through the *chlorine intermediate* path. It is quite likely that changes in the experimental conditions would change not only the actual values of these three rate constants but also the relative amounts going by the two paths.

By calculating, according to the combined mechanisms of the preceding paragraph, $z/(y + z)$ for $t = 30$ minutes we obtain the value, 48.2%. The experimental value of this quantity, taken from Table II, is 40.5%. Considering the inaccuracies of this particular determination we feel that the check is sufficiently close.

In all of this work we must not overlook the fact that we are placing a heavy burden on the single determination of k_2. However, calculations show that a 100% change in the value of this rate constant will not affect our conclusions materially.

Summary

The rearrangement of ordinary acetylchloroaminobenzene has been induced by the action of radioactive hydrochloric acid.

The time rates of change of the percentages of radioactivity in the products have been measured. The rate with which the chlorine on the nitrogen of acetylchloroaminobenzene interchanges with the chloride ion in solution also has been measured.

For these measurements it has been shown that under the conditions of this experiment the rearrangement of acetylchloroaminobenzene does not proceed exclusively either by an intramolecular rearrangement or by a chlorine intermediate.

A combination of these two mechanisms, with 43% of the reaction going by direct rearrangement, and 57% through a chlorine intermediate, will explain all our results.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OHIO STATE UNIVERSITY]

Vapor Pressures of Saturated Solutions

BY ALFRED E. HIRSCHLER

Roehl[1] has pointed out the interesting fact that when all the scanty available data on vapor pressures of saturated aqueous salt solutions are plotted as log P against $1/T$, straight lines are obtained which are all parallel to the water curve. He was unable to offer an explanation for this "unexpected" result.

While this fact does seem somewhat surprising at first sight, it is the purpose of this paper to show that a closer scrutiny reveals that this is just what would be expected from the magnitudes of the heat effects involved.

The change in fugacity of water from a continuously saturated solution of a solid solute as the temperature rises is given by the equation[2a]

$$\mathrm{d}\ln f_1/\mathrm{d}T = (H_1^* - \overline{H}_1)/RT^2 + N_2(H_2' - \overline{H}_2)/N_1RT^2 \tag{1}$$

where f_1 is the fugacity of water from the solution, H_1^* the molal heat content of attenuated water vapor, H_2' the molal heat content of the solid salt, $\overline{H}_1$, N_1 and $\overline{H}_2$, N_2 the partial molal heat contents and mole fractions of water and solute, respectively. In this equation and those to follow, constant pressure is assumed. We may choose pure liquid water, and an infinitely dilute

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[1] Roehl, THIS JOURNAL, **58**, 1291 (1936).

(2) (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, 1923, p. 220; (b) p. 222; (c) p. 201; (d) p. 92; (e) p. 477.

aqueous solution as standard states for solvent and solute, respectively, and represent the corresponding molal heat contents by H_1^0 and H_2^0. We then have

$$\begin{aligned} \mathrm{d}\ln f_1/\mathrm{d}T &= [(H_1^* - H_1^0) - (\overline{H}_1 - H_1^0)]/RT^2 + \\ &\quad N_2[(H_2' - H_2^0) - (\overline{H}_2 - H_2^0)]/N_1RT^2 \\ &= (\Delta H_\mathrm{i} - \overline{L}_1)/RT^2 + N_2(L_2' - \overline{L}_2)/N_1RT^2 \end{aligned}$$

where ΔH_i is the molal heat of vaporization of water into a vacuum (the so-called ideal heat of vaporization), and $\overline{L}_1$, $\overline{L}_2$ and L_2' are the relative heat contents of the substances involved. Rearranging slightly

$$\begin{aligned} \mathrm{d}\ln f_1/\mathrm{d}T &= \Delta H_\mathrm{i}/RT^2 - (N_1\overline{L}_1 + N_2\overline{L}_2 - N_2L_2')/N_1RT^2 \\ &= \Delta H_\mathrm{i}/RT^2 - (L - N_2L_2')/N_1RT^2 \qquad (2) \end{aligned}$$

where L is the relative heat content of one mole of the solution.

Now, $L - N_2L_2'$ is the total or integral heat of solution involved in the formation of one mole of the saturated solution. The mole fraction is numerically equal to the number of moles of each substance taken. Using sodium chloride as an example, we may write

$$N_2\,\mathrm{NaCl(s)} + N_1\mathrm{H_2O(l)} = 1 \text{ mole saturated solution}$$

The integral heat of solution is the value of $\Delta H_\mathrm{s} = \Delta L$ for this process, where the symbol ΔH_s represents the heat absorbed in the formation of one mole of the saturated solution from its components.

$$\Delta H_\mathrm{s} = \Delta L = L - N_2L' - N_1L_1 = L - N_2L$$

since L_1 for the liquid water is zero by choice of standard state.

Hence

$$\mathrm{d}\ln f_1/\mathrm{d}T = (\Delta H_\mathrm{i} - \Delta H_\mathrm{s}/N_1)/RT^2 \qquad (3)$$

The corresponding equation for pure water is[2c]

$$\mathrm{d}\ln f_1/\mathrm{d}T = \Delta H_\mathrm{i}/RT^2 \qquad (4)$$

These equations are exact. For practical purposes they may be modified slightly. Assuming water vapor to be a perfect gas, we can replace the fugacity by the vapor pressure, and the latter by the total pressure P if the solute is not appreciably volatile. At the same time, to be consistent, we may replace the ideal heat of vaporization by that ordinarily determined.[3] Then

$$\mathrm{d}\ln P/\mathrm{d}T = (\Delta H - \Delta H_\mathrm{s}/N_1)/RT^2 \qquad (5)$$

$$\mathrm{d}\ln P/\mathrm{d}T = \Delta H/RT^2 \qquad (6)$$

If we plot log P against $1/T$ for equations (5) and (6), the plot in each case should be a straight line of slope $-(\Delta H - \Delta H_\mathrm{s}/N_1)/2.303R$ in the case of equation (5) and of slope $-\Delta H/2.303R$ for equation (6).

It is now obvious that if the term $\Delta H_\mathrm{s}/N_1$ is small compared to ΔH, the vapor pressure curves of saturated solution and pure solvent will be nearly parallel, the more nearly so the smaller the integral heat of solution. For a solution of a non-volatile solid which forms a perfect solution the two curves should be exactly parallel, as the heat of solution is then zero.[2b]

For most aqueous salt solutions, N_1 is not far from unity, so that the magnitude of ΔH_s practically determines the size of the correction factor, the solubility having small effect. Further, the heat effect in forming one mole of solution must always involve less than 18 g. of water. Since most heats of solution, expressed in terms of 1000 g. of water, are much smaller than the heat of vaporization of water, it can be seen that $\Delta H_\mathrm{s}/N_1$ usually will be quite small compared to ΔH.

This conclusion may be illustrated by a specific example. The necessary heat quantities for sodium chloride, one of the cases cited by Roehl, have been determined.[2d] The saturated solution is 6.12 *m* at 25° $\overline{L}_1 = 11.5$ cal., $\overline{L}_2 = -702$ cal., $L' = -1019$ cal., $N_1 = 0.9007$ and $N_2 = 0.0993$.

$$\Delta H_\mathrm{s} = N_1\overline{L}_1 + N_2\overline{L}_2 - N_2L' = 42.6 \text{ cal.}$$

$$\Delta H_\mathrm{s}/N_1 = 47.3 \text{ cal.}$$

We may take the molal heat of vaporization of water at 25° as 10,450 cal.[2e] The difference in slope of the vapor pressure curves for pure water and for saturated solution at 25° should thus only differ by 47.3/10,450, or 0.45%, which is less than the usual experimental error.

In the foregoing discussion it has been assumed that ΔH and ΔH_s are independent of temperature. This is only true as a first approximation. ΔH at 100° is 9730 cal.[2e] While exact data on ΔH_s are lacking, it is known that in general solutions become more ideal as the temperature is raised, so that we would expect ΔH_s to decrease also. The percentage deviation of the slopes of the vapor pressure curves might well remain sensibly constant up to the boiling point of the solution.

Sodium chloride may be taken as typical of a strong electrolyte in aqueous solution. The heats of solution of many electrolytes will be found to be of the same order of magnitude. However, a heat of solution eleven times that of sodium chloride will give rise to a difference in slope of only 5%. We may thus state as a working rule that vapor pressures of saturated aqueous salt solutions plotted as log P *vs.* $1/T$ will be parallel

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(3) Since pressure has such a small effect on vapor pressures, we may apply the equation to a liquid under a variable vapor pressure.

to the curve for pure water. In the absence of data a determination of the vapor pressure of the saturated solution at any one temperature will enable the entire curve to be drawn with a good degree of approximation.

It may be remarked that equations (5) and (6) apply equally well to the case of non-aqueous solutions, with the same assumptions, when the corresponding heat quantities are used. We may again predict a fairly close parallelism between the log P–$1/T$ curves for pure solvent and saturated solution. For a given value of ΔH_s, we would expect the deviation in slope for a non-aqueous solution to be much greater than for an aqueous solution. The heat of vaporization of water is abnormally high, and the solubility of electrolytes (or other solutes) expressed in terms of mole fractions are lower in water than in most other liquids. Consequently, for non-aqueous solutions, $\Delta H_s/N_1$ would be larger, and at the same time ΔH smaller, than for water. On the other hand, it must be pointed out that deviations of solutions from ideality are as a rule much less in other liquids than in water, particularly in the case of organic liquids, where many approximately ideal solutions are known. Therefore, for a great many solutions of organic substances, ΔH_s will be very small or zero, and for them the slopes of the vapor pressure curves will be sensibly parallel.

Finally, the assumptions under which equation (1) was derived make it possible to apply it to the case where a liquid is the saturating phase, provided only that its composition does not change with temperature. Owing to the phenomenon of mutual solubility, this will not ordinarily be true. Nevertheless, if the change in composition is not great, we may expect an approximate parallelism between the log P–$1/T$ curves if the "solute" is non-volatile; and between the log p_1–$1/T$ curves for the instance of an appreciably volatile solute.

Summary

1. An explanation is offered for the parallelism of the log P–$1/T$ curves for some saturated aqueous solutions and pure water.

2. An equation is developed from which it is predicted that this phenomenon will be true in general for saturated solutions, both aqueous and non-aqueous.

3. It is suggested that in the absence of data, a knowledge of the vapor pressure of a saturated solution at one temperature will make it possible to obtain the entire curve to a good degree of approximation.

BLUFFTON, OHIO

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The Acetyl Derivatives of Gluconic and Xylonic Acids

BY RANDOLPH T. MAJOR AND ELMER W. COOK

The only record in the literature of an acetylated sugar acid is that described by Upson and Bartz. These investigators prepared 2,3,4,6-tetraacetyl-*d*-gluconic acid monohydrate by the acetylation of δ-*d*-gluconolactone.[1] This reaction has been repeated in this Laboratory. Tetraacetyl-*d*-gluconic acid monohydrate with practically the same melting point reported by the previous workers was obtained but the optical activity found was different. Since the previous investigators did not report the solvent used for the measurement of the optical activity it seems probable that a different solvent was used in this Laboratory than the one used by Upson and Bartz. Tetraacetyl-*d*-gluconic acid monohydrate was also prepared by the oxidation of tetraacetyl-*d*-glucose.

Pentaacetyl-*d*-gluconic acid has been prepared by two different processes. The first was by the oxidation of aldehydo-*d*-glucose pentaacetate.[2] In the course of attempts to improve the methods of obtaining aldehydo-*d*-glucose pentaacetate, it was found that *d*-glucose tetraacetate gave the ring form of tetraacetyl-*d*-glucose semicarbazone with semicarbazide. This had been prepared previously by Wolfrom, Georges and Soltzberg by acetylation of *d*-glucose semicarbazone.[2b]

The second method of preparing pentaacetyl-*d*-gluconic acid was by further acetylation of

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[1] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[2] (a) Wolfrom, *ibid.*, **51**, 2190 (1929); (b) Wolfrom, Georges and Soltzberg, *ibid.*, **56**, 1795 (1934).