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

K. F. LIU and W. T. ZIEGLER
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Ga.

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)

Table I. (*Continued*)

Melting Region Traverses—Series A		
-109.662	-107.719	19.467
-105.776	-103.622	19.963
-101.467	-99.372	20.697
-97.278	-95.430	22.380
-93.583	-92.037	36.188
-90.492	-90.024	509.989
-89.555	-89.525	11940.194
-89.494	-89.487	49820.636
-89.479	-89.475	30824.612
-89.470	-87.731	58.390
-85.993	-84.340	31.582
-82.687	-81.102	31.509
Series B		
-105.431	-103.277	19.988
-101.124	-99.046	20.782
-96.968	-95.117	22.631
-93.263	-91.824	38.997
-90.384	-89.946	828.007
-89.508	-89.489	19482.125
-89.471	-89.466	53994.163
-89.462	-89.458	39765.154
-89.454	-87.786	48.659
-86.117	-84.533	31.537
-82.948	-81.321	31.474
-79.694	-77.862	31.379
-76.031	-73.656	31.264
-71.280	-68.890	31.195
Run 3		
-76.183	-74.417	31.248
-72.651	-70.907	31.203
-69.163	-67.361	31.156
-65.558	-63.714	31.096
-61.871	-59.898	31.073
-57.924	-55.937	31.036
-53.950	-51.929	31.026
-49.908	-47.885	31.011
-45.863	-43.748	31.002
-41.634	-39.342	31.032
-37.049	-34.811	31.035
-32.574	-30.197	31.090
-40.137	-37.571	31.048
-35.005	-32.395	31.064
-29.784	-26.864	31.111
-23.943	-21.433	31.175
-18.924	-16.350	31.224
-13.777	-11.286	31.307
-8.796	-6.168	31.384
-3.539	-0.988	31.493
1.564	4.037	31.580
6.511	8.741	31.690

reported here is practically the same as C_p. The reproducibility of the measurements was about 0.03 cal. per gram mole ° K. The error in the reported heat capacity values is believed to be less than 0.4%.

The experimental heat capacity data (Table I) was fitted with polynominals in T(° K.) by the least-squares method. Equations 1 and 2 represent the data in the solid and liquid regions, respectively.

$$C_{\text{satd}}(\text{solid}) = 0.87836230 + 0.18523983\,T - 7.5973292 \times 10^{-4}\,T^2 + 1.9315512 \times 10^{-6}\,T^3 \quad (1)$$

$$C_{\text{satd}}(\text{liquid}) = 117.11037 - 1.2690254\,T + 7.0229342 \times 10^{-3}\,T^2 - 1.7448255 \times 10^{-5}\,T^3 + 1.6638328 \times 10^{-8}\,T^4 \quad (2)$$

The root-mean-square deviation of Equation 1 is 0.019 cal. per gram mole ° K., and that of Equation 2 is 0.016 cal. per gram mole ° K. Smoothed values calculated with Equations 1 and 2 are presented in Table II. The maximum deviation of the smoothed values from the experimental heat capacity data is 0.28% in the solid range and 0.14% in the liquid range.

The only previous measurements of the heat capacity of nitroethane appear to be the limited measurements (25° to 50° C.) of Beard (*1*). His value at 25° C. is about 3.3% higher than that given in Table II.

Table II. Smoothed Heat Capacity of Nitroethane[a]

T	C_{satd}	T	C_{satd}
80	11.82	205	31.17
85	12.32	210	31.10
90	12.80	215	31.05
95	13.28	220	31.02
100	13.74	225	31.01
105	14.19	230	31.02
110	14.63	235	31.03
115	15.07	240	31.06
120	15.50	245	31.10
125	15.94	250	31.15
130	16.36	255	31.21
135	16.79	260	31.28
140	17.22	265	31.35
145	17.65	270	31.43
150	18.09	275	31.53
155	18.53	280	31.63
160	18.98	285	31.74
165	19.44	290	31.86
170	19.90[b]	295	31.99
175	20.38[b]	300	32.13
180	20.87[b]		
183.69	M.P.[c]		
185	31.71		
190	31.53		
195	31.38		
200	31.26		

[a] Units: cal., gram mole, ° K. [b] Corrected for premelting. [c] Melting point.

Table III. Determination of Purity, Melting Point, and Heat of Fusion

Equilibrium Temp., ° C.	Fraction Melted
Series A	
-90.492	0.024
-89.555	0.219
-89.494	0.527
-89.479	0.843
-89.470	0.961

Melting point = -89.474° C.
Heat of fusion = 2360 cal. per gram mole
Purity = 99.92 mole %

Equilibrium Temp., ° C.	Fraction Melted
Series B	
-90.384	0.027
-89.508	0.328
-89.471	0.634
-89.462	0.841
-89.454	0.976

Melting point = -89.457° C.
Heat of fusion = 2351 cal. per gram mole
Purity = 99.91 mole %

Average melting point = -89.46 ± 0.02° C.
Average heat of fusion = 2355 ± 4 cal. per gram mole
Average purity = 99.92 mole %

The heat capacity of liquid nitroethane exhibits a minimum near 228° K. This may be associated, at least in part, with the contribution to the heat capacity arising from internal rotation about the C—N bond.

Purity, Melting Point, and Heat of Fusion. Two traverses of the melting region were carried out. These data are shown in Table I. During each series of measurements a record was kept of the energy input as a function of equilibrium temperature. From these data the heat of fusion, fraction melted, and melting point presented in Table III were obtained following the treatment given by Rossini (*5*). The melting point found (-89.46 ± 0.02° C.) may be compared with the value of -89.52° C. reported by Toops (*7*) for a sample of 99.9 + % purity. The heat of fusion found was 2355 ± 4 cal. per gram mole.

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An Isothermal Dilution Calorimeter for Exothermic Heats of Mixing

D. R. WINTERHALTER[1] and H. C. VAN NESS
Chemical Engineering Department, Rensselaer Polytechnic Institute, Troy, N. Y.

An isothermal dilution calorimeter is described which allows rapid and routine collection of accurate heat-of-mixing data for both exothermic and endothermic systems. Data are reported for the endothermic system benzene–carbon tetrachloride at 25° C. and for the exothermic systems acetone-dichloromethane at 0°, 15°, 30°, and 45° C.; methyl acetate–dichloromethane at 30° and 45° C.; and 1,4-dioxane–dichloromethane at 30° and 45° C.

THE isothermal dilution calorimeter for heats of mixing described by Savini *et al.* (*6*) has been modified so that it is now capable of measuring both exothermic and endothermic heats of mixing. This paper describes the modifications which have been made to Savini's endothermic calorimeter and presents some exothermic heat-of-mixing data which have been obtained with the new instrument. A detailed description of the present calorimeter and the associated instrumentation and operating procedures is given elsewhere (*8*).

EXPERIMENTAL

Use of an isothermal dilution calorimeter to determine exothermic heats of mixing requires removal of heat from the vessel in which the mixing occurs. In the present calorimeter, heat is removed from the mixing vessel at a constant rate by a thermoelectric cooling device. Before the mixing process is begun, heat is simultaneously added to the vessel at the same constant rate by means of an electric resistance heater. During the mixing process, the heater is turned off with the result that heat is removed from the mixing vessel at a net rate equal to the rate of energy addition by the heater before mixing. This type of cooling system can be made physically small; it has a very small thermal lag corresponding to the response time of the heater only; it can be made virtually independent of small (0.01° C.) variations in solution temperature during mixing; it does not require external calibration.

APPARATUS

Figure 1 shows the Teflon calorimeter plug in two views taken at right angles to each other. The drawing is somewhat schematic, and many of the components are shown in only one view. The figure shows the Teflon plug, *E*, supported by a 2-inch diameter stainless-steel tube, *A*, which is, in turn, attached to a support rack (not shown). View *b* of this figure shows the cooling system itself housed within the support tube *A*. The warm junctions of the 6-couple, 15-ampere cooling module *Z* (Frigistors Ltd., Montreal, Canada Type 1FB - 06 - 015 - G1) are in thermal contact with a copper heat sink *R* through which water from the thermostated bath in which the calorimeter is immersed is circulated. The cold junctions of the module are in thermal contact with a coin-silver bar, *Y*, which is, in turn, connected to a ⅛-inch diameter coin-silver rod, *U*, which passes through the Teflon plug into the mixing vessel. The lower end of the silver rod is surrounded by a small copper cup, *V*, the inside surface of which is amalgamated and which is filled with mercury. The mercury acts as a heat-transfer agent and as a bearing for the stirrer assembly. Two coin-silver paddles, shown at *L* in view *a*, are attached to the copper cup and act both as a heat transfer surface and as a stirrer for the solution in the Dewar flask, *S*. The entire cooling assembly is surrounded by a copper heat shield, *X*, which is an extension of the heat sink, *R*, to prevent inadvertent cooling of adjacent calorimeter parts. The free space within the support tube, *A*, is entirely filled with Santocell A insulating dust to reduce further the possibility of unwanted heat transfer. The cooling module is powered by a home-built current-regulated D.C. supply. This arrangement is capable of removing heat from the mixing vessel at a sufficiently constant rate to allow the collection of reliable exothermic heat-of-mixing data.

RESULTS AND DISCUSSION

The system benzene–carbon tetrachloride at 25° C. was studied to provide a basis for the comparison of this calorimeter with other calorimeters. When the calorimeter is used for endothermic systems such as this, the cooling rate is set to a low value which just compensates for the rate of energy addition by the stirrer thus avoiding the problem encountered by Savini and coworkers of having the temperature within the Dewar flask rise to a value slightly greater than that of the thermostated bath. The results of

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[1] Present address: Chemical Engineering Department, University of California, Berkeley, Calif.