From this standpoint, the low value for $\partial\Phi/\partial C^{1/2}$ for hydrochloric acid is due to the ease with which the hydrogen ion fits into the existing structure of water, and only the chloride ion is effective in changing that structure.

The observed increase in the partial molal volume of hydrochloric acid at constant total volume ionic strength when the hydrogen ion is replaced by sodium ion must be due to the greater effect of the sodium ion on the water structure. The fact that the increase is a linear function of the amount of sodium ion added is in harmony with this view. The decrease in the partial molal volume of sodium chloride on replacing the sodium ion with hydrogen ion is explained in the same manner.

Summary

The apparent and partial molal volumes of sodium chloride and hydrochloric acid have been determined in water and in mixed solutions.

The partial molal volumes of sodium chloride are decreased at constant total volume ionic strength by the addition of hydrochloric acid. The decrease is a linear function of the acid concentration.

The partial molal volumes of hydrochloric acid are increased at constant total concentration by the addition of sodium chloride. The increase is a linear function of the sodium chloride concentration.

The partial molal volumes of water have been determined in the mixed solutions. At a given concentration they are largest in solutions of pure hydrochloric acid and least in pure sodium chloride solutions.

The observed behavior may be interpreted in terms of changes in the structure of water caused by ions in solution.

An X-Ray Investigation of the System Cr2O3-NiO[1]

BY L. THOMASSEN

The present work has for its purpose to investigate the phases that are present in the above system. This equilibrium diagram is of considerable practical interest since the scale formed on the common electric resistance wires of nominal composition 80% Ni 20% Cr mainly consists of these oxides.

An earlier investigation[1a] has shown that the compound $NiO\cdot Cr_2O_3$ is formed when mixtures of this composition are heated with a mineralizer such as potassium chloride. This compound crystallizes in the widely distributed spinel type of structure.[2] Regarding the rest of the system, no information seems to be available. Similar systems with ferric oxide as the trivalent metal oxide have been investigated.[3]

Experimental Procedure

Most of the samples were made by mixing the oxides in the proper proportions, grinding them intimately and heat-

ing them with potassium chloride in platinum crucibles at 1000° for one to two hours. An electric furnace with automatic temperature control was used for the heating. After fusion, the crucibles were taken out and allowed to cool rapidly in the air. Unless changes take place very rapidly, the material as investigated would represent equilibrium conditions at 1000°.

The chromic oxide used was obtained by heating c. p. ammonium chromate to 900°. Upon heating a sample to 1000° for ten hours, a loss of 0.2% was obtained. According to Wretblad[4] there is no danger of forming CrO_2 when heating Cr_2O_3 to 1000° in oxygen and there should be still less chance of forming such a compound in air.

The nickel oxide was obtained by heating c. p. nickel nitrate, cobalt free, to 400°. The oxide obtained analyzed 77.3% Ni instead of 78.5% theoretically. Both the weight loss of the chromic oxide and this deviation from the theoretical composition were taken into account when making up mixtures to be fused.

After fusion the samples were washed carefully to remove all the potassium chloride present. Invariably, the first wash water was yellow, showing that some chromic oxide was oxidized to chromate.

Boric oxide was also tried as a mineralizer but with the straight $NiO\cdot Cr_2O_3$ composition, a number of extra lines appeared on the X-ray diagram. This observation confirmed the doubts expressed by Holgersson[1a] regarding the advisability in using boric oxide in this synthesis.

(1) Original manuscript received July 31, 1939.

(1a) S. Holgersson, Z. anorg. allgem. Chem., 204, 382 (1932).

(2) See for instance S. Holgersson, "Lunds Universitetets Arsskrift," N. F. Avd. 2, Vol. 23, Nr. 9; G. L. Clark, Am. J. Sci., 22, 539 (1931).

(3) A. E. van Arkel, E. J. W. Verwey and M. G. van Bruggen, Rec. trav. chim., 55, 331, 340 (1936).

(4) Wretblad, Z. anorg. allgem. Chem., 189, 329 (1930).

The method of grinding and pressing together the oxides in the proportions to form spinel and heating them at 1000° for two hours did not produce complete combination since both the nickel and chromium oxide lines were present besides the spinel lines.

Some of the samples used were produced by co-precipitation of nickel carbonate and chromium hydroxide with sodium carbonate. Proper proportions were taken out of solutions of known contents of $NiCl_2$ and Cr_2Cl_6, precipitated out of hot diluted solutions, filtered, washed carefully, dried and ignited, keeping the samples at 1000° for ten hours.

The porportions used may be seen from Table I. The samples with an asterisk are those prepared by co-precipitation. The sample of straight spinel composition was analyzed for nickel and gave 33.0% NiO instead of theoretically 32.6%.

The phases present were identified by X-ray diffraction patterns, using filtered chromium radiation. The X-rays were produced by a modified Siegbahn–Hadding tube with a plated chromium target. The samples were made up by mixing the powders with Duco Household Cement and rolling them out into rods of about $^3/_{10}$ mm. diameter. For lattice parameter determinations c. p. sodium chloride was mixed with the sample to provide a variable correction factor. The lattice constant of sodium chloride was taken to be 5.626 Å.[5]

Computations of lattice parameters are not given in this work since the lattice constants of the substances investigated are all known, and the precision determinations did not differ much from those in the literature. For more detailed information on the method of computation, see for instance L. Thomassen, Z. physik. Chem., 135, 388 (1928); ibid., B2, 340 (1929).

Discussion of Results

The results obtained are shown in Table I. It will be seen that the only compound in the system is the spinel. A separate experiment shows that this compound remains cubic when cooled slowly from 1000° in the electric furnace. It also will be noticed that chromic oxide on one side of the spinel composition and nickel oxide on the other side appear when present in small excess over the 1:1 ratio. This means that if solid solubility exists, the amounts dissolved are small at the temperature of formation.

In order to investigate whether solid solubility could be detected in lattice dimensions, diffraction diagrams of the samples 0.95 $NiO·Cr_2O_3$, $NiO·Cr_2O_3$ and 1.1 $NiO·Cr_2O_3$ were made, using sodium chloride as reference substance. Within experimental error, the measurements gave the same results, namely, 8.282, 8.282 and 8.284 Å., respectively, with an error of ±0.003 Å. This compares to the lattice constant given by Holgersson[1a] of 8.30 Å., also using sodium chloride as a

(5) T. Barth and O. Lunde, Z. physik. Chem., 126, 417 (1927).

reference substance. Since the lines were comparatively broad, no precision back reflection pictures were taken.

TABLE I

Mols of NiO per Mol Cr₂O₃	Phases present
0.25	Cr₂O₃
* .25	Cr₂O₃ + spinel
* .30	Cr₂O₃ + spinel
.375	
.50	
.75	Cr₂O₃ + increasing amount of spinel on increasing NiO
.87	
.95	
1.0	Spinel only
1.1	
1.25	
1.50	
1.75	
2.0	NiO + decreasing amount of spinel on increasing NiO
4.0	
8.0	
*20	
*50	
*100	NiO

From the table it will be seen that the samples with high chromic oxide content give conflicting results regarding phases present, depending on whether they are produced by co-precipitation or by fusion. The meaning of this observation is not clear and this question of the solubility of nickel oxide in chromium oxide will be treated in another paper.

Among the samples with high nickel oxide content, the one with 100 mols of nickel oxide is the only one which does not show spinel lines. By the technique used in this investigation the diffraction method will not detect phases present below one to three per cent. The one mol spinel which would be formed would hardly register in a diffraction diagram when diluted with 99 mols of NiO. Taking into account that the spinel lines were hardly discernible when present in the double concentration and in amounts which are at the threshold of detection, it seems probable that the solubility of Cr_2O_3 in NiO is very small.

As is well known, the nickel oxide crystallizes in the sodium chloride type of structure, and several investigators have found a lattice constant $a = 4.17$ Å.[6,7] The present investigation also gave $a = 4.170 ± 0.003$Å.

(6) G. Lunde, Z. anorg. allgem. Chem., 163, 345 (1927).
(7) S. B. Hendricks, M. E. Jefferson and J. F. Schultz, Z. Krist., 73, 376 (1930).

It is a pleasure to acknowledge the assistance of Mr. George Manning who made up most of the preparations and also took some of the X-ray diagrams.

Summary

1.   In the equilibrium diagram Cr_2O_3–NiO the spinel $NiO\cdot Cr_2O_3$ is the only compound present.

2.   At 1000° the solubility of nickel and chromium oxide in the spinel is small.

3.   Nickel oxide does not dissolve chromium oxide.

The Acid Catalyzed Esterification of Aliphatic Acids

BY HILTON A. SMITH

In two previous papers the effect of the alkyl chain of an aliphatic organic acid on its velocity of esterification in methanol was discussed. The first[1] dealt with normal acids only, and the second included simple methyl substituted acids.[2] The present paper reports a study of the velocity of esterification of certain other branched-chain aliphatic acids, together with a discussion of the general effect of alkyl substitution on reaction velocity.

Experimental

Methanol was obtained in a pure dry state, as in previously reported work, by careful fractionation of 99.5% methyl alcohol using a 5-foot (1.5-meter) spiral column. The material used distilled at a constant head temperature.

Trimethylacetic acid and diethylacetic acid were obtained by fractionation of the Eastman Kodak Co. acids in a 5-ft. (1.5-meter) Vigreux type column. The former analyzed 99.5% by titration with standard base and melted at 35.4°. The latter analyzed 99.9%.

β-Methylvaleric acid[3] was prepared by the malonic ester synthesis from diethyl malonate, s-butyl bromide and sodium ethylate. Ethyl s-butylmalonate was prepared by the method indicated in "Organic Syntheses" for its normal isomer,[4] and this ester converted to β-methylvaleric acid by hydrolysis and decarboxylation. The crude acid was purified by fractionation in a 5-ft. Vigreux type column. The sample used for esterification purposes distilled at constant head temperature (±0.05°) and analyzed 100.0% by titration with standard base.

Dipropylacetic acid, dibutylacetic acid, and di-isobutylacetic acid were prepared in a manner similar to that used for β-methylvaleric acid. The di-alkyl substituted ethyl malonates were prepared by introducing two alkyl groups into the ester using sodium ethylate and the necessary alkyl iodide. The substituted malonic ester was hydrolyzed and decarboxylated, and the crude acids purified by reduced pressure distillation in a 5-ft. Vigreux column.

Each of the samples used in the esterification studies analyzed at least 99.6% by titration with standard base.

The method employed to obtain the rate constants for the hydrion-catalyzed esterification of these acids was similar to that previously described[1] with the exception that the glass-stoppered bottles were replaced by small Pyrex vials the openings of which were fitted with a glass plug. A rubber sleeve around the opening and the plug prevented possible loss of solvent by evaporation. This was necessary because of the slowness of the runs, some of them lasting for several weeks.

Experimental Results and Calculations

The rate constants were calculated from Goldschmidt's equation

$$k = \frac{(r + a) \ln [a/(a - x)] - x}{(\text{catalyst})rt}$$

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst is hydrogen chloride. The values of the constant r used were those obtained in earlier work for normal aliphatic acids.[1]

The values of the reaction velocity constant, k, were quite constant for reactions run at the lower temperatures. This is illustrated in Table I for the esterification of trimethylacetic acid at 20°.

TABLE I

ESTERIFICATION OF CH_3OH AND $(CH_3)_3CCOOH$ AT 20°
$a = 0.500$, $(HCl) = 0.005$

t, min.	$(a - x)$	k (liters $\times$ moles^{-1} $\times$ sec.$^{-1}$)
190	0.465	0.00139
1047	.361	.00141
1897	.298	.00140
3304	.227	.00141
5611	.157	.00139
11593	.073	.00133

For the slower runs at elevated temperatures, the rate constants fall off consistently with increasing reaction. The greatest falling off oc-

(1)   Smith, THIS JOURNAL, **61**, 254 (1939).
(2)   Smith, *ibid.*, **61**, 1176 (1939).
(3)   The author is greatly indebted to Mr. A. S. Raff for his aid in the preparation of this compound.
(4)   "Organic Syntheses," Coll. Vol. I, p. 245.