Summary

1. Adsorption isotherms on activated carbon were determined for *cis* and *trans*-dichloroethylene over a range of temperatures in the gas phase.

2. The adsorption for both isomers followed the B.E.T. theory if the number of layers possible in adsorption was taken as 1.6. The surface areas and heats of adsorption based on the theory were determined.

3. Isosteric heats of adsorption based on a constant fraction of the surface covered rather than constant weight adsorbed were calculated.

4. The adsorption of the *cis* and *trans* isomers were found to be the same when a comparison of surface area covered at fixed relative pressures was made.

5. It was concluded that the condensation properties of molecules adequately determine the adsorption where the only intermolecular forces are van der Waals with or without permanent dipole interaction.

6. It was shown that the separation of *cis–trans* isomers by adsorption on charcoal from the gas phase could be effected only in a multi-stage apparatus.

The Partial Molal Volume of Acetic Acid in Sodium Acetate and in Sodium Chloride Solutions[1]

BY HENRY E. WIRTH

It has been shown[2] that the partial molal volumes of certain electrolytes depend on the total (volume) ionic strength of the solution as predicted by the Debye–Hückel theory. Redlich and Klinger[3] and Gucker[4] have shown experimentally that the apparent molal volumes of certain non-electrolytes are linear functions of the volume concentration. Redlich and Nielsen[5] found that the apparent molal volume of acetic acid (Φ_3)[6] could be represented by the equation

$$\Phi_3 = 51.8397 + 0.14184 m_3 \qquad (1)$$

in the range 0.2–5 m, where m is the molality. Since the partial molal volume $(\overline{V}_3)$ can be obtained from the apparent molal volume by the relation

$$\overline{V}_3 = \Phi_3 + m_3 \partial \Phi_3 / \partial m_3 \qquad (2)$$

$\overline{V}_3$ is also a linear function of the molality in this concentration range. In this paper the effects of electrolytes on the partial molal volume of acetic acid are reported.

Methods.—Densities at 25° were determined by the sinker method using apparatus described previously.[2] A stock solution of acetic acid was analyzed by adding a weighed excess of standard carbonate-free sodium hydroxide solution and titrating the excess base with dilute hydrochloric acid solution using phenolphthalein as the indicator. The stock solution contained 0.37584 ± 0.00004 g. of acetic acid per gram of solution.

Solutions for the density determination were prepared by weight from the stock acetic acid. Sufficient anhydrous salt (sodium chloride or sodium acetate, previously dried at 200° for six hours) was added to give the required concentration of electrolyte.

The observed density differences were used to calculate the volume of solution containing 1000 grams of water (V) and the apparent molal volume of acetic acid in each of the solutions investigated. The partial molal volumes were obtained from the apparent molal volumes by use of equation 2.

Results

The equation

$$V = 1002.935 + 51.832 m_3 + 0.1394 m_3^2 \qquad (3)$$

which represents the experimental values of V in an aqueous acetic acid solution (Table I) with an average deviation of ±0.004 ml. can be arranged to give $\Phi_3 = 51.832 + 0.1394 m_3$. The values of Φ_3 reported here average 0.013 ml. per mole less than those reported by Redlich and Nielsen.[5] This compares to the probable experimental error of 0.008 ml. per mole due to errors in concentration alone quoted by these authors.

Differentiation of equation 3 gives

$$\overline{V}_3 = 51.832 + 0.2788 m_3 \qquad (4)$$

which agrees with the values of $\overline{V}_3$ calculated directly from the data with an average deviation of ±0.008 ml. per mole. Equations 2, 3 and 4 are valid only in the concentration range 0.16–2.5 molal, since in solutions less than 0.16 m the increased ionization of acetic acid causes Φ_3 and $\overline{V}_3$ to decrease toward the limiting value (40.68) characteristic of H^+ and $C_2H_3O_2^-$ at infinite dilution.

For aqueous sodium chloride solutions the equation

$$V = 1002.935 + 16.670 m_2 + 1.6363 m_2^{3/2} + 0.1705 m_2^2 \qquad (5)$$

represents the experimental results with an aver-

(1) Presented at the Chicago meeting of the American Chemical Society, September, 1946.

(2) Wirth, THIS JOURNAL, **59**, 2549 (1937).

(3) Redlich and Klinger, *Sitzb. Akad. Wiss. Wien, Abt. IIb.* **143**, 489 (1934).

(4) Gucker, Gage and Moser, THIS JOURNAL, **60**, 2582 (1938).

(5) Redlich and Nielsen, *ibid.*, **64**, 761 (1942).

(6) In this paper the subscript 3 refers to acetic acid, the subscript 2 to sodium chloride or sodium acetate.

TABLE I

PARTIAL MOLAL VOLUME OF ACETIC ACID (MOL. WT. 60.052) IN WATER SOLUTION AT 25°

m_3	$\dfrac{(d_1 - d_1)}{1000}$	V, ml.	$\Delta V \times 10^3$ (Eq. 3)	Φ_3	$\overline{V}_3$	$\dfrac{\Delta \overline{V}_3 \times 10^3}{\text{(Eq. 4)}}$
0.04269	0.360	1005.143	−5	51.72	51.8	
.04129	0.353	1005.066	−9	51.62	51.7	
.16317	1.351	1011.390	−6	51.829	51.90	20
.16889	1.399	1011.687	−6	51.824	51.90	20
.38251	3.110	1022.782	1	51.887	51.942	3
.36874	3.003	1022.065	−2	51.881	51.934	−1
1.0724	8.327	1058.688	3	51.983	52.137	5
1.0015	7.814	1054.985	1	51.972	52.115	3
2.4360	17.319	1130.028	2	52.171	52.520	8
2.5225	17.837	1134.569	3	52.182	52.544	7

age deviation of ±0.001 ml. In addition to those terms involved in equations 3 and 5, only two additional terms are required to represent all the data on mixed solutions of acetic acid and sodium chloride with an average deviation of ±0.005₆ ml. (Table II). The complete equation is

$$V = 1002.935 + 16.670 m_2 + 1.636_3 m_2^{3/2} + 0.170_5 m_2^2 +$$
$$51.832 m_3 + 0.1394 m_3^2 + 0.3070 m_2 m_3 - 0.1212 m_2^{1/2} m_3 \quad (6)$$

The addition of another term involving either

TABLE II

PARTIAL MOLAL VOLUMES OF ACETIC ACID IN SODIUM CHLORIDE (MOL. WT. 58.454) SOLUTIONS AT 25°

m_1	$\dfrac{(d_1 - d_2)}{1000}$	V, ml.	$\Delta V \times 10^3$ eq. 6	Φ_3	$\overline{V}_3$	$\dfrac{\Delta \overline{V}_3 \times 10^3}{\text{eq. 7}}$
		$m_2 = 0.04000_5$, $d_2 = 0.998729$				
0.12152	1.000	1009.910	−6	51.806	51.910	33
0.31724	2.561	1020.073	−2	51.884	51.930	−1
0.63508	5.017	1036.593	−1	51.929	52.023	−8
1.0389	7.986	1057.625	1	51.989	52.141	7
		$m_2 = 0.1600_3$, $d_2 = 1.003620$				
0.21053	1.645	1016.645	8	51.920	51.947	15
0.50702	3.899	1032.042	−5	51.927	51.995	−19
0.86000	6.449	1050.422	−3	51.987	52.102	−14
1.3822	10.017	1077.659	−14	52.054	52.238	−21
		$m_2 = 0.3590_3$, $d_2 = 1.011587$				
0.29433	2.159	1024.578	−8	51.934	51.979	−21
0.71168	5.058	1046.309	−3	52.013	52.121	5
1.1991	8.249	1071.734	−10	52.075	52.256	3
2.1263	13.715	1120.328	16	52.216	52.538	26
		$m_2 = 1.0002$, $d_2 = 1.036276$				
0.21005	1.242	1032.346	3	52.059	52.087	10
0.44013	2.565	1044.332	−1	52.074	52.133	−8
1.0070	5.622	1073.940	6	52.164	52.299	0
1.5840	8.496	1104.150	−6	52.235	52.448	−12
		$m_2 = 2.1884$, $d_2 = 1.078813$				
0.31104	1.112	1061.739	−4	52.147	52.189	−10
0.66947	2.307	1080.476	6	52.213	52.305	−2
1.4378	4.644	1120.733	−2	52.309	52.506	−7

$m_2 m_3^2$ or $m_2^2 m_3$ does not improve the fit. Differentiation of equation 6 gives

$$\overline{V}_3 = 51.832 + 0.2788 m_3 + 0.3070 m_2 - 0.1212 m_2^{1/2} \quad (7)$$

The average deviation between the partial molal volumes of acetic acid calculated directly from the data and calculated from equation 7 is ±0.012 ml. per mole.

Figure 1 shows that in dilute sodium chloride solutions (0.04–0.36 molal) the partial molal volume of acetic acid in a solution of given total molality $(m_2 + m_3)$ is the same as in an aqueous solution of the same molality. At higher sodium chloride concentrations (1.0 and 2.2 molal) $\overline{V}_3$ is less than in solutions of equal molality containing only acetic acid.
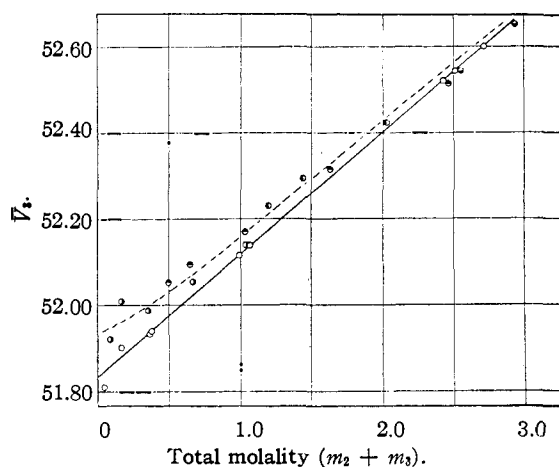

Fig. 1.—Partial molal volume of acetic acid in sodium chloride solution: O, $m_2 = 0.04$; ◑, $m_2 = 0.16$; ◕, $m_2 = 0.36$; ◓, $m_2 = 1.0$; ◐, $m_2 = 2.19$. The solid line represents the partial molal volume of acetic acid in aqueous solution.

In aqueous solutions containing only sodium acetate the equation

$$V = 1002.935 + 39.274 m_2 + 1.881 m_2^{1/2} + 0.114 m_2^2 \quad (8)$$

represents the experimental values with an average deviation of ±0.001₆ ml. Values of Φ_3 calculated from the derived relation $\Phi_3 = 39.274 + 1.881 m_2^{1/2} + 0.114 m_2$ deviate from the values reported by Redlich and Nielsen[6] by ±0.040 ml. per mole as compared to a deviation of ±0.029 ml. per mole found for their equation: $\Phi_3 = 39.244 + 1.86 c_3^{1/2} + 0.209 c_3$.

An equation similar to equation 6 was found to

$$V = 1002.935 + 39.274 m_2 + 1.881 m_2^{1/2} + 0.114 m_2^2 +$$
$$51.832 m_3 + 0.1394 m_3^2 + \alpha m_2 m_3 + \beta (m_2 m_3)^{1/2} \quad (9)$$

represent the experimental values for a given sodium acetate concentration but was not valid for all sodium acetate concentrations. Values of α and β are: 3.464, −10.13 $(m_2 = 0.04)$; 0.9968, −0.920 $(m_2 = 0.16)$; 0.5855, −0.2255$(m_2 = 0.365)$; 0.3733, −0.0461 $(m_2 = 1.0)$; and 0.3094, −0.0193 $(m_2 = 2.25)$, respectively.

TABLE III

PARTIAL MOLAL VOLUMES OF ACETIC ACID IN SODIUM ACETATE (MOL. WT. 82.041) SOLUTIONS AT 25°

m_3	$\dfrac{(d_1 - d_2)}{1000}$	V, ml.	$\Delta V \times 10^3$ Eq. 9	Eq. 10	Φ_3	$\overline{V}_3$	$\Delta \overline{V}_3 \times 10^3$ Eq. 11	Eq. 12
			$m_2 = 0.039966$, $d_2 = 0.998761$					
0.04897	0.401	1007.064	−1	1	51.86	51.92	−40	−50
.12234	0.989	1010.878	1	1	51.94	52.01	50	30
.31453	2.515	1020.864	−2	8	51.954	51.988	−3	−17
.63121	4.948	1037.337	−2	−1	51.985	52.055	4	15
1.0037	7.682	1056.746	3	−8	52.029	52.138	8	57
			$m_2 = 0.15960$, $d_2 = 1.003730$					
0.09512	0.741	1014.270	−2	0	51.96	52.01	20	40
.20270	1.562	1019.868	2	−6	52.00	52.02	−10	20
.49001	3.716	1034.814	−2	−2	52.011	52.062	−3	−5
.82430	6.113	1052.236	2	−6	52.054	52.140	0	−6
1.3487	9.697	1079.608	−1	0	52.110	52.250	−15	−20
			$m_2 = 0.36553$, $d_2 = 1.012050$					
0.13415	0.968	1024.705	3	−7	52.04	52.05	0	20
.28443	2.029	1032.531	2	−8	52.061	52.094	9	22
.67014	4.668	1052.634	−1	−7	52.093	52.172	0	−1
1.2652	8.476	1083.722	−2	−1	52.163	52.313	−1	−15
2.1066	13.363	1127.832	3	10	52.268	52.516	−8	−31
			$m_2 = 0.99911$, $d_2 = 1.036202$					
0.20864	1.178	1055.058	−1	−5	52.20	52.23	0	20
0.44858	2.488	1067.600	2	−11	52.239	52.294	10	17
1.0387	5.543	1098.488	−6	−4	52.297	52.424	0	−12
1.7214	8.750	1134.346	8	0	52.390	52.601	7	−22
			$m_2 = 2.2541$, $d_2 = 1.078767$					
0.30881	0.944	1114.625	−5	−6	52.51	52.55	−10	0
0.68920	2.028	1134.642	4	−16	52.573	52.653	13	4
1.5026	4.144	1177.530	0	10	52.657	52.832	4	42

The simplest equation that would represent all the data was found to be

$$V = 1002.935 + 39.274m_2 + 1.881m_2^{1/2} + 0.114m_2^2 + 51.931m_3 + 0.1394m_3^2 + 0.2391m_2m_3 + 0.005187m_2^{-1}m_3 - 0.02000m_2^{-1/2}m_3 - 0.00338m_2^{-1}m_3^2 \quad (10)$$

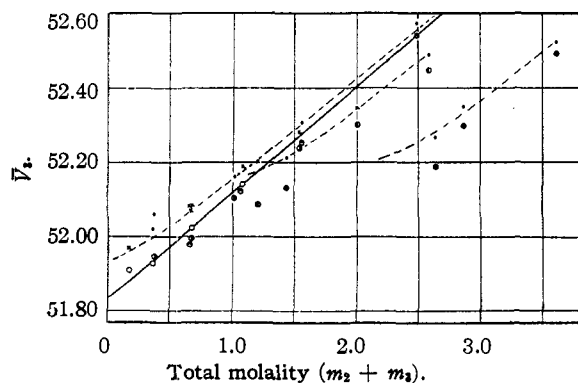The average deviation between observed and calculated values is ±0.005 ml. This equation is

Fig. 2.—Partial molal volume of acetic acid in sodium acetate solution: O, $m_2 = 0.04$; ◑, $m_2 = 0.16$; ◕, $m_2 = 0.365$; ◐, $m_2 = 1.0$; ◓, $m_2 = 2.25$. The solid line represents the partial molal volume of acetic acid in aqueous solution.

adequate for interpolation but cannot be used for extrapolation to solutions more dilute in acetic acid and sodium acetate than those used in this work.

By differentiation of equations 9 and 10 the following equations for the partial molal volume were obtained:

$$\overline{V}_3 = 51.832 + 0.2788m_3 + \alpha m_2 + 3/2\beta m_2^{1/2}m_3^{1/2} \quad (11)$$

(average deviation ±0.010 ml. per mole) and

$$\overline{V}_3 = 51.931 + 0.2788m_3 + 0.2391m_2 + 0.005187m_2^{-1} - 0.02000m_2^{-1/2} - 0.00676m_2^{-1}m_3 \quad (12)$$

(average deviation ±0.021 ml. per mole) (Table III).

The observed values of $\overline{V}_3$ in sodium acetate solutions are greater than in aqueous acetic acid solutions of equal molality (Fig. 2). The greatest differences are found in the more dilute solutions. This is to be expected from the decreased ionization of acetic acid in the sodium acetate solutions.

Summary

The volume of solution containing 1000 g. of water, the apparent molal volume of acetic acid, and the partial molal volume of acetic acid are reported for solutions containing acetic acid and

either sodium chloride or sodium acetate. Empirical equations representing the data are developed.

As a rough approximation the partial molal volume of acetic acid in a solution containing electrolyte is the same as in an aqueous solution of the same total molality. This approximation does not hold in solutions of sodium chloride with molalities greater than 0.4.

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Long Life Zirconium from Uranium 235 Fission

BY A. V. GROSSE[1] AND E. T. BOOTH

In our first paper on radioactive zirconium and columbium from uranium fission[1a] we described, outside of the 17.0-hour zirconium, also a long life zirconium, with a period of more than twenty days. In the following few months additional evidence was obtained, but publication was postponed due to other urgent atomic energy investigations. In the intervening years this fission product was investigated as part of the Plutonium Project,[2] but no details have appeared as yet. In 1940 Hahn and Strassmann[3] claimed to have discovered a 26-day zirconium. This they cancelled, however, in a short note in 1943[4] and simultaneously announced the long life zirconium to be described below. In the recently published Nuclear Physics Tables[5] the properties of our isotope have been inadvertently mixed with those of Hahn and Strassmann's 26-day zirconium. It thus seems worthwhile to publish our original findings.

Our zirconium proved to have a half-period of sixty-six days; this was followed for nearly three hundred days. As mentioned previously, it emitted electrons of about 0.25 MEV. energy. Chemical evidence proved unambiguously that the carrier of β-activity was the element zirconium. It produced a long life columbium isotope with very soft radiation, whose period was not determined.

Experimental Part

A typical experiment was carried out as follows: A 100-cc. solution of 70 g. of uranyl nitrate was bombarded by slow neutrons from the Columbia cyclotron on and off for a number of days. This was diluted to 1000 cc. of a 25% hydrochloric acid solution (by adding 588 cc. of 36% hydrochloric acid). Ten cc. of zirconium oxychloride solution, containing 135 mg. of zirconium dioxide, was added as carrier, together with various solutions containing a few milligrams each of stable isotopes to act as carriers for the radioactive fission products (i. e., Rb, Cs, Sr, Ba, Y, La, Mo, Sb, Te, Ce, Cb, Br and I). On addition of 10-fold molar excess of phosphoric acid a fine, nicely settling precipitate of zirconium phosphate (ZrP_2O_7)

was obtained, containing some insoluble columbic acid $(HCbO_3)$.

This precipitate was washed with 25% hydrochloric acid and then purified twice from possible natural radioactive contaminations by addition of a few milligrams of Th, Bi, Pb, La + Ba and Fe as carriers. The radio-pure zirconium phosphate, still containing the added columbic acid and some iron oxide, was converted to zirconium dioxide by melting with a 10-fold quantity of sodium potassium carbonate in a platinum–gold dish; 143 mg. of zirconium dioxide and a trace of ferric oxide were obtained. These were further purified and fractionated as shown in Fig. 1; 19.0 mg. was painted on an aluminum disc (Al, 45) and measured. The rest was converted into acid soluble zirconium hydroxide (by sodium bisulfate melt and ammonia precipitation) and fractionally crystallized as $ZrOCl_2 \cdot 8H_2O$ from concentrated hydrochloric acid. The head or purest fraction of oxychloride was converted to oxide (56.5 mg. of snow white zirconium dioxide) and all of it painted on Al 47. Intermediate fractions were discarded. The residual zirconium was precipitated from the mother liquor, after diluting with hydrochloric acid, as a pure zirconium phosphate; all of it, equivalent to 16.7 mg. of zirconium dioxide, was painted on Al 48. The columbium was precipitated, from the sodium potassium carbonate-melt solution, with dilute acid; 51 mg. of columbium pentoxide, containing small amounts of zirconium dioxide, was obtained and painted on Al 46 for measurement.[5a] The scheme of the chemical separation is illustrated in Fig. 1. All measurements were made using an F. P. 54 amplifier and through 1 or 5 mil Al foil. The results of our measurements through 1 mil aluminum are plotted in Fig. 2. We see that all three zirconium preparations decay with the same period, namely, sixty-six days.

The specific activity per 1.0 mg. of zirconium dioxide of all three preparations, after correcting to zero time, was as follows:

Al 45, initial material = 4.9×10^{-3} div./sec.
Al 47, head fraction = 4.9×10^{-3} div./sec.
Al 48, tail end = 5.2×10^{-3} div./sec.

Thus, they are, within experimental error, identical. Zirconium is the only element, except ekatantalum (no. 91) and hafnium, which is precipitated from concentrated hydrochloric acid by phosphoric acid. Ekatantalum can be carefully separated from zirconium by the procedure we originally used to separate protactinium[6] and as was also subsequently demonstrated by the separation of ekatantalum[233] from thorium + n products.[7] Hafnium is only separated slowly from zirconium by tedious fractionation.[8] Thus the constancy of the specific activity, together with the other chemical evidence, is strong proof

(1) Present address: Houdry Process Corp., Marcus Hook, Pa.

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(5a) Data on this columbium isotope will be published later. Hahn and Strassmann[4] give it a half life of fifty-five days.

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