ON THE FREE ENERGY OF NICKEL CHLORIDE.

By M. deKay Thompson and M. W. Sage.

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1. Introduction.

In a previous paper[1] by one of the authors, calculations of the free energy have been made, from potential measurements, of all compounds for which the necessary data already existed, but so far no direct free energy determinations of salts have been made on the principle underlying these computations. The object of the following investigation is to determine the free energy of nickel chloride by this method, for a full description of which reference may be made to the above paper. Briefly, for the salt here investigated it consists in measuring the electromotive force of the cell:

$$\text{Nickel} \mid \text{Saturated sol. of } NiCl_2 \mid Pt + Cl_2.$$

If the salt contained no water of crystallization and the chlorine were at a pressure of 76.0 cm. of mercury the free energy increase of one mol of the salt would be

$$\Delta F = -2EF$$

where E is the measured electromotive force and F is one faraday.[2] On account of the fact, however, that nickel chloride takes on water of crystallization, a slight modification of the ideal process by which the nickel and chlorine are allowed to unite reversibly is necessary.

Nickel chloride, in contact with water, forms the hydrate $NiCl_2.6H_2O$.[3] A hydrate with four molecules has also been detected,[4] but this existed in contact with a saturated solution at a temperature about 80° and, consequently, would not enter into this process. According to Lescoeur, the anhydrous salt is produced directly on dehydrating that with two molecules of water. This conclusion is based on vapor pressure measurements at 100°, starting with $NiCl_2.2H_2O$ and making measurements after successive evacuations of the apparatus. The final analysis of the hydrate gave $NiCl_2.1.45H_2O$, which might be a mixture of $NiCl_2.2H_2O$—$NiCl_2.1H_2O$ or $NiCl_2.2H_2O$—$NiCl_2$. Although this point is doubtful, it will be assumed that there is no hydrate with one molecule of water.

The salt in contact with the saturated solution of nickel chloride is then $NiCl_2.6H_2O$, and in the ideal process, as nickel and chlorine unite and precipitate from the solution, water would be removed from the solution, and in order to keep the amount of water in the solution con-

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[1] This Journal, 28, 731 (1906).

[2] To bring the conception of free energy increase into conformity with the present more general usage, the terms involving RT are included in ΔF. See Haber, "Thermodynamik technischer Gaserak," p. 9.

[3] Lescoeur, *Ann. chim. phys.* [6], 19, 533 (1890).

[4] Etard, *Ibid.* [7], 2, 545 (1894).

stant, this has to be supplied reversibly and isothermally at the same rate at which it is removed. This may be accomplished by means of isothermal distillation, as follows: Consider water at the temperature in question enclosed in a cylinder with a frictionless piston. Allow six moles to evaporate reversibly and isothermally. The free energy increase of the system is $-6RT$. Now separate the six mols and allow them to expand reversibly and isothermally until the pressure is equal to the vapor pressure of a saturated solution of $NiCl_2.6H_2O$. The free energy increase of the system in expansion is

$$-6RT \log \frac{p_{H_2O}}{p_{sol}},$$

if p_{H_2O} is the vapor pressure of water at T° absolute and p_{sol} is the vapor pressure of the solution. The water vapor may now be condensed reversibly into the solution, at the same rate at which it is removed by the salt crystallizing out. The free energy increase of the system in this last step is $+6RT$, so that the net result is the free energy increase, $-6RT \log \frac{p_{H_2O}}{p_{sol}}$.

$$\Delta F_1 = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} \qquad (1)$$

is therefore the free energy of $NiCl_2.6H_2O$, referred to gaseous chlorine at atmospheric pressure and liquid water, both at T° absolute.

The free energy of $NiCl_2.2H_2O$ may be obtained from this by allowing $NiCl_2.6H_2O$ to change reversibly into $NiCl_2.2H_2O$ and four molecules of liquid water. To do this allow four mols of water to evaporate at the vapor pressure p_1 of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$, whereby ΔF is $-4RT$. The water vapor must now be compressed to the vapor pressure p_{H_2O} of water, in which process ΔF is

$$+ 4RT \log \frac{p_{H_2O}}{p_1}.$$

The water vapor is then condensed to liquid water, in which ΔF is $+4RT$.

The free energy increase then of $NiCl_2.2H_2O$ is

$$\Delta F_2 = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1}. \qquad (2)$$

By an exactly similar process the free energy increase caused by $NiCl_2.2H_2O$ going over to $NiCl_2$ and $2H_2O$ is

$$+2RT \log \frac{p_{H_2O}}{p_2},$$

where p_2 is the vapor pressure of the system $NiCl_2.2H_2O$—$NiCl_2$, and hence the free energy increase of formation of $NiCl_2$ is

$$\Delta F = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1} + 2RT \log \frac{p_{H_2O}}{p_2} = -2EF + RT \log \frac{(p_{sol})^6}{p_1^4 \cdot p^2}. \qquad (3)$$

To all the above expressions a small correction must be made for the gaseous chlorine, whose pressure will in general not be 76 cm. of mercury. Assuming the vapor pressure of the solution to be unaffected by the presence of the chlorine in the enclosed space above the chlorine couple[1] would be $b - p_{sol}$ where b = barometric pressure. The increase in free energy of the system when the chlorine expands from 76 cm. to $b - p_{sol}$ is

$$\Delta F = -RT \log \frac{760}{b - p_{sol}},$$

which must be added to the right-hand side of equation (3).

2. Potential Measurements.

The apparatus in which the potential measurements were carried out consisted of an H tube 15 cm. high with a glass stop-cock in the horizontal arm. The tubes of the vertical arms were 2 to 3 cm. in diameter. The stop-cock was not lubricated and the potential of the cell was usually measured with the stop-cock turned off.

The chlorine electrode was a smooth sheet of platinum with 10 per cent. iridium, 10 cm. long by 3 cm. wide. This was half way immersed in the solution, and chlorine gas, generated by the electrolysis of strong hydrochloric acid, bubbled over it from below. The chlorine was led from the cell by a rubber tube to a bottle containing potassium hydroxide, where it was absorbed. The pressure of the gas over the chlorine electrode was determined by a small manometer in the escape tube and by the barometer reading. The nickel electrode was formed by electrolytic deposition of nickel on platinum or copper. It is known that nickel exists both in the active and passive states and that active nickel rapidly changes over to the passive state if exposed to the oxygen of the air. Pure nickel immersed in molal nickel sulphate gives about —0.2 volt[2] while according to Muthmann and Frauenberger[3] active nickel has a potential of +0.32 volt. The nickel having this potential was prepared by electrolytic deposition on platinum "according to the directions for electro-analysis." This statement, and that which follows later, according to which the solution used was neutral nickel sulphate and the impressed voltage eight volts, are all the directions given for obtaining a nickel deposit giving the voltage quoted above. The first measurements of the nickel couple were attempts to reproduce this potential in a molal solution of neutral nickel sulphate. The measurements were made by the Poggendorf method with a Weston standard cell and Lippmann electrometer. The potential between the nickel sulphate and

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[1] See THIS JOURNAL, 28, 733.

[2] All single potentials in this paper refer to the "normal electrode" as —0.560 volt at 20°.

[3] *Sitzungsber. kgl. Bayr. Akad. Wiss.*, 34, 201 (1904).

normal potassium chloride was eliminated by a saturated solution of potassium chloride or ammonium nitrate placed between the two.[1] The potential was measured within thirty seconds after plating. It was found that on electrolyzing a neutral sulphate solution at room temperature with eight volts a green deposit appeared on the cathode whose potential was about that given by Muthmann and Frauenberger, and which decreased rapidly. On heating a solution containing 60 grams $NiCl_2.6H_2O$ per liter to 90° and electrolyzing with 12.5 volts the nickel came down in a black spongy form, and no green compound was visible. The highest potential obtained was +0.112 volt. Many other solutions were used, but none gave such high results as the neutral sulphate. For example, a solution containing 60 grams $NiSO_4.6H_2O + 20$ grams $(NH_4)_2SO_4$ + 40 cc. NH_4OH per liter, electrolyzed at 20° with eight volts, gave a deposit of nickel whose potential was +0.017 volt. This was a gray, firm deposit, and could be easily duplicated. Our only explanation of Muthmann and Frauenberger's high value for nickel is that some of this green precipitate came down with the nickel. If this nickel was obtained in a cold solution with eight volts, this is certain to have happened. The nickel deposits obtained in the hot solution did not maintain a constant voltage, but fell off as rapidly as in the case of the green precipitate obtained in the cold. Attempts to increase the voltage by polarizing with hydrogen were not successful. In preparing the nickel electrodes for the final measurements the anode and cathode were separated by the wall of a porcelain cup and in all cases pure electrolytic nickel anodes were used. This cup was to protect the cathode from any sulphuric acid set free at the anode, as it was found, as stated by Muthmann and Frauenberger, that any free acid reduced the potential.

The actual measurement of the cell

$$\text{Nickel} \mid \text{Sat. sol. } NiCl_2.6H_2O \mid Pt + Cl_2$$

at 20° was now taken up. A saturated solution of the chloride was prepared by rotating bottles for several days in a thermostat maintained at 20° by means of a mercury regulator and electric lamps. The dissolved nickel was determined by electro-analysis and three determinations gave 60.5, 60.6 and 60.9 grams of anhydrous salt per hundred grams of water. This is somewhat less than 64 g. chloride to 100 g. water as found by Etard.[2] The density of this solution referred to water at 4° was 1.474.

Before making measurements, chlorine was allowed to bubble over the platinum-iridium plate for an hour or so, so as to give the solution in this arm of the H tube time to get saturated with chlorine and to drive out all air above the solution. After leaving the cell it was tested by

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[1] Bjerrum: *Z. physik. Chem.*, **53**, 428 (1905).

[2] Landolt-Börnstein-Meyerhoffer Tables, 3rd Edition, p. 562.

absorbing in potassium iodide in an inverted test tube. The absence of bubbles showed the gas to be pure chlorine. The electromotive force of this couple was measured against the "normal electrode" and was found to be —1.59 volt. The nickel electrode was now prepared as described above and changed from the plating solution to the cell as quickly as possible and the reading on the bridge taken immediately. This could be done within thirty seconds from the time the plating was finished. Cleaning off the sulphate adhering to the elctrode by dipping in water did not affect the result. The electromotive force of the cell thus measured varied between 1.65 and 1.707 volts, the latter being the highest value obtained in a large number of measurements. This, therefore, corresponds to the most active nickel obtained above. The pressure of the chlorine gas at the time of the latter measurement was 752 mm. mercury.

As there is approximately 0.2 volt difference between the highest value here obtained and that which would have resulted if the nickel couples had as high a value as that assigned them by Muthmann and Freuenberger, some decomposition point determinations of the saturated solution between small platinum plates were made for the purpose of determining whether the above measured value is reversible. The values obtained were not used for computing the free energy, but were simply to decide whether an error of 0.2 volt in the above value were possible. The values found were 1.61, 1.63, 1.60 and 1.60 volts. These are somewhat less than the highest value found above, but the agreement indicates that 1.7 volts and not 1.9 volts is the voltage of the cell.

3. Vapor Pressures.

The vapor pressure of the saturated solution of nickel chloride has been found by Lescoeur[1] to be 8.0 mm. Hg and that of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$ to be 4.6 mg, Hg, both at 20°. The system $NiCl_2.2H_2O$—$NiCl_2$ was found to have a vapor pressure at 100° of 123 mm. No measurement is given of this quantity at 20°, but the statement is made that it is zero, which is, of course, impossible.

By means of the integrated van't Hoff formula this pressure could be calculated, however, from the pressure at 100°, if the heat of hydration of $NiCl_2.2H_2O$ were accurately known. This is equal to the difference between the heat of hydration of $NiCl_2.6H_2O$ starting from $NiCl_2$ and from $NiCl_2.2H_2O$. The former quantity is 20,330 calories.[2] The following table shows the latter value, q, obtained from Lescoeur's vapor pressure of the system $NiCl_2.6H_2O$—$NiCl.2H_2O$ by the formula:

$$4.57 \log_{10} \frac{p_2}{p_1} = q_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

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[1] *Ann. chim. phys.* [6], 19, 533 (1890).

[2] Landolt-Börnstein-Meyerhoffer Tabellen, p. 461.

All except the last column are taken from Lescoeur.

Temp.	Pres. in mm. Hg.	q_1.
15°	3.4	10540
25°	6.3	
20°	4.6	14760
30°	10.5	
40°	24.0	14000
15°	3.4	
30°	10.5	15470
40°	24.0	

Subtracting the average value of q_1 from 20,330, the heat of hydration of $NiCl_2.2H_2O$ is obtained. Computing this from the value of the vapor pressure of $NiCl_2.2H_2O$ at 20°, 11.5 mm. results, which is greater than that of $NiCl_2.6H_2O$, and is therefore impossible. It is evident, therefore, that this value of the heat of hydration is not accurate enough for this purpose.

The value of this pressure was obtained directly by the tensimeter method. For this purpose one tensimeter was filled in June and three in July.[1] One bulb contained phosphorus pentoxide and the other the salt. The liquid in the manometer was cottonseed oil of specific gravity 0.9185. The tensimeters were placed on their side, carefully pumped out, and at the same time warmed. They were then left several hours in connection with the pump and again pumped out and warmed before sealing off. In October they were placed in a thermostat at 20° and allowed to remain until January. The following table gives the readings in mm. of oil:

Date.	No. 1.	No. 2.	No. 3.	No. 4.
Dec. 30	11.4	7.0	3.6	5.4
Jan. 7	....	6.3	broken	6.4
Jan. 25	11.6	6.8	....	6.1
Mol water to 1 mol salt	2.06	2.05	....	1.99

Dec. 30, after the measurements, the bulbs of Nos. 2 and 5 containing the $NiCl_2$ were placed in a beaker of hot water for a few minutes to see if the evolution of water vapor could not be accelerated. The pressure increased to 10 to 15 cm. of oil, due evidently to the expansion of water vapor already present, but went back to nearly the same values afterwards. The water in the salt in the tensimeters was determined by analyzing for the amount of nickel present subsequent to these measurements, and the results were those shown in the table above. It is evident from the above that No. 1 was not properly filled, and is therefore omitted in taking the mean. The average of Nos. 2 and 4 is 0.43 mm. of mercury.

In order to check this value by a different method it was decided to

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[1] See Findlay, "The Phase Rule", p. 88.

measure it at 110° and compute by the van't Hoff equation from this and from Lescoeur's value at 100°, the value at 20°.

For this purpose a tensimeter was filled with some nickel chloride that had been in the drying closet for more than a week at 100°. Mercury was used in the manometer and phosphorus pentoxide in the drying bulb. It was first placed in a steam-bath to see that it checked with Lescoeur's value. The tensimeter was left at four in the afternoon, and next morning was found at 123 mm. Hg, reduced to zero degrees, at which pressure it remained constant for the following twenty-four hours. This agrees identically with Lescoeur's value. It was then placed in a bath of vapor from boiling toluene and in a few hours reached a constant pressure of 218 mm. Hg., at a temperature of 110.7° as obtained from a thermometer corrected at this point by a standard from the Reichsanstalt. The value at 20° computed from this is 0.46 mm.

The tensimeter was then opened and heated while exhausted and connected to the air pump for an hour and a half at a temperature varying from between 90° and 120°, thereby driving off some water. It was sealed off while hot and again placed in the bath of toluene vapor. The constant pressure reached as before in a few hours was 216 mm. Hg., at 110.6°. The pressure computed from this measurement for 20° is 0.47 mm.

These values agree well enough for the present purpose with the average of those from direct measurements. The best value to adopt is the average of the four which is 0.45 of mercury. It is interesting to note that on cooling, the mercury in the tensimeter immediately goes back to nearly a zero pressure, showing that water is taken up by the chloride more rapidly than it is evolved.

Substituting in formula (3) $E = 1.71$ volts, $p_{sol} = 8.0$, $p_1 = 4.6$ and $p_2 = 0.45$, $\Delta F = -74{,}400$ cal. The correction due to the pressure of the chlorine not being 760 mm. is negligible.

The heat of the reaction, or the increase in total energy, is —74,500 cal., assuming the compound to be formed from gaseous chlorine. If the chlorine were solid and superheated to this temperature, the total energy increase is obtained by increasing the above value by the sum of the heat of fusion and the heat of vaporization of chlorine which has been estimated at 7000 cal.[1] This gives —67,500 cal. as the total energy change, starting with solid chlorine. Likewise, if the chlorine were solid the free energy increase ΔF would be diminished by the quantity RT, or approximately 600 cal., giving the value $F = -75{,}000$. The ratio of free to total energy, for chlorine in the solid state, consequently is 1.11, while the ratio of the same quantities with chlorine in the gaseous state is 1.00. The free energy and the total energy of this salt, therefore, are

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[1] THIS JOURNAL, 28, 741 (1906).

approximately equal, as was found to be true in all other cases for which this calculation has been made.

4. Precision Discussion.

The term $2EF$ in formula (3) amounts to 79,040 calories, the second term to only 4600 cal., from which it is evident that even a large error in the vapor pressures would have only a relatively small effect on the final result. Assuming an error of 0.1 mm. in p_{sol}, p_2 and 0.1 mm. in p, which seems an outside limit, the resultant effect is 600 calories, or about 0.8 per cent. error in ΔF. Assuming a possible error of 0.02 volt in E the combined error in ΔF would be 990 cal., or 1.3 per cent.

5. Summary.

The free energy ΔF of $NiCl_2$ was determined by measuring the potential of the cell.

$$Ni \mid \text{Sat. sol. of } NiCl_2.6H_2O \mid Cl_2 + Pt.$$

A formula for ΔF was deduced, involving this potential, the vapor pressure of the saturated solution, of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$ and of $NiCl_2.2H_2O$—$NiCl_2$. The pressure of the last system was obtained both by direct and by indirect measurement. The free energy and total energy of $NiCl_2$ were found to be approximately equal.

ELECTROCHEMICAL LABORATORY,
MASS. INST. OF TECH., BOSTON.

A STUDY OF THE SOLUTIONS OF SOME SALTS EXHIBITING NEGATIVE VISCOSITY.

FREDERICK H. GETMAN.

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In 1873 Hübner[1] determined the viscosities of a series of solutions of alkaline halides of equal densities and observed that some of the salts diminished the viscosity of water.

Subsequently Sprung[2] made an extensive study of the viscosities of saline solutions between the temperatures 0° and 60° C.

He divided the salts examined into two groups as follows:

(1) KCl, KBr, KI, KNO_3, $KClO_3$, NH_4Cl, NH_4Br, NH_4NO_3.

(2) K_2SO_4, $NaCl$, $NaBr$, NaI, $NaNO_3$, $NaClO_3$, Na_2SO_4, $(NH_4)_2SO_4$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $LiCl$, $MgSO_4$.

He pointed out that at low temperatures the salts of the first group lower the viscosity of water and at higher temperatures they increase it. The salts of the second group always increase the viscosity of the solvent, the viscosity of the solution becoming less as the temperature is raised.

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[1] *Pogg. Ann.*, 157, 130.

[2] *Ibid.*, 159, 1.