chloride in absolute ethyl alcohol in the molar ratios of two to one and four to one.

(3) Exposure of anhydrous ferric chloride crystals to aniline vapor in a desiccator, in the presence of P_2O_5.

Anhydrous ferric chloride was obtained in 1-oz. bottles from Eimer and Amend Co. and freshly opened for each solution. Solution concentrations were obtained by chloride analysis. Samples precipitated in benzene or made from the vapor reaction were subjected to X-ray diffraction without recrystallization. Samples precipitated from alcohol were recrystallized from 95% benzene–5% absolute alcohol solvent.

The X-ray diffraction photographs were taken with CuK_α radiation using a nickel foil filter and a 14.32-cm. diameter camera. Two distinct crystalline patterns appeared from the samples. The complex formed from the aniline vapor and ferric chloride and from the one to one molar ratio in benzene had the following pattern.

d	I/I_0	d	I/I_0	d	I/I_0
11.27	0.07	2.14	0.67	1.64	.35
5.53	.86	2.05	.20	1.53	.45
4.40	.25	1.99	.14	1.48	.15
4.05	.54	1.96	.04	1.39	.17
3.52	.25	1.88	.17	1.37	.31
3.03	.96	1.83	.32	1.28	.12
2.79	.37	1.80	.36	1.24	.04
2.21	1.00	1.74	.27		

d = interplanar spacing measured in ångstrom units
I = intensity of the diffraction line (arbitrary units)
I_0 = intensity of the strongest line

The complex precipitated by the reaction of two and four moles of aniline to one of ferric chloride in alcohol, and six and twelve moles of aniline to one of ferric chloride in benzene had the following pattern.

d	I/I_0	d	I/I_0	d	I/I_0
11.27	1.00	3.90	0.57	2.29	0.58
10.32	.98	3.70	.38	2.14	.25
8.63	.98	3.52	.38	2.05	.38
7.70	.52	3.34	.49	1.96	.45
6.66	.36	3.15	.50	1.88	.45
5.65	.43	3.03	.61	1.83	.32
5.25	.54	2.89	.42	1.76	.25
4.99	.36	2.79	.18	1.72	.14
4.78	.34	2.70	.50	1.64	33
4.40	.66	2.59	.32	1.61	.33
4.05	.30	2.53	.78		

Relative intensities were taken from densitometer tracings of the film, treated according to the method described by Gardner, Cohen and Antia.[6] The relative intensities vary to some extent for different preparations. However, the specimens were packed on a wedge holder without standardization of dimensions or shape beyond the limits imposed by packing the specimen in place. The intensities given were taken from the photographs of the aniline vapor reaction and of the precipitate from the one to six molar ratio in benzene.

The line of the 11.27 Å. plane was just barely visible in the first pattern ($I//I_0$ = 0.07) and may have been due to traces of the second complex where I/I_0 = 1.00 for the 11.27 plane. Lines representing the 10.32 and 8.63 Å. planes of the second pattern (I/I_0 = 0.98) were not visible on the first pattern, but corresponded to small rises in the densitometer tracings. The lines of 1.00 and 0.86 relative intensity of the first pattern were missing in the second pattern, although some of the less intense lines are common to both. In comparing the patterns given here with spacings listed for anhydrous $FeCl_3$,[7] it is found that the 5.9 Å. spacing (I/I_0 = 0.32) of $FeCl_3$ is missing in both patterns, while the 2.68 Å. (I/I_0 = 1.00) and 5.7 Å. (I/I_0 = 0.32) spacings are missing in the first pattern. Some of the other spacings are close enough to possibly coincide, but a number of the more intense lines of the ferric chloride–aniline complexes are not listed, or are of very low intensity, for $FeCl_3$.

Iron analysis, by reduction with $SnCl_2$ and oxidation with dichromate showed 21.8% Fe for the sample from a one to one molar ratio solution in benzene and 16.3 and 17.0% Fe for the samples from six to one and twelve to one ratios of aniline to ferric chloride in benzene. The theoretical amount of iron in a one to one molar ratio compound would be 21.9% and in a two to one molar ratio compound 16.7%. The absence of solvent of crystallization in the samples was indicated by the identity of diffraction patterns for the first compound formed both with and without solvent and by the identity of the diffraction patterns of the second compound made from both alcohol and benzene solutions. The results indicate that the molar ratios one to one and two to one of aniline to ferric chloride were the compounds formed and there was no evidence of any higher ratios comparable to the acid hexa-anilinium salts reported by previous investigators.[2-4]

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The Specific Heats of Concentrated Sodium and Potassium Bromide Solutions at 25 and 30°

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The range of concentration covered in the specific heat measurements on dilute sodium and potassium bromide solutions made by Randall and Rossini[1] extended to the one molal level. Results are here reported for higher concentrations.

Experimental Details

Calorimeter.—An isothermal-jacket calorimeter of essentially conventional design was employed. The calorimeter vessel, which held about 730 ml. of solution, was made of brass and heavily silver plated; it was supported, on three Micalex cones, in a submarine jacket in an oil thermostat controlled by a mercury thermoregulator.

The calorimeter heater was made from enameled constantan wire, wound over thin mica insulation on a brass spool and covered with a close-fitting brass sleeve which was soldered in place. One end of the coil was connected directly to the brass shell; the other lead was taken out of the housing through a Kovar hermetic seal, and thence out of the calorimeter vessel through a brass tube which was one of the supports holding the heater assembly to the vessel cover. The calorimeter stirrer operated inside the cylindrical heater unit. The calibrations of the standard cell, standard resistance and voltage divider used in the electrical measurements were checked by the Electrical Standards Laboratory

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(1) M. Randall and F. D. Rossini, This Journal, **51**, 323 (1929).

of the University of Wisconsin. The frequency of the tuning-fork controlled power supply used to operate the timing clock was determined by use of the time signals from station WWV.

Temperature measurements were made by use of a Leeds and Northrup Co. calorimetric type platinum resistance thermometer, calibrated by the National Bureau of Standards. The Rubicon Company Mueller bridge employed was also calibrated. The corrected temperature rise was calculated on the standard assumptions of Newton's law and a constant heat of stirring. The required time–temperature readings were recorded photographically.[2] A temperature rise of about three degrees was regularly used; the initial conditions were adjusted so that the mean temperature of the interval was very close to 25 or 30°. The heat capacity of the calorimeter was determined with a precision of ±0.03%, by use of water as a standard; the reference data were those of Osborne, *et al.*[3]

Solutions.—Concentrated stock solutions of reagent grade sodium and potassium bromide were diluted quantitatively to lower concentrations as required. All solutions used were analyzed gravimetrically by the silver bromide method, to avoid the uncertainty otherwise present due to the water retained by the salts even after prolonged drying. The molalities specified are considered accurate to ±0.03% or better; calibrated weights were employed, and all results correspond to weights *in vacuo*.

Experimental Results

The results obtained are presented in Table I. Except where noted the values given represent the average of duplicate or (usually) triplicate determinations in which the deviation from the mean averaged ±0.05%. The apparent molal heat capacity of the solute, in defined calories deg.$^{-1}$ mole^{-1}, was calculated for each solution (for the solvent the specific heat data of Osborne, *et al.*,[3] were used) and by the method of least squares there were obtained the following equations, which are presented for interpolation purposes only:

$$\text{KBr: }\begin{cases}25°,\ \phi_{c_p} = -38.167 + 20.460m^{1/2} - 2.645m\\ 30°,\ \phi_{c_p} = -31.135 + 14.111m^{1/2} - 1.133m\end{cases}$$

$$\text{NaBr: }\begin{cases}25°,\ \phi_{c_p} = -29.715 + 20.049m^{1/2} - 1.625m\\ 30°,\ \phi_{c_p} = -24.467 + 16.453m^{1/2} - 1.034m\end{cases}$$

The deviations of the experimental values for the specific heats from the comparison values given by the preceding equations average ±0.04%, in confirmation of the internal consistency of the results at the different concentrations involved. It is considered that an accuracy of the order of ±0.15% can be assigned to the specific heat data reported. This claim is supported by a comparison of the present results with those derived from the work of Randall and Rossini[1]; for one molal solutions at 25°, the deviation between the two sets of results amounts to 0.16% for the potassium bromide solution, and 0.08% for the sodium bromide solution, the present results being the lower in each case. For proper comparison, the apparent molal heat capacities given by Randall and Rossini were converted to defined calories, and the specific heats calculated by use of the data of Osborne, *et al.*,[3] for the solvent.

TABLE I

SPECIFIC HEATS OF SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS

m = molality solute, C_p = specific heat, defined calories deg.$^{-1}$ g.$^{-1}$.

m	C_p, 25°	C_p, 30°
A. Sodium Bromide Solutions		
0.9675[a]	0.8983	....
0.9990	.8955	0.8973
2.2050	.8078	.8102
2.2165[a]	.8076	....
3.8495	.7247	.7256
5.9985	.6534	.6528
8.3735	.6028	.6020
B. Potassium Bromide Solutions		
0.9985	0.8746	0.8764
1.9960	.7838	.7850
2.9945	.7133	.7142
3.9795	.6561	.6576
4.9985	.6082	.6095
5.5245	.5875	.5885

[a] One run only.

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Polarographic Reduction of the Nitrobenzaldehydes

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Korshunov and Sazanova recently[1] reported a study of the polarography of *o*-, *m*- and *p*-nitrobenzaldehydes in buffered ethanol–water media. They found abnormally high diffusion currents for the *ortho* isomer and three waves for the *para* isomer in basic solution, suggesting secondary reactions between the groups in the molecule and reduction of the resulting products.[2] Since these results do not appear consistent with usual carbonyl behavior we decided to repeat these experiments. We found that the behavior of these compounds upon polarographic reduction is consistent with the known behavior of both the nitro and carbonyl groups.

The results are given in Table I for the *meta* and *para* isomers and in Table II for the *ortho* isomer. The *meta* compound reduces in two steps at low *p*H values. The first wave corresponds to the reduction of the nitro group to the hydroxylamine, four electrons being consumed. The second wave is a combination of the second nitro wave (reduction of the hydroxylamine to the amino group) and the first acid carbonyl wave. The second acid carbonyl wave is masked by liberation of hydrogen in these solutions. Since the hydroxylamine is stable toward further reduction at higher *p*H values, the second wave at *p*H 6.1 is evidently the first carbonyl wave alone. The current at this *p*H corresponds to this interpretation. At still higher *p*H values the second wave corresponds to the complete reduction of the carbonyl group to the carbinol. The current does not drop to half-value, as with the *ortho* and *para* isomers (below) and a wave at higher poten-

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