Table II. Diffusivities at Infinite Dilution

	100 Mole % Toluene		100 Mole % *n*-Propanol	
Ref.	$D \times 10^5$ cm.^{2}/sec.	Dev. from exptl., %	$D \times 10^5$ cm.^{2}/sec.	Dev. from exptl., %
This work	3.56	0	1.35	0
(*4*)	1.08	70	0.35	67
(*10*)	1.44	60	1.64	22
(*14*)	1.96	45	0.53	61
(*15*)	2.15	40	0.32	77
(*19*)	2.70	24	0.52	62
(*17*)	2.32	35	0.57	58

ACKNOWLEDGMENT

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NOMENCLATURE

a = thermodynamic activity, mole fraction scale
$\bar{C}', \bar{C}''$ = mean concentrations in the closed and open compartments, respectively, gram per ml.
$\Delta C_o, \Delta C_f$ = initial and final concentration difference between the two compartments of the diffusion cell, gram per ml.
$\bar{D}$ = integral concentration-based diffusivity, cm.^{2} per sec.
D_a = activity-based differential diffusivity, cm.^{2} per sec.
D = concentration-based differential diffusivity, cm.^{2} per sec.
x = mole fraction *n*-propanol

Greek Letters

β = diaphragm cell constant, cm.$^{-2}$
θ = diffusion time, sec.

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Solubilities of Disodium Terephthalate in Aqueous Solutions of Sodium Carbonate and Sodium Bicarbonate

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Solubility data have been obtained for disodium terephthalate in aqueous solutions of carbonate and sodium bicarbonate. The temperature range for carbonate was 40° to 91° C. and for bicarbonate, 40° to 66° C. At higher temperatures, the bicarbonate decomposed. The solubility changes due to temperature were insignificant. The data are shown in tabular form and by triangular phase diagrams.

THE SOLUBILTY of disodium terephthalate in aqueous solutions of sodium carbonate and sodium bicarbonate was determined. The temperature range covered for carbonate was 40° to 91°C. and for bicarbonate, 40° to 66°C. The sodium bicarbonate solutions were unstable at higher temperatures; the bicarbonate decomposed. With both systems, the solubility changes due to temperature were insignificant. The pH of the carbonate solutions was about 10.7 and that of the bicarbonate solutions, 8.1.

Smith and Hoebery (*4*) studied the solubility of disodium phthalate in solium carbonate solutions. Disodium phthalate is much more soluble than disodium terephthalate in water. This is true for the free acids also.

EXPERIMENTAL PROCEDURE

Apparatus. Samples were allowed to reach equilibrium in a shaking, constant-temperature bath. The bath used was a Model 2156-1 temperature-controlled water bath shaker, manufactured by Research Specialties Co., Richmond, Calif.

Reagents. SODIUM CARBONATE. Mallinckrodt Primary Standard grade.

SODIUM BICARBONATE. Mallinckrodt Analytical Reagent grade.

TEREPHTHALIC ACID. Eastman Kodak.

Preparation of Disodium Terephthalate. A 10% excess of the stoichiometric amount of sodium hydroxide to convert therephthalic acid to disodium terephthalate was mixed with terephthalic acid in distilled water. The quantity of water used was insufficient to dissolve all of the disodium terephthalate produced. The mixture was stirred for 24 hours, the disodium terephthalate was removed by filtering and was washed several times with a 1 to 2 mixture of water and methanol.

Sample Preparation and Sampling. The salt sloutions plus the solid phase salt were placed in rubber-stoppered Erlenmeyer flasks in the bath. Mineral oil was used as the bath

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Table I. Solubility Data: Disodium Terephthalate–Sodium Carbonate

Solution Composition, Wt. %			
Disodium Terephthalate	Na_2CO_3	H_2O	Solid Phase
		40° C.	
...	32.25	67.75	$Na_2CO_3 \cdot H_2O$
0.72	21.87	77.41	$Na_2CO_3 \cdot H_2O$
2.04	16.76	81.20	$Na_2CO_3 \cdot H_2O$
4.03	12.20	83.77	$Na_2CO_3 \cdot H_2O$
5.07	10.91	84.02	Mixture
5.84	9.37	84.79	$C_8H_4O_4Na_2$
7.11	4.35	88.54	$C_8H_4O_4Na_2$
12.04	1.28	86.68	$C_8H_4O_4Na_2$
13.26	...	86.74	$C_8H_4O_4Na_2$
		66° C.	
...	31.44	68.56	$Na_2CO_3 \cdot H_2O$
0.38	22.80	76.82	$Na_2CO_3 \cdot H_2O$
2.00	17.36	80.64	$Na_2CO_3 \cdot H_2O$
4.27	12.34	83.39	$Na_2CO_3 \cdot H_2O$
4.89	10.59	84.52	$Na_2CO_3 \cdot H_2O$
5.62	9.41	84.97	Mixture
8.74	5.40	85.86	$C_8H_4O_4Na_2$
11.48	1.92	86.60	$C_8H_4O_4Na_2$
13.49	...	86.51	$C_8H_4O_4Na_2$
		91° C.	
...	30.90	69.10	$Na_2CO_3 \cdot H_2O$
0.63	22.56	76.81	$Na_2CO_3 \cdot H_2O$
1.04	18.55	80.41	$Na_2CO_3 \cdot H_2O$
2.95	14.66	82.39	$Na_2CO_3 \cdot H_2O$
5.81	10.21	83.98	$Na_2CO_3 \cdot H_2O$
6.16	9.89	83.95	Mixture
8.88	5.20	85.92	$C_8H_4O_4Na_2$
12.60	1.29	86.11	$C_8H_4O_4Na_2$
13.65	...	86.35	$C_8H_4O_4Na_2$

Table II. Solubility Data: Disodium Terephthalate–Sodium Bicarbonate

Solution Composition, Wt. %			
Disodium Terephthalate	$NaHCO_3$	H_2O	Solid Phase
		40° C.	
...	13.40	86.60	$NaHCO_3$
1.92	12.31	85.77	$NaHCO_3$
4.48	10.93	84.59	$NaHCO_3$
6.40	9.17	84.43	Mixture
10.37	4.47	85.16	$C_8H_4O_4Na_2$
13.05	1.33	85.62	$C_8H_4O_4Na_2$
13.26	...	86.74	$C_8H_4O_4Na_2$
		66° C.	
...	14.71	85.29	$NaHCO_3$
1.67	13.59	84.74	$NaHCO_3$
4.57	11.55	83.88	$NaHCO_3$
5.51	10.73	83.76	Mixture
7.79	7.12	85.09	$C_8H_4O_4Na_2$
11.08	3.18	85.74	$C_8H_4O_4Na_2$
12.98	0.82	86.20	$C_8H_4O_4Na_2$
13.49	...	86.51	$C_8H_4O_4Na_2$

liquid, and the temperature was maintained to within ±0.5° C. of the specified temperature.

After 5 days, aliquots were analyzed. Aliquots were then taken for analysis every day until equilibrium was attained.

Chemical Analysis. Terephthalic acid was determined gravimetrically by precipitaing the free acid with hydrochloric acid. The pK_{a_1} for terephthalic acid is 3.82 (*2*) which makes it considerably stronger than carbonec acid with a pK_{a_1} of 6.46.

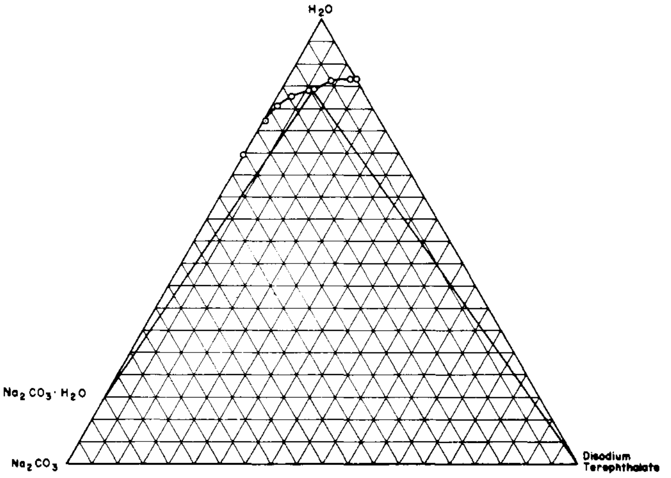

Figure 1. Phase diagram for the disodium terephthalate–Na_2CO_3–H_2O system at 91° C.

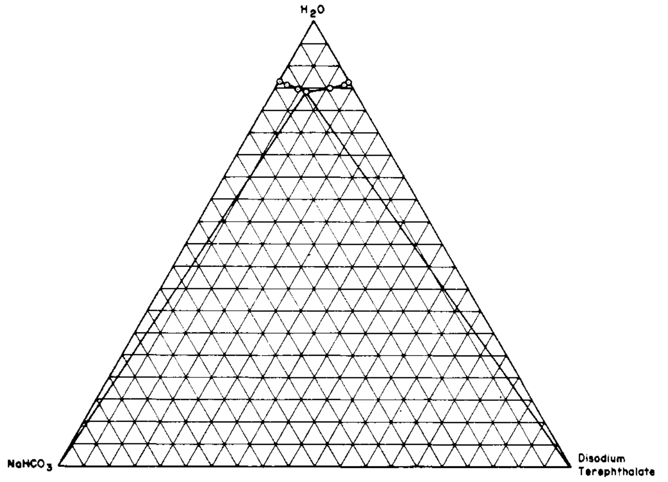

Figure 2. Phase diagram for the disodium terephthalate–$NaHCO_3$–H_2O system at 40° C.

Terephthalic acid is almost completely insoluble in water Lange's Handbook reports a value of 0.001 gram per 100 grams of cold water (*3*).

Sodium carbonate was determined by a potentiometric titration using standard sodium hydroxide. The titration curves were plotted and the end points determined graphically.

RESULTS

Table I shows the solubility of disodium terephthalate in sodium carbonate solutions at three temperatures. The solid phase for sodium carbonate in the monohydrate while the solid phase of disodium terephthalate is not hydrated. The triangular phase diagrams are almost superimposable and are therefore, represented by the one shown in Figure 1, plotted from data given in Table I.

Table II. gives the solution and solid phase composition for the sodium bicarbonate-disodium terephthalate-water system. Again, temperature changes over the limited range covered cause little change in the solubilities. Figure 2 is plotted from data shown in Table II. The solid phases formed were anhydrous sodium bicarbonate and anhydrous disodium terephthalate.

CONCLUSIONS

The solubility of disodium terephthalate is about the same in both sodium carbonate and bicarbonate solutions. The differences in the triangular phase diagrams are primarily due to the differences in the solubilities of carbonate and bicarbonate in water.

Temperature, over the range covered, has very little effect on the solubility of disodium terephthalate. Also, once the disodium salt has been formed, pH has no effect on the solubility.

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Heat Capacity from 80° to 300° K., Melting Point and Heat of Fusion of Nitroethane

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The heat capacity of nitroethane has been determined by adiabatic calorimetry from 80° to 300° K. The heat capacity of the liquid exhibits a minimum in the vicinity of 228° K. The melting point was 183.69 ± 0.02° K. The heat of fusion was 2355 ± 4 cal. per gram mole.

NITROPARAFFINS are widely used as industrial solvents and are of interest in the study of solutions. However, except for nitromethane (2), relatively little is known about the thermal properties of these materials. The present measurements were undertaken to add to the thermal data for nitroethane (3).

EXPERIMENTAL

Calorimeter. The apparatus used was an adiabatic-shield high vacuum calorimeter. A description of this equipment has been given elsewhere (*4, 8*). Temperatures were determined with a capsule-type, platinum resistance thermometer calibrated by the National Bureau of Standards on the International Temperature Scale. The heat capacity of the empty calorimeter was determined separately.

Preparation and Purity of the Sample. The nitroethane sample was prepared from commercially available material by distillation at reduced pressure (92 mm. of Hg). Chromatographic analysis indicated a purity of 99.2 + %. The principal impurity was 2-nitropropane. The calorimetric purity (see below) was 99.9%. The calorimetric sample had a mass of 156.007 grams, corresponding to 2.0782 moles (mol. wt. = 75.070).

RESULTS AND DISCUSSION

Heat Capacities. Heat capacity measurements were made over the entire range from −193.622° to 27.111° C. using 3 to 4° temperature intervals. The experimental results are shown in Table I. The actual temperature intervals used may be computed from the temperature data given. Temperatures were converted to the International Practical Kelvin Scale using the relation T° K. = 273.15 + t° C. The data are based upon a defined thermochemical calorie equal to 4.1840 joules. The maximum effect of partial vaporization and the contribution of the 10 ml. of nitrogen gas above the sample was estimated to be 0.01 cal. per ° K. at 30° C. The measured heat capacity is essentially the heat capacity of the saturated condensed phase and is so reported in Table I. From the data of Toops (7) and the relation between C_p and C_{satd} given in Rowlinson (6), the difference between C_p and C_{satd} at 27.00° C. (the highest experimental temperature) is 0.001 cal. per gram mole ° K. Thus, the C_{satd}

Table I. Experimental Heat Capacity of Nitroethane

Initial Temp., ° C.	Mean Temp., ° C.	$C_{satd.}$ Cal./ Gram Mole ° C.
	Run 1	
0.037	1.557	31.513
3.078	4.806	31.561
6.534	8.144	31.658
9.754	11.296	31.713
12.838	14.414	31.781
15.989	17.542	31.877
19.095	20.728	31.942
22.362	23.998	32.048
25.634	27.111	32.155
	Run 2	
−195.642	−193.622	11.782
−191.602	−190.137	12.145
−188.672	−187.303	12.398
−185.935	−184.530	12.658
−183.125	−181.930	12.915
−180.734	−179.369	13.153
−178.003	−176.794	13.389
−175.585	−174.136	13.642
−172.686	−171.229	13.902
−169.776	−168.224	14.172
−166.782	−165.440	14.433
−164.098	−162.511	14.724
−160.925	−159.170	15.001
−157.416	−156.036	15.275
−154.655	−153.159	15.498
−154.402	−152.763	15.555
−151.123	−149.326	15.847
−147.529	−145.666	16.140
−143.802	−141.936	16.422
−140.147	−138.361	16.756
−136.576	−134.850	17.070
−133.125	−131.548	17.345
−129.972	−128.302	17.637
−126.633	−125.000	17.935
−123.368	−121.725	18.240
−120.083	−118.446	18.550
−116.810	−115.259	18.783
−113.762	−112.228	19.027
−110.693	−109.191	19.333
−107.688	−106.022	19.652
−104.356	−102.728	20.838
−101.101	−99.454	19.809
−97.808	−96.265	21.635
−94.721	−93.492	24.519
−92.262	−91.369	40.060

(Continued)