Table II. Experimental Results, Cal. per Gram-Atom

$x_{Zn} = 0.198$		$x_{Zn} = 0.291$		$x_{Zn} = 0.342$	
T, °K.	$H^\circ_T - H^\circ_{298.15}$	T, °K.	$H^\circ_T - H^\circ_{298.15}$	T, °K.	$H^\circ_T - H^\circ_{298.15}$
373.8	438	373.9	450	373.8	450
403.7	638	403.9	646	403.4	635
451.4	928	403.7	625	403.9	635
498.3	1226	451.4	942	451.0	929
565.0	1644	...	...	496.4	1175
611.4	1931	564.9	1647	498.0	1220
637.5	2117	564.8	1663	565.0	1658
699.4	2525	611.4	1964	611.0	1977
752.6	2874	637.9	2142	638.1	2137
806.0	3243	699.3	2540	699.6	2559
807.3	3222	752.1	2909	752.5	2903
756.0	2912	805.7	3248	806.5	3302
697.1	2529	808.3	3296	807.4	3322
656.3	2235	755.6	2898	755.7	2933
606.7	1886	697.6	2544	697.4	2517
552.0	1577	656.1	2220	655.3	2281
488.9	1166	606.8	1937	606.3	1931
446.7	897	552.2	1571	...	...
405.7	639	488.8	1160	488.8	1169
345.3	276	447.0	899	447.3	898
...	...	405.8	643	405.7	643
...	...	...	...	344.9	275

Table III. Thermal Properties of Alpha Brass Alloys

	$x_{Zn} = 0.198$		$x_{Zn} = 0.291$		$x_{Zn} = 0.342$	
T, °K.	$H_T - H^{a}_{298.1}$	$C_p^{\,b}$	$H_T - H^{a}_{298.1}$	$C_p^{\,b}$	$H_T - H^{a}_{298.1}$	$C_p^{\,b}$
298.15	0	5.80	0	5.80	0	5.81
400	602	6.01	603	6.04	603	6.04
450	908	6.21	909	6.18	910	6.26
483	...	...	...	...	1129	6.98
500	1224	6.48	1233	7.14	1246	6.74
513	1310	6.70	...	...	...	...
550	1553	6.43	1568	6.43	1570	6.43
600	1873	6.42	1890	6.48	1893	6.52
700	2526	6.64	2549	6.70	2559	6.80
800	3195	6.75	3225	6.82	3249	7.00

[a] Calories per gram-atom. [b] Calories per degree per gram-atom.

sion which was measured from mercury displaced into a capillary tube. Each gram of mercury displaced represents 18.91 calories (*4*). The performance of the calorimeter was checked frequently by dropping a solid platinum capsule (*5*).

The experimental results are given in Table II. The heat contents are approximately 3% higher than results reported by Ruer and Kremers (*7*) and are much lower than the integrated C_p values measured by Kussmann and Wollenberger (*6*).

DISCUSSION

Manifestly, the results of Kussmann and Wollenberger are too high. No doubt there was a systematic error in their differential calorimeter. However, there seems to be no reason to doubt the validity of the anomalies found by them. The latent heat of their anomalies amount only to approximately 30 calories per gram-atom for each composition. There are indications of such anomalies in the heat content data but the effect is not so large. It is likely that in a drop calorimeter the alloys dropped from a disordered state would not become fully ordered during cooling, so that the high temperature measured heat contents would be low by perhaps 10 calories per gram-atom. The effect in this case can hardly be greater than the precision of the measurement, which amounts to ±15 calories per gram-atom.

The following procedure was adopted in obtaining the smoothed values of Table III. Heat capacity *vs.* temperature curves were drawn with values lower than those of Kussmann and Wollenberger, but having anomalies of the same shape. Integrated heat contents derived from these curves agreed with heat contents obtained more directly with deviations never more than 10 calories per gram-atom.

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Some New Unsymmetrically Disubstituted *N*-Nitroso Compounds, Hydrazines, and 5-Nitro-2-hydroxybenzal Derivatives

GEORG NEURATH and MICHAEL DÜNGER
Research Department, Zentrallaboratorium H. F. & Ph. F. Reemtsma, Hamburg, Germany

IDENTIFICATION of *N*-nitroso compounds via reduction by means of lithium aluminum hydride to hydrazines and formation of the 5-nitro-2-hydroxybenzal derivatives has been described earlier (*2, 3*). The properties of some new *N*-nitroso compounds, unsymmetrical hydrazines, and 5-nitro-2-hydroxybenzal derivatives are given.

EXPERIMENTAL

The unsymmetrical secondary ethylamines have been prepared by acetylation of primary amines followed by reduction with lithium aluminum hydride. This rarely used reaction for the preparation of secondary ethyl alkyl amines

Some new *N*-nitroso compounds, unsymmetrical hydrazines, and 5 nitro-2-hydroxybenzal derivatives therefrom have been prepared from a number of aliphatic, alicyclic, and heterocyclic secondary amines.

Table I. Unsymmetrical *N*-Nitroso Compounds, Hydrazines, and 5-Nitro-2-hydroxybenzal Derivatives

Amine Used	*N*-Nitroso-B.P., ° C./Mm. Hg	*N*-Amino-B.P., ° C./Mm. Hg	5-Nitro-2-hydroxybenzal Derivatives: M.P., ° C.	$\lambda_{max.}$[a] (nm): Neutral	$\lambda_{max.}$[a] (nm): Alkaline	Molar Extinction: Neutral	Molar Extinction: Alkaline	Formula	Analysis[b]: C	Analysis[b]: H	Analysis[b]: N
Ethyl-*n*-propyl	72–73/$_{12}$	115–118/$_{760}$	45–46	297	340	30,100	18,900	$C_{12}H_{17}N_3O_3$	57.42	6.83	16.74
					420		11,200		57.30	6.78	16.89
Ethyl-iso-propyl	70/$_{12}$	110/$_{760}$	64–67	296	338	26,000	13,700	$C_{12}H_{17}N_3O_3$	57.42	6.83	16.74
					420		12,100		57.14	7.00	16.80
Ethyl-*n*-butyl	87–90/$_{14}$	140–145/$_{760}$	43–44	298	340	29,700	18,700	$C_{13}H_{19}N_3O_3$	58.92	7.23	15.86
					420		10,700		59.65	7.21	15.59
Ethyl-iso-butyl	81–83/$_{12}$	135/$_{760}$	28–28.5	298	340	30,800	18,900	$C_{13}H_{19}N_3O_3$	58.92	7.23	15.86
					432		9,600		58.44	7.11	15.67
Ethyl-*sec*-butyl	79–81/$_{12}$	140–145/$_{760}$	40–42	299	338	30,200	21,200	$C_{13}H_{19}N_3O_3$	58.92	7.23	15.86
					430		9,800		59.69	7.26	15.61
Ethyl-*tert*-butyl	75–77/$_{15}$	120/$_{760}$	92	298	340	33,200	21,000	$C_{13}H_{19}N_3O_3$	58.92	7.23	15.86
					430		9,300		59.14	7.08	15.65
Ethyl-*n*-pentyl	95–97/$_{14}$	157–160/$_{760}$	liquid								
Ethyl-iso-pentyl	95–99/$_{15}$	153–160/$_{760}$	liquid								
Ethyl-allyl	68–69/$_{14}$	115–120/$_{760}$	35.5–36	296	340	29,800	17,600	$C_{12}H_{15}N_3O_3$	57.88	6.07	16.88
					420		11,400		57.59	6.04	17.06
Methyl-(β-phenethyl)	85/$_{0.15}$	130/$_{30}$	108–109	295	340	32,900	18,400	$C_{16}H_{17}N_3O_3$	64.27	5.73	14.05
					420		11,050		64.30	5.71	14.16
2-Methylpyrrolidine	113/$_{27}$	131–133/$_{760}$	110.5–111.5	298	343	29,600	19,300	$C_{12}H_{15}N_3O_3$	57.88	6.07	16.88
					424		11,700		57.86	6.03	16.78
2,5-Dimethylpyrrolidine	87–89/$_{12}$	140–144/$_{760}$	102–103	300	343	28,100	18,600	$C_{13}H_{17}N_3O_3$	59.37	6.52	15.98
					425		9,700		59.80	6.45	15.41
2-Pipecoline	100–101/$_{13}$	157–161/$_{760}$	143–144	294	347	27,000	15,100	$C_{13}H_{17}N_3O_3$	59.37	6.52	15.98
					413		12,100		59.34	6.60	16.10
3-Pipecoline	99/$_{13}$	165–168/$_{760}$	143–144	292	344	27,200	15,000	$C_{13}H_{17}N_3O_3$	59.37	6.52	15.98
					415		12,500		59.43	6.58	15.90
4-Pipecoline	100/$_{13}$	165–168/$_{760}$	155–156	292	345	27,200	14,800	$C_{13}H_{17}N_3O_3$	59.37	6.52	15.98
					418		12,500		59.16	6.60	15.93
2,6-Lupetidine	103–104/$_{12}$	169–173/$_{760}$	112–114	302	351	23,100	13,500	$C_{14}H_{19}N_3O_3$	60.70	6.91	
					401		14,700		60.07	6.67	
2-(Methylaminomethyl)-pyridine	142–144/$_{12}$	100–110/$_{11}$	137–138.5	293	343	28,500	17,300	$C_{14}H_{14}N_4O_3$	58.79	4.93	19.59
					421		11,600		58.96	5.00	19.79
3-(Methylaminomethyl)-pyridine	160–161/$_{13}$	120–125/$_{15}$	92–93	292	343	28,800	16,600	$C_{14}H_{14}N_4O_3$	58.79	4.93	19.59
					420		11,800		58.71	5.08	19.47
4-(Methylaminomethyl)-pyridine	167–168/$_{16}$	115–120/$_{12}$	134	292	343	27,900	16,400	$C_{14}H_{14}N_4O_3$	58.79	4.93	19.59
					420		11,300		58.93	5.05	19.56
6-(Methylaminomethyl)-2-methylpyridine	144–146/$_{11}$	115–120/$_{12}$	107–109	293	342	27,600	16,800	$C_{15}H_{16}N_4O_3$	60.05	5.38	18.68
					421		11,100		60.02	5.40	18.60

[a] Measured in methanol respectively after adding 3 drops of 3% methanolic sodium hydroxide solution to a 0.002% solution of substance. Cell volume 2 cc., thickness of layer 1 cm. [b] The first value given is calculated; the second, found.

delivered the amines in an easy manner, however, with yields of 15 to 35% only.

The *N*-nitroso compounds were obtained from aqueous hydrochloric acid solutions of secondary amines by reaction with sodium nitrite. After the addition of sodium nitrite, the mixture was heated to 50° C. for 1 hour, extracted with dichloromethane after cooling, and the solutions were dried with calcium chloride. The solvent was evaporated, and the *N*-nitroso compounds were purified by vacuum distillation.

The *N*-amino compounds—unsymmetrical hydrazines—have been prepared by reduction of the corresponding *N*-nitroso compounds with lithium aluminum hydride as described earlier (*1-4*).

5-Nitro-2-hydroxybenzal derivatives have been obtained from the reaction with 5-nitro-2-hydroxybenzaldehyde—Schuchardt, Munich, Germany—in ethanol (*3*). UV and visible measurements were taken with a spectrophotometer Beckman DK 1. The ultraviolet spectra and elemental analyses are given in Table I. Boiling and melting points are uncorrected.

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Thermodynamic Properties of Sea Salt Solutions

R. W. STOUGHTON AND M. H. LIETZKE
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Thermodynamic properties of sea salt solutions have been recalculated in view of re-evaluations of the properties of NaCl solutions as a function of temperature and an experimental comparison of the osmotic coefficients of NaCl and sea salt solutions at 25° C. Boiling point elevations (BPE's) were evaluated in the ranges 2 to 28 wt. % salts and 25° to 260° C.; theoretical minimum energies of recovery of water from sea water, in the ranges of 0 to 100% recovery and 25° to 200° C.; and osmotic pressures, in the ranges 1 to 25 wt. % solids and 25° to 100° C. The new values show greatest deviations from the previous calculations at high concentrations and low temperatures. The largest change is a 12% increase in BPE at 25° C. and 28 wt. % solids. In general, where there is a change, the new values are higher; the values of BPE at the highest concentrations and temperature are exceptions—e.g., a 2% decrease at 28 wt. % solids at 260° C.

IN PREVIOUS WORK (*15, 16*) vapor pressures of sea salt solutions were calculated from 25° to 175° C. and from 1 to 28 wt. % solids by using the following extended Debye-Hückel equation and parameters obtained from measured osmotic coefficients of sodium chloride solutions.

$$\phi = 1 - \frac{S}{A^3 I}\left\{\left[1 + A\,(I)^{1/2}\right] - 2\ln\left[1 + A\,(I)^{1/2}\right] - \frac{1}{1 + A\,(I)^{1/2}}\right\} + BI' + CI'^2 \quad (1)$$

In Equation 1, S is the appropriate Debye-Hückel limiting slope for either a single electrolyte or an electrolyte mixture, A is the Debye-Hückel parameter (here set equal to 1.5), I is the ionic strength, I' is a concentration term discussed below, while B and C are adjustable parameters. The latter parameters for NaCl solutions were evaluated to 270° C. (*15, 16*) from osmotic or activity coefficients from the literature up to 4*m* to 100° (*11*) and up to 3*m* from 100° to 270° C. (*4*).

In applying Equation 1 to sea salt solutions, the values of B and C for NaCl solutions were used with three different concentration terms for I':

$$I' = \tfrac{1}{2}\sum_i m_i Z_i^2 = I \quad (2a)$$

$$= \tfrac{1}{2}\sum m_i\,|Z_i| \quad (2b)$$

$$= \tfrac{1}{2}\sum m_i \quad (2c)$$

where m_i is the molality and Z_i the charge of any ionic constituent. (For a 1-to-1 electrolyte all three expressions are equal to the molality.)

The calculated vapor pressures were compared with the measured values of Arons and Kientzler (*1*) at 25° and 35° C. and those of Higashi, Nakamura, and Hara (*8*) from 25° to 175° C. and to 28 wt. % solids. The agreement was best when Equation 2c was used and poorest when 2a was used. Vapor pressure measurements of Forrest and Worthley (*2*) from 25° to 100° C. gave better agreement with Equation 2a than with 2b or 2c, although the scatter of the various experimental values (*1, 2, 8*) was much greater than the difference between the values calculated using Equations 2a and 2c; even at 28 wt. % solids the scatter was greater by at least a factor of two than the difference between the two sets of calculated values. Because the measurements of Arons and Kientzler (*1*) appeared to be the most precise ones available, the authors concluded (*15, 16*) that Equation 2c gave best results for the thermodynamic properties of sea salt solutions.

Recently, Rush and Johnson (*12*) have measured osmotic coefficients of synthetic sea salt solutions in the ionic