857. *The Partial Molar Heats of Solution of Water in Dinitrogen Pentoxide Solutions and of Potassium Nitrate and Sulphuric Acid in Nitric Acid at 0°.*

By L. Lloyd and P. A. H. Wyatt.

Specific heats and partial molar heats of solution of water are reported for dinitrogen pentoxide solutions in the range 78·8—89·5% N_2O_5. For potassium nitrate and sulphuric acid, specific heats and heats of solution have been determined up to concentrations of about 2 molal in pure nitric acid.

The derived values of the differential heat of dilution of nitric acid for the solutes water, dinitrogen pentoxide, and potassium nitrate are at variance with the results expected from a simple solvent dissociation involving dissociation products of fixed solvation number.

On the basis of spectroscopy [1] and cryoscopy [2,3] it is generally accepted that the main dissociation of nitric acid is represented by the equation

$$2HNO_3 \qquad NO_2^+ + NO_3^- + H_2O$$

By treating deviations from Raoult's law in chemical terms, some details have been added to this conclusion. Thus, water is said to be almost unprotonated [4] and dinitrogen pentoxide completely dissociated [1,2] in dilute solutions, whilst all the products of dissociation are regarded as being more or less solvated with nitric acid molecules. The nitrate ion has been assigned a solvation number of 2,[5] and water a solvation number of 1,[4] or perhaps 2 [2,6] near the composition of pure nitric acid.

Since these solvation numbers were calculated on the assumption that deviations from ideality may be treated chemically, the partial molar heats of solution of the dissociation products should depend upon the concentration in a characteristic way.[7] For, if it is assumed that the degree of solvation does not vary markedly with concentration (this has been assumed over considerable concentration ranges for the nitrate ion [5] and water [4,8]), the partial molar heats of solution of water, dinitrogen pentoxide, or an alkali-metal nitrate should decrease with increasing concentration, but tend towards a constant value as the solvent dissociation is suppressed. Further, the derived partial molar heat content of the solvent should tend towards the *same* constant value for all three solutes at high concentrations.

As the existing data on heats of solution in nitric acid are too few near the composition

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[1] Ingold and Millen, *J.*, 1950, 2612.

[2] Gillespie, Hughes, and Ingold, *J.*, 1950, 2552.

[3] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.

[4] Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722.

[5] Chédin and Vandoni, *ibid.*, 1948, **227**, 1232.

[6] Fénéant and Chédin, *ibid.*, 1956, **243**, 41.

[7] Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 806.

[8] Chédin, *J. Chim. phys.*, 1952, **49**, 109.

of the pure acid to apply this test, we have made some new measurements on the partial molar heats of solution (at 0°) of potassium nitrate and sulphuric acid in pure nitric acid, and on the partial molar heat of solution of water in dinitrogen pentoxide solutions at concentrations on both sides of the composition of the pure acid. Apart from measurements on the solute water at 20° by Leclerc and Chédin,[9] which have already been interpreted in the way outlined above,[7] a number of determinations of heats of solution at isolated concentrations have been recorded and used to interpret the constitution of nitric acid solutions.[2] But the latter interpretations have been based upon the *total* value of the heat of solution, whilst for the present purposes attention is directed to the *variation* of the heat of solution with composition, which clearly requires a more extensive set of measurements.

EXPERIMENTAL

The 1-pint Pyrex Dewar flask used as a calorimeter was stoppered at the mouth with a Polythene bung, bored to carry five tubes. A short tube in the centre of the bung terminated at its upper end in a B14 joint, into which a tube carrying the thermocouples could be fitted: this extended to within a few mm. of the bottom of the Dewar flask and was closed at its lower end. Around this central tube were grouped a glass cooling "finger," into which pieces of solid carbon dioxide could be dropped to cool the contents of the calorimeter; a tube carrying the electrical heater for specific-heat measurements; a B10 socket, into which a device for adding solids or liquids could be fitted; and a long tube sealed at its upper end in which the arm of a magnetic stirrer could slide freely. This stirrer was similar to that used in vapour-pressure[10] and cryoscopic [2, 11] work. When measurements were about to be made the Polythene bung was always wired into position and greased externally so that the calorimeter was air-tight, and the whole calorimeter was surrounded by a metal jacket rising above the level of the cap so that it could be immersed in an ice-bath without direct contact with moisture.

Five copper–constantan thermocouple junctions, insulated from each other and embedded in naphthalene in a thin-walled glass tube, enabled temperature measurements to be made to within 0·001° when used in conjunction with a Cambridge Vernier Potentiometer. Since the temperature changes to be recorded were of the order of 1°, this degree of precision was quite sufficient to ensure that temperature errors were not limiting. (The overall experimental error was of the order of 1%, most of which probably arose from the fact that the surroundings of the ice-bath were at room temperature.) The ice-point, the sodium sulphate hydrate transition at 32·388°, and the freezing point of sulphuric acid [11, 12] were used in calibrating the thermocouples. A separate Dewar flask containing pure ice was immersed in the ice-bath alongside the calorimeter and housed the cold junctions.

The heating element, consisting of a small coil of resistance wire constructed so that it would produce a temperature rise in the calorimeter of about 0·6° in 10 min., was immersed in transformer oil in a thin-walled glass tube, the main length of which was packed with wax around the leads. Two copper leads were silver-soldered at each end of the heating coil, one pair serving to carry the heating current and the other to tap off the potential drop across the heater. Before the heater was switched on, the potential source (two 90 ampère-hour 2-volt accumulators in parallel) was always connected through an identical resistance coil (the "ballast") for about an hour to stabilize the potential. During a heating period the observed potential drop across the heater never changed by more than 0·05%, and the heat input was calculated from the average potential drop, the time, and the resistance of the heater, which was calibrated by comparison with a standard 1 ohm resistance.

When a measurement was to be made, nitric acid was weighed into the calorimeter at about −5°, after which the calorimeter was sealed and kept in the ice-bath for at least 1 hr. As the temperature approached 0°, readings were taken every minute for a period of 8—10 min. to establish the rate of leakage before heating. Then either the electrical heater was switched on or an addition of solute was made, after which further readings were taken at intervals of 1 min.

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[9] Leclerc and Chédin, *Mém. Services chim. État*, 1945, **32**, 87.
[10] Lloyd and Wyatt, *J.*, 1955, 2248.
[11] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.
[12] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 297.

to establish the rate of leakage after the change of temperature By extrapolating the readings for the pre- and post-periods to the time when the temperature of the calorimeter had risen half-way to the final temperature, a corrected value of the temperature rise was obtained. A correction was made for the temperature of the added solute, which was measured by a single-junction thermocouple in the adding device.

A further complication is introduced by the variability of the water equivalent of a Dewar flask with the extent to which it is filled.[13] The calorimeter used had a water equivalent which varied from 25·8 g. when it contained 140 g. of water to 34·4 g. when it contained 230 g. To find the volume of liquid, nitric acid solutions being unstable, the density of some solutions was determined with a form of pyknometer which permitted rapid reading; this consisted of a glass bulb and stem with a total capacity of about 10 c.c. The stem was graduated and could be read to 0·001 c.c., so that, after calibration with water at various points on the scale and at different temperatures, the volume of a known weight of solution could always be read without the necessity for adjusting the meniscus to a fixed mark at each temperature.

Materials.—The dinitrogen pentoxide solutions and pure nitric acid were prepared by standard methods,[10] and the sulphuric acid cryoscopically. Potassium nitrate was " AnalaR."

RESULTS

The results for the partial molar heats of solution are collected in Tables 1, 2, and 3, and those for specific heats and densities in Tables 4, 5, and 6. Specific-heat measurements were made at definite compositions before and after the addition of solutes: the compositions quoted for the partial molar heats of solution, on the other hand, represent the average of the compositions before and after an addition of the solute. It was assumed that the quantities of solute added were small enough to give a direct estimate of the partial molar heat of solution at this

TABLE 1. *Partial molar heats of solution of water in dinitrogen pentoxide solutions at 0°, and the derived differential heats of dilution of nitric acid.*

N_2O_5 (% by wt.)	H_2O (m)	N_2O_5 (m)	$\frac{m_{H_2O}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{H_2O}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$ (cal. mole^{-1})
89·5	−2·34	1·80	−0·147	5897	−532·9
89·2	−2·19	1·72	−0·138	4984	−402·6
88·8	−1·93	1·54	−0·122	3976	−271·8
88·4	−1·72	1·41	−0·108	2998	−159·3
88·0	−1·46	1·24	−0·092	2206	− 80·1
87·5	−1·14	1·00	−0·072	1423	− 15·9
87·0	−0·82	0·74	−0·052	885	+ 17·5
86·5	−0·50	0·47	−0·032	857	19·5
86·1	−0·28	0·27	−0·018	1736	—
$86{\cdot}0_3$	−0·22	0·21	−0·014	1446	6·0
$85{\cdot}9_6$	−0·17	0·17	−0·011	1582	4·1
$85{\cdot}9_3$	−0·11	0·11	−0·007	1769	2·4
$85{\cdot}8_1$	−0·06	0·06	−0·004	2114	0·5
$85{\cdot}6_3$	+0·06	—	+0·004	2626	0·5
85·5	0·11	—	0·007	3176	—
$85{\cdot}3_5$	0·22	—	0·014	3368	7·3
85·2	0·28	—	0·018	3575	10·5
84·9	0·56	—	0·035	3986	21·6
84·5	0·85	—	0·054	4124	27·7
84·1	1·08	—	0·068	4157	29·7
83·8	1·25	—	0·079	4157	—
83·6	1·42	—	0·090	4198	32·9
83·5	1·48	—	0·093	4202	33·2
83·2	1·72	—	0·108	4171	30·2
80·2	3·86	—	0·244	4141	+24·9
79·8	4·18	—	0·264	4029	− 3·6
79·3	4·57	—	0·288	3990	−14·4
78·8	4·90	—	0·309	3836	−60·4

TABLE 2. *Partial molar heats of solution of potassium nitrate in nitric acid solutions at 0°, and the derived differential heats of dilution of nitric acid.*

KNO_3 (m)	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{KNO_3}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$ (cal. mole^{-1})
0·10	0·006	6590	—
0·22	0·014	6770	—
0·03	0·002	6540	—
0·095	0·006	6690	+1·0
0·35	0·022	6650(?)	—
0·51	0·032	6810	+2·4
0·21	0·013	6830	—
0·83	0·052	6490	−10·5
1·02	0·064	6330	−19·5
0·32	0·020	6840	+2·5
1·50	0·094	6200	−28·8
1·57	0·099	6140	−33·8
2·27	0·143	5240	−145

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[13] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 3472.

TABLE 3. *Partial molar heats of solution of sulphuric acid in nitric acid solutions at 0°, and the derived differential heats of dilution of nitric acid.*

H_2SO_4 (m)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\overline{H}_{H_2SO_4}$ (cal. mole^{-1})	$\overline{L}_{HNO_3}$ (cal. mole^{-1})	H_2SO_4 (m)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\overline{H}_{H_2SO_4}$ (cal. mole^{-1})	$\overline{L}_{HNO_3}$ (cal. mole^{-1})
0·05	0·003	6750	+0·2	1·11	0·070	4800	−131
0·19	0·012	7070	+2·0	1·78	0·112	3550	−238
0·35	0·022	7360	+7·5	1·91	0·120	3540	−241

TABLE 4. *Specific heats of nitric acid solutions.*

N_2O_5 as solute		N_2O_5 as solute		N_2O_5 as solute		N_2O_5 as solute	
N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)
89·7	0·424	86·7	0·396	85·5	0·415	83·4	0·423
89·3	0·425	86·3	0·404	85·2	0·420	83·0	0·422
89·0	0·413	86·1	0·407	84·6	0·428	80·4	0·448
88·6	0·408	86·0	0·408	84·0	0·426	80·0	0·456
88·2	0·399	85·9	0·410	83·9	0·424	79·5	0·462
87·7	0·392	85·8	0·412	83·7	0·420	79·0	0·465
87·2	0·394	85·7 *	0·413	83·5	0·423	78·6	0·467

* *I.e.*, 100% HNO_3.

KNO_3 as solute		KNO_3 as solute		H_2SO_4 as solute	
$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)
0·000	0·413	0·037	0·380	0·007	0·412
0·003	0·410	0·060	0·354	0·017	0·422(?)
0·004	0·412	0·092	0·388	0·026	0·414
0·009	0·408	0·096	0·384	0·065	0·419
0·010	0·407	0·102	0·376	0·108	0·422
0·018	0·404	0·142	0·375	0·116	0·423
0·024	0·400	0·283	0·366	0·125	0·425
0·027	0·391				

TABLE 5. *Densities* (*d*) *of potassium nitrate–nitric acid solutions* (*in g. cm.*$^{-3}$) *at* 0°, 10°, *and* 20°.

$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}
0·000	$1{\cdot}547_0$	$1{\cdot}529_3$	$1{\cdot}513_8$	0·225	$1{\cdot}732_3$	$1{\cdot}719_4$	$1{\cdot}709_0$
0·066	$1{\cdot}612_0$	$1{\cdot}596_7$	$1{\cdot}583_4$	0·283	$1{\cdot}756_5$	$1{\cdot}744_0$	$1{\cdot}733_4$
0·123	$1{\cdot}661_9$	$1{\cdot}647_9$	$1{\cdot}636_0$	0·416	$1{\cdot}817_8$	$1{\cdot}806_1$	$1{\cdot}797_1$

TABLE 6. *Densities* (*d*) *of sulphuric acid–nitric acid solutions* (*in g. cm.*$^{-3}$) *at* 0°, 10°, *and* 20°.

$\frac{m_{H_2SO_4}}{m_{H_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}
0·040	$1{\cdot}581_9$	$1{\cdot}565_6$	$1{\cdot}551_5$	0·273	$1{\cdot}700_5$	$1{\cdot}685_4$	$1{\cdot}673_3$
0·074	$1{\cdot}609_2$	$1{\cdot}592_7$	$1{\cdot}579_0$	0·373	$1{\cdot}729_2$	$1{\cdot}714_3$	$1{\cdot}702_4$
0·174	$1{\cdot}664_0$	$1{\cdot}648_0$	$1{\cdot}634_7$				

average composition. Values of the differential heat of dilution of nitric acid relative to pure nitric acid ($\overline{L}_{HNO_3}$) were estimated by the standard graphical method [14] using the formula

$$\overline{L}_1 = -\int_{m_2=0}^{m_2} (m_2/m_1)\,d\overline{H}_2 \qquad (m = \text{molality})$$

Values of this quantity are necessarily very sensitive to the shape of the $\overline{H}_2$ curve, especially as m_2/m_1 tends to zero. Since the points for potassium nitrate were more than usually scattered

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[14] Lewis and Randall, " Thermodynamics," McGraw-Hill, New York, 1923, p. 92.

in this region of composition (probably because it was added as a solid), it is difficult to assess the reliability of the solvent heats of dilution in this case. Nevertheless, the $\bar{L}_{HNO_3}$ values quoted would have to be several hundred per cent. in error to have the slighest effect upon the conclusions drawn in this work.

In the case of the water–dinitrogen pentoxide system, the specific heat was studied in detail in the neighbourhood of the composition of 100% nitric acid (85·7% N_2O_5) in order to see if a maximum occurred at this point, as has been recorded for 100% sulphuric acid.[13] Our observations show that no such maximum occurs at 0°, although a point of inflexion can be detected. Maxima do, however, occur at 84·9% and 89·5% N_2O_5, and minima at about 82% and 87·7% N_2O_5. Comparison with the very accurate determination of the specific heat of pure nitric acid by Forsythe and Giauque,[15] 0·420 cal. g.$^{-1}$ deg.$^{-1}$, suggests that the specific-heat data quoted here are probably low by 1·7% owing to a systematic error. The data were nevertheless used as they stood in the calculation of the heats of solution, since these measurements were made under the same experimental conditions.

Our results for the heats of solution of water agree well as to general trend and order of magnitude with those of Leclerc and Chédin[9] at 20°, but show some differences in detail, particularly between 84 and 85% N_2O_5, where their values are 200—500 cal. mole^{-1} more positive. The fact that our results show far less change in $\bar{H}_{H_2O}$ in the region 80—85% N_2O_5 can probably be explained by the difference in temperature of the measurements, since results showing the same trend as Leclerc and Chédin's can be obtained from the results at 0° and graphical estimates of the partial molar specific heat of water.

DISCUSSION

The differential heats of dilution of nitric acid have been plotted in the Figure. Water is the only one of the solutes which even approximates to the simple behaviour expected from a dissociation product. The curve for dinitrogen pentoxide begins very similarly to that for water, but diverges markedly at relatively low concentrations (~0·6 molal) and shows values of the solvent heat of dilution of hundreds of calories at concentrations less than 2 molal. The initial positive portion of the curve is very much less marked for potassium nitrate, whose behaviour differs considerably from that of water and dinitrogen pentoxide even in dilute solutions, whilst at greater concentrations this solute also produces large negative heats of dilution of the solvent.

If it is accepted that the main dissociation reaction for nitric acid is represented by the equation

$$s\mathrm{HNO_3} \rightleftharpoons \mathrm{H_2O} + \mathrm{NO_2}^+ + \mathrm{NO_3}^- + (s - 2)(\mathrm{HNO_3}\text{ of solvation})$$

the methods described in a former paper[7] can be used to show that it is improbable that even the water curve can be regarded as "ideal." From the differences between the partial heat contents of both the solute and the solvent at the composition of the pure solvent and at concentrations of solute high enough to suppress the solvent dissociation, the following results can be deduced (equations 25 and 29 of ref. 7 being applied to the results of this paper):

$$\Delta_d H \,.\, as/(a + b) = -1850 \text{ cal. mole}^{-1}$$
$$\alpha_0 \Delta_d H = -33 \text{ cal. mole}^{-1}$$

As in ref. 7, $\Delta_d H$ represents the heat of dissociation per mole of solvent, s the total number of molecules of nitric acid involved in the dissociation reaction, a and b the numbers of particles given per molecule of water and dinitrogen pentoxide respectively, and α_0 the fraction of solvent molecules dissociated in pure nitric acid. Combining the two equations, we have $\alpha_0/s = 0{\cdot}018a/(a + b)$, and on substitution of $a = 1$, $b = 2$, α_0/s becomes 0·006. The corresponding value of α_0/s at 0° derived from vapour-pressure determinations[16] is 0·04/3 × 0·96, *i.e.*, 0·014. Further, by applying the van't Hoff isochore, the vapour-pressure results at 0°, 10°, and 20° can be shown to yield a value of the total heat of the

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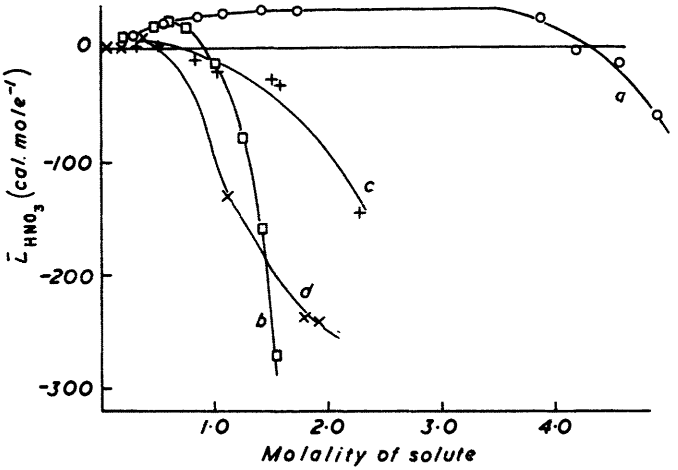
[15] Forsythe and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48.

[16] Lloyd and Wyatt, following paper.

dissociation reaction (*i.e.*, $s\Delta_dH$) which is practically independent of s and is about $-8{\cdot}9$ kcal. mole^{-1}. Thus the vapour-pressure data yield $\alpha_0\Delta_dH = -0{\cdot}014 \times 8900 = -124$ cal. mole^{-1}. That the thermal result is much smaller (-33 cal. mole^{-1}) suggests that the flattening of the partial molar heat content curve for water is probably deceptive, and that a thermal effect of opposite sign to the suppression of solvent dissociation is masking the latter effect even in the case of water.

This opposing thermal effect might, of course, be due to variable solvation, though it is rather unsatisfactory that considerable variation is required in regions of composition for which *fixed* solvation numbers were originally suggested by Chédin and his co-workers to explain their vapour-pressure data.[4, 5] Nevertheless, the thermal changes in these solutions are so large that it seems likely that some form of " chemical " explanation is necessary, as can be seen by comparison with the case of the solute sulphuric acid, in which changes in the extent of conventional chemical reactions are thought to be occurring.[6, 16] The simplest chemical explanation for dinitrogen pentoxide would be that it is not a completely strong electrolyte, but such an explanation contradicts the strong Raman evidence[1] for its complete ionisation.

The relative heat of dilution of nitric acid in the presence of various solutes.



Curve *a*, H_2O; curve *b*, N_2O_5; curve *c*, KNO_3; curve *d*, H_2SO_4.

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