Thermodynamic Properties of Import to Environmental Processes and Remediation. II. Previous Thermodynamic Property Values for Nickel and Some of its Compounds

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Thermodynamic Properties of Import to Environmental Processes and Remediation. II. Previous Thermodynamic Property Values for Nickel and Some of its Compounds

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The sources of previous thermodynamic property values are detailed for nickel and some compounds of nickel that might be expected as derived from anthropogenic introduction of nickel into the environment or are required for calculation of thermodynamic properties of nickel-containing systems. Included are descriptions of the sources of information and the methodology used to obtain the values for these compounds reported in the NBS series of publications loosely and collectively referred to as the NBS Thermodynamics Tables. © *2000 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00306-2]

Contents

1. Introduction

This is the second in a series of articles that describe some of the sources of values of thermodynamic properties of materials and systems that are essential in the calculation and prediction of environmental fates of particular materials in environmental remediation technologies. This series of articles contains information required to assess the reliability of values calculated from some process or environment simulators. These articles describe, as best as can be discerned, determination of the values in the thermodynamic compendium known colloquially as the NBS Tables, in the present case 69WAG/EVA and 82WAG/EVA.

The organization of the current series of articles is as follows. Under each substance described will be six sections. The first section, A, will describe the methodology and the measurements that led to the value given in the NBS Tables. This information was kept on loose papers, ''worksheets,'' that have been kept in file cabinets at the National Institute of Standards and Technology (NIST). Not all of the worksheets were equally understandable. As such, we have not been able to discern sources for all values; sometimes the worksheets have been too cryptic to be understood. This also applies to some of the auxiliary values; many of these were not listed on the worksheets. Tracing all auxiliary values (osmotic coefficients, saturation molalities, etc.) and in many cases making assumptions from whence they may have come did not seem a wise investiture of resources. Therefore, the sources of these values were not guessed if they were not identified on a worksheet. The second section, B, contains comments by the author of the article regarding the methodology used in generation of the NBS Tables values. In Sec. B, such things as arithmetic errors, erroneous auxiliary values that might have been used, etc. will be identified. Section C details the auxiliary substances required to obtain the NBS Tables thermodynamic property values for the title substance. The measurements examined by the NBS Tables staff, but not used in their final assessment, are described in Sec. D. Section E describes more recent measurements that could lead to thermodynamic property values. Other evaluations or compendia of thermodynamic properties of the substances are not listed in this section, regardless of quality. This is due to the large number of such evaluations. Finally, references are given in Sec. F for each title substance. For all sections, if a temperature is not specified, it is to be assumed that the relevant temperature is 298.15 K.

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It is not always clear cut for which substance one might place some of the new measurements in a document such as this. Thus, one reader might consider inclusion of, say, osmotic coefficient measurements for aqueous nickel chloride underneath $Ni^{2+}(aq)$ as correct, whereas another might consider entry under $NiCl^+(aq)$ to be more correct. We chose not to involve ourselves with that level of minutiae.

Some of the thermodynamic properties described in Sec. A were calculated by 69WAG/EVA from decomposition pressures. In cases where only one component was believed to have been present in the gas phase, for example, the hydrates of $NiCl_2$ and $NiSO_4$, the thermodynamic property for the reaction was calculated on the original worksheets on a *per mole of gas basis, regardless of the assumed stoichiometry written for the reaction*. The ratio of moles of gas to moles of desired substance, or to the reaction as it had been written, was accommodated at a later step in the calculations. The descriptions of calculations given in Sec. A have attempted to represent as accurately as possible the calculations as they were performed. This faithfulness in reproduction of the original calculations is often useful where one must describe arithmetic or other errors that affected a tabulated value. Therefore, these particular calculations, as well as others, have been described on the same basis as that used on the original worksheets. Because the pressure of the gas-phase species and also the property of the reaction calculated therefrom are both given in Sec. A for these cases and because the combination of the two uniquely describes the calculation, we have not belabored the reader by constantly repeating ''per mole of water'' or ''per mole of nickel'' for each numerical value given.

There are numerous high-temperature measurements of electrochemical cells involving a nickel+nickel oxide half cell. In many of the electrochemical measurements, the other half cell involved some other metal-oxide system. The nickel+nickel oxide half cell was taken to be the reference electrode for many of those measurements. Therefore, only those measurements that might lead to description of nickel as a reference electrode were included in this article. As examples, the electrochemical cell in which the nickel half cell is coupled to an oxygen cell [Pt in air or in pure $O_2(g)$ of established oxygen fugacity] was included in this article, whereas the electrochemical cell composed of the nickel half cell coupled to a half cell containing wüstite was not. This is because the present author presumed the properties of wüstite to have been less well known than were those of nickel oxide. This presumption might be considered by some to be an arbitrary decision.

The compounds considered in this first series of papers are those that arise from combination of the titled metal species with the most common components of groundwaters, namely, chloride, sulfate, carbonate, and those species affected by hydroxide concentrations. The author does not contend and has not contended that these are the only species that are important in environmental and/or remediation considerations. Rather, it is a starting point from which one es-

tablishes a set of accurate and thermodynamically consistent properties.

The present document is relevant to the origin of values from both 69WAG/EVA and 82WAG/EVA. Some of the 82WAG/EVA values are slightly different than the 69WAG/EVA values because the former chose to tabulate values relative to 1 bar standard pressure, whereas the latter chose 1 atm. The effect of this small pressure difference on the tabulated values is described in 82WAG/EVA. The specific calculations in the following pages should give the numerical values in 69WAG/EVA, rather than those in 82WAG/EVA. This is because the calculations on the worksheets corresponded to the 1 atm standard pressure.

1.1 References for the Introduction

69WAG/EVA Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., Selected Values of Chemical Thermodynamic Properties. Tables for Elements 35–53 in the Standard Order of Arrangement (NBS Tech. Note 270-4, 1969).

82WAG/EVA Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. L., J. Phys. Chem. Ref. Data **11**, Suppl. 2 (1982).

2. Ni(cr)

A. Selected Values, NBS Tables

The entropy, the enthalpy relative to 0 K, and the heat capacity were all taken from 63HUL/ORR; $S_m^\circ = 29.87$ $J \cdot K^{-1} \cdot mol^{-1}$ (7.14 $cal \cdot K^{-1} \cdot mol^{-1}$).

B. Comments

No examination of the measured values appeared to have been performed.

C. Auxiliary Values Required for Data Pathway

None.

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties of Ni(cr)

76VEC/GUS reported measurement of the heat capacity of Ni(cr) from 45 to 700 K by low-temperature adiabatic calorimetric and a ''triple thermal bridge method.'' They reported a value of $S_m^\circ = (29.92 \pm 0.08)$ $J \cdot K^{-1} \cdot mol^{-1}$. The measurements were not included in the published article.

F. Bibliography

63HUL/ORR Hultgren, R. R., Orr, R. L., Anderson, P. D., and Kelley, K. K., Selected Values of Thermodynamic Prop-

erties of Metals and Alloys (Wiley, New York, 1963).
76VEC/GUS Vecher, A. A., Gusakov, A. G., and Kozyro, A. A., Zh. Fiz. Khim. **50**, 1626 (1976).

3. Ni^{2+}(aq)

A. Selected Values, NBS Tables

29HAR/VAN measured potentials of cells of the type

$$Ni|NiSO_4(m)|Hg_2SO_4|Hg \qquad (3.1)$$

for values of m ranging from 0.05 to 0.16 mol·kg^{-1}. The worksheet indicated that activity coefficients were taken from Robinson and Stokes, with no further citation information given. The Gibbs energy of reaction corresponding to the reaction

$$Ni(cr)+Hg_2SO_4(cr)=NiSO_4(aq)+2Hg(l) \qquad (3.2)$$

was taken as the average of the values for 26 cells; $\Delta_r G_m° = -164.272$ kJ·mol^{-1} (-39.262 kcal·mol^{-1}). This value was combined with $\Delta_f G_m°[Hg_2SO_4(cr)] = -625.880$ kJ·mol^{-1} (-149.589 kcal·mol^{-1}) to obtain $\Delta_f G_m°[NiSO_4(aq)] = -790.15$ kJ·mol^{-1} (-188.85 kcal·mol^{-1}). Combination of this value with $\Delta_f G_m°[SO_4^{2-}(aq)] = -744.63$ kJ·mol^{-1} (-177.97 kcal·mol^{-1}) gave $\Delta_f G_m°[Ni^{2+}(aq)] = -45.52$ kJ·mol^{-1} (-10.88 kcal·mol^{-1}).

58MUL measured the enthalpy of solution of $NiCl_2$ in water for $T=(298.15\pm0.3)$K for molalities ranging from 0.001453 to 0.01025 mol·kg^{-1}. Two measurements were also made in dilute acid solutions for $m=0.007\,232$ and 0.010 94 mol·kg^{-1}. Of these measurements, the enthalpy of solution-molality pair $\Delta_{sol}H_m = -19.73$ kcal·mol^{-1}, 0.002 775 mol·kg^{-1} was selected:

$$NiCl_2(cr)=NiCl_2(20\,000H_2O). \qquad (3.3)$$

This was combined with an L_ϕ value of 0.481 kJ·mol^{-1} (0.115 kcal·mol^{-1}) to obtain $\Delta_{sol}H_m° = -83.03$ kJ·mol^{-1} (-19.84 kcal·mol^{-1}), where L_ϕ is the relative apparent molar enthalpy. This value was combined with $\Delta_f H_m°[NiCl_2(cr)] = -305.332$ kJ·mol^{-1} (-72.976 kcal·mol^{-1}) and $\Delta_f H_m°[Cl^-(aq)] = -167.159$ kJ·mol^{-1} (-39.952 kcal·mol^{-1}) to obtain $\Delta_f H_m°[Ni^{2+}(aq)] = -54.04$ kJ·mol^{-1} (-12.92 kcal·mol^{-1}).

The entropy, $S_m°[Ni^{2+}(aq)]$, was calculated from $S_m°[Ni^{2+}(aq)] = -(\Delta_f G_m° - \Delta_f H_m°)/(298.15\ \text{K}) + S_m°(Ni) - S_m°[H_2(g)]$ and resulted in $S_m°[Ni^{2+}(aq)] = -128.9$ J·K^{-1}·mol^{-1} (-30.8 cal·K^{-1}·mol^{-1}).

B. Comments

The value described as having been from 58MUL was not tabulated in that reference; however, it was reasonably close to one of the measured pairs. If one applies the same calculational pathway to all of the 58MUL measured values (for solution in water), then the values of the standard-state enthalpy of solution ranged from -82.30 (0.001 453 mol·kg$^{-1}$) to -84.56 kJ·mol^{-1} (0.010 25 mol·kg^{-1}). This dependence of calculated standard-state enthalpy of solution upon the measured concentration reflects either that the NBS-tabulated concentration dependence for the enthalpy of formation is in error or that some concentration-dependent bias existed within 58MUL's series of measurements. In either case, the minimum uncertainties in the tabulated $\Delta_f H_m°$ and $S_m°$ were somewhat larger than 2 kJ·mol^{-1} and 7.6 J·K^{-1}·mol^{-1}.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f G_m°[Hg_2SO_4(cr)],$$
$$\Delta_f G_m°[SO_4^{2-}(aq)],$$
$$\Delta_f H_m°[NiCl_2(cr)],$$
$$\Delta_f H_m°[Cl^-(aq)],$$
$$S_m°[Ni(cr)],$$
$$S_m°[H_2(g)].$$

D. Other Thermodynamic Measurements Considered

52CAR/BON measured the emf of electrochemical cells

$$Ni|NiSO_4(aq)\|Hg_2Cl_2(cr)|Hg(l) \qquad (3.4)$$
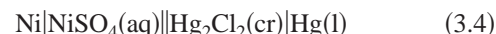
at 298.15 K. 52CAR/BON used the Debye-Hückel limiting law to calculate activity coefficients of $NiSO_4(aq)$ and obtained a calculated value of $E° = -0.231$ V. The worksheets indicated this emf led to $\Delta_f G_m°[Ni^{2+}(aq)] = -44.56$ kJ·mol^{-1} (-10.65 kcal·mol^{-1}). 52CAR/BON also measured the thermoelectric voltages of cells of the type

$$Ni|NiSO_4(aq,T=T_1)\|NiSO_4(aq,T=T_2)|Ni \qquad (3.5)$$

for temperatures from 303.15 to 373.15 K. These measurements were not considered further.

1882THO measured the enthalpy change for the reaction

$$NiCl_2(cr)=NiCl_2(400\ H_2O) \qquad (3.6)$$

at 292.15 K; $\Delta_{sol}H_m = -80.21$ kJ·mol^{-1}. The heat capacity change of the reaction was assumed to be -418 J·K^{-1}·mol^{-1}, giving $\Delta_{sol}H_m = -82.30$ kJ·mol^{-1} for $T = 298.15$ K. This value was then used to calculate $\Delta_f H_m°[Ni^{2+}(aq)] = -56.82$ kJ·mol^{-1}.

50BOB/LAI measured the enthalpy change for solution of $NiCl_2 \cdot 6H_2O(cr)$ in water. The NBS Tables staff assumed the reaction to be

$$NiCl_2 \cdot 6H_2O(cr)=NiCl_2(270\ H_2O) \qquad (3.7)$$
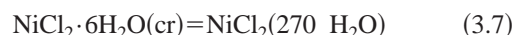
and used $\Delta_{sol}H_m = 6.07$ kJ·mol^{-1} for $T = 298.15$ K. The NBS Tables staff adjusted this value to infinite dilution by subtracting 3.703 kJ·mol^{-1}. The resultant value, 2.364 kJ·mol^{-1}, was then combined with a value of the Gibbs energy of solution of the hexahydrate crystal, -17.544 kJ·mol^{-1}, to obtain the entropy of solution, which was then combined with the entropies of the hexahydrate crystal (see below), two moles of chloride ions, and six moles of water to obtain the entropy of the aqueous nickel ion.

$S_m°[Ni^{2+}(aq)] = -121.3$ J·K^{-1}·mol^{-1}. [Author's note: 50BOB/LAI measured the enthalpy of solution at 295.65, not 298.15 K. Additionally, 50BOB/LAI did not describe an exact final composition, writing instead that the final solutions were ''very dilute.'' They gave general representative conditions for the measurements of 2–15 g of solute dissolved into 200 ''or'' 300 g of water, with amounts selected so as to obtain a temperature change of 1–2 K. This would place compositions in the (0.2–0.3) mol·kg^{-1} range or higher. These compositions are not very dilute from the perspective of determination of an accurate $\Delta_{sol}H_m°$ and insufficient information exists to determine a sufficiently accurate value from the published article.]

E. More Recent Determinations of the Thermodynamic Properties of Ni²⁺(aq)

81HOL/MES measured isopiestic molalities of NiCl$_2$(aq) with NaCl(aq) as reference for temperatures of 382.96 and 413.36 K.

87RAR measured isopiestic ratios of aqueous nickel chloride against sodium chloride and calcium chloride as reference solutes over the range of NiCl$_2$ compositions, from 0.3 to 4.78 mol·kg^{-1}.

92RAR measured isopiestic ratios of aqueous nickel chloride against sodium chloride and calcium chloride as reference solutes over the range of NiCl$_2$ compositions from 1.6 to 5.15 mol·kg^{-1}.

81PER/ROU measured the apparent molar heat capacity of NiCl$_2$(aq) at 298.15 K with a Picker mass-flow calorimeter. The molality range spanned 0.1–5.4 mol·kg^{-1}. From their treatment of their measurements they gave $C_{p,\phi}°$ = (-306 ± 1)J·K^{-1}·mol^{-1}.

78SPI/SIN measured the apparent molar heat capacity of NiCl$_2$(aq) at 298.15 K with a Picker mass-flow calorimeter. Concentrations ranged from 0.045 to 0.2 mol·kg^{-1}. From their treatment of their measurements they gave $C_{p,\phi}°$ = -294 J·K^{-1}·mol^{-1}.

77KAR/VAS measured the specific heat capacity of NiCl$_2$(aq) at 298.15 K for molalities from 3.91 to 0.03 mol·kg^{-1}.

82SMI/WOO measured apparent molar heat capacities for NiCl$_2$(aq) for temperatures from 321 to 572 K and for molalities from 0.13 to 3.0 mol·kg^{-1} with a mass-flow calorimeter.

92SCH/SCH measured the enthalpy of dilution of aqueous NiCl$_2$ at 298.15 K for concentrations of 0.1–1 mol·kg^{-1}.

84VAS/VAS measured the enthalpy of solution of nickel into aqueous solutions of HCl+H$_2$O$_2$ and of HClO$_4$+H$_2$O$_2$. The concentrations of the acids ranged from 1 to 6 mol·kg^{-1} and the concentration of hydrogen peroxide was 1% or 1.5%. The observed enthalpies of solution were extrapolated to I =0 and then averaged to give the enthalpy of reaction, (-432.59 ± 0.43) kJ·mol^{-1} for

$$Ni(cr) + 2H^+(aq) + H_2O_2(aq) = Ni^{2+}(aq) + 2H_2O(l). \quad (8)$$
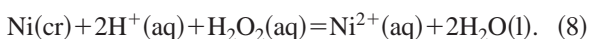
They combined this result with enthalpies of formation of water and hydrogen peroxide to calculate $\Delta_fH_m°[Ni^{2+}(aq)]$ = -52.22 ± 0.47 kJ·mol^{-1}.

86VAS/DMI measured the enthalpy of solution of nickel in aqueous mixtures of Br$_2$ and NaBr acidified to 0.05 M HClO$_4$. The concentration of Br$_2$ was 0.3 M and the concentration of NaBr was varied from 0.95 to 3.95 M. The final state was 1.4567 mol NiBr$_2$/kg of solution. They also measured enthalpies of mixing NiBr$_2$ solutions with the Br$_2$–NaBr solutions and enthalpies of dilution of NiBr$_2$ in 0.05 M HClO$_4$. From these measurements, 86VAS/DMI calculated $\Delta_fH_m°[Ni^{2+}(aq)] = (-52.17 \pm 0.38)$ kJ·mol^1.

90EFI/FUR measured the enthalpy of solution of NiCl$_2$(cr) in dilute aqueous solutions of HClO$_4$ (0.001 N). They used a Debye-Hückel expression to calculate the extrapolation to infinite dilution and averaged the resulting values to obtain $\Delta_{sol}H° = (-84.868 \pm 0.168)$ kJ·mol^{-1}. They then combined that value with an enthalpy of formation for NiCl$_2$(cr) that they had determined independently to calculate $\Delta_fH_m°[Ni^{2+}(aq)] = (-55.67 \pm 0.28)$ kJ·mol^{-1}.

F. Bibliography

1882THO Thomsen, J., Thermochemische Untersuchungen (Barth, Leipzig, 1882–1886).

29HAR/VAN Haring, M. M., and Vanden Bosche, E. G., J. Phys. Chem. **33**, 161 (1929).

50BOB/LAI Bobtelsky, M., and Lairsch, R. D., J. Chem. Soc. 3612 (1950).

52CAR/BON Carr, D. S., and Bonilla, C. F., J. Electrochem. Soc. **99**, 475 (1952).

58MUL Muldrow, C. N., Ph.D. dissertation, University of Virginia, 1958.

77KAR/VAS Karapet'yants, M. Kh., Vasilev, V. A., and Sanaev, E. S., Zh. Fiz. Khim. **51**, 2180 (1977).

78SPI/SIN Spitzer, J. J., Singh, P. P., McCurdy, K. G., and Hepler, L. G., J. Solution Chem. **7**, 81 (1978).

81HOL/MES Holmes, H. F., and Mesmer, R. E., J. Chem. Thermodyn. **13**, 131 (1981).

81PER/ROU Perron, G., Roux, A., and Desnoyers, J. E., Can. J. Chem. **59**, 3049 (1981).

82SMI/WOO Smith-Magowan, D., Wood, R. H., and Tillett, D. M., J. Chem. Eng. Data **27**, 335 (1982).

84VAS/VAS Vasil'ev, V. P., Vasil'eva, V. N., and Dmitrieva, N. G., Zh. Neorg. Khim. **29**, 1123 (1984).

86VAS/DMI Vasil'ev, V. P., Dmitrieva, N. G., Vasil'eva, V. N., Yashkova, V. I., and Belokurova, N. A., Zh. Neorg. Khim. **31**, 3044 (1986).

87RAR Rard, J. A., J. Chem. Eng. Data **32**, 334 (1987).

90EFI/FUR Efimov, M. E., and Furkalyuk, M. Yu. Zh. Fiz. Khim. **64**, 2560 (1990).

92RAR Rard, J. A., J. Chem. Eng. Data **37**, 433 (1992).

92SCH/SCH Schreiber, D. R., and Schreiber, L. C., J. Solution Chem. **21**, 249 (1992).

4. NiO(cr)

A. Selected Values, NBS Tables

The 298.15 K entropy and heat capacity of NiO(cr) were taken from 57KIN to be $S_m° = 37.99$ J·K^{-1}·mol^{-1} (9.08 cal·K^{-1}·mol^{-1}) and $C_{p,m}° = 44.31$ J·K^{-1}·mol^{-1} (10.59 cal·K^{-1}·mol^{-1}). Measurements reported in 57KIN were for temperatures from 54 to 296 K.

The enthalpy of formation, -239.7 kJ·mol^{-1} (-57.3 kcal·mol^{-1}), was taken from 54BOY/KIN's measurement of the energy of combustion of nickel in oxygen. The Gibbs energy of formation was calculated from the usual combination of the enthalpy of formation and the entropy of formation.

B. Comments

54BOY/KIN estimated the uncertainty of their enthalpy of formation value to be 0.4 kJ·mol^{-1}.

C. Auxiliary Values Required for Data Pathway

$$S_m°[O_2(g)],$$

$$S_m°[Ni(cr)].$$

D. Other Thermodynamic Measurements Considered

40SEL/DEW measured the heat capacity of NiO from 68 to 298.1 K. They gave $S_m° = 38.58$ J·K^{-1}·mol^{-1}.

29ROT/MUL measured the energy of combustion of nickel in oxygen. Their measured value led to $\Delta_f H_m° = -246.6$ kJ·mol^{-1}.

13RUF/GER measured the energy of combustion of nickel in oxygen. Their measured value was used to calculate $\Delta_f H_m° = -219.2$ kJ·mol^{-1}.

10MIX measured the energy of combustion of nickel in oxygen. 10MIX's measured values led to $\Delta_f H_m° = -242.2$ kJ·mol^{-1}.

60AND/DEL measured the emf of cells

$$Ni|NiO|O_2(Pt) \tag{4.1}$$
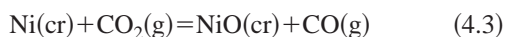
for temperatures of 993–1173 K. The worksheets indicated these measurements led to an average value of $\Delta_f H_m°(298.15 \text{ K}) = -242.806$ kJ·mol^{-1}.

58PET/MAN measured the potentials of cells of the type

$$Pt|Ni+NiO|\text{solid electrolyte}|CO+CO_2+FeO|Pt \tag{4.2}$$

in the temperature range of 1153–1573 K. The worksheets indicated that one of these measurements led to $\Delta_f H_m°(298.15 \text{ K}) = -235.31$ kJ·mol^{-1}.

42FRI/WEI measured the carbon monoxide fraction in the vapor phase for the reaction

$$Ni(cr)+CO_2(g)=NiO(cr)+CO(g) \tag{4.3}$$

for temperatures from 1044 to 1289 K. The worksheets indicated that these values led to $\Delta_f H_m°(298.15 \text{ K}) = -241.62$ kJ·mol^{-1}.

30WAT measured the equilibrium mole fractions of the components of the gas phase for the reaction in Eq. (4.3) for temperatures from 936 to 1125 K. His values led to $\Delta_f H_m°(298.15 \text{ K}) = -238.65$ kJ·mol^{-1}.

29SCH/WES measured the equilibrium mole fractions of the components of the gas phase for the reaction of Eq. (4.3) for 1173 K. The worksheet indicated this measurement led to $\Delta_f H_m°(298.15 \text{ K}) = -241.62$ kJ·mol^{-1}.

38BOG measured the equilibrium mole fractions of the components of the gas phase for the reaction in Eq. (4.3) for 773–1373 K. The worksheets indicated these measurements led to $\Delta_f H_m°(298.15 \text{ K})$ values that ranged from -245.8 to -239.5 kJ·mol^{-1}.

36KAP/SIL measured the equilibrium mole fractions of the components of the gas phase for the reaction in Eq. (4.3) for 885–1216 K. The worksheets indicated these measurements led to $\Delta_f H_m°(298.15 \text{ K}) = -256.14$ kJ·mol^{-1}.

60BRA/RIE measured the equilibrium mole fractions of the components of the gas phase for the reaction in Eq. (4.3) for 1258–1336 K. The worksheets indicated these measurements led to $\Delta_f H_m°(298.15 \text{ K}) = -242.43$ kJ·mol^{-1}.

37BOG determined the composition of the equilibrium gas phase in the reaction

$$NiO(s)+H_2(g)=Ni(s)+H_2O(g) \tag{4.4}$$
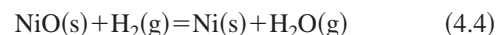
for temperatures from 723 to 1273 K. Values for the 298 K enthalpy were found to vary by about 12 kJ·mol^{-1} and were considered no further.

26PEA/COO passed hydrogen, water, or a mixture of the two over either nickel or nickel oxide and determined the composition of the gas phase for the reaction in Eq. (4.4) for 758 and 873 K. They approached equilibrium from both directions. Their measured values were used to compute $\Delta_f H_m°(298.15 \text{ K}) = -239.12$ kJ·mol^{-1}.

33KAP/SCH measured the decomposition pressure over nickel oxide,

$$NiO(s)=Ni(s)+1/2O_2(g). \tag{4.5}$$

Their measured values were used to compute $\Delta_f H_m°(298.15 \text{ K}) = -243.93$ kJ·mol^{-1}.

62EFI measured the decomposition pressure over nickel oxide by means of an adaptation of a Knudsen effusion method. His values were used to compute $\Delta_f H_m°(298.15 \text{ K}) = -226.65$ kJ·mol^{-1}.

E. More Recent Determinations of the Thermodynamic Properties of NiO(cr)

67ANT/WAR measured the equilibrium composition of a carbon dioxide+carbon monoxide gas mixture over (Ni+NiO) for temperatures from 853 to 1289 K. They obtained for the Gibbs energy change for the reaction of Eq. (4.3) $\Delta_r G_m° = (45.564+4.6\times10^{-4}T/T°)$ kJ·mol^{-1}, where $T° = 1$ K.

70NAV/MUA also measured the equilibrium composition of a carbon dioxide+carbon monoxide gas mixture over (Ni+NiO) at 1323 K. They obtained $p(CO_2)/p(CO) = 58.00 \pm 0.25$.

61HAH/MUA measured the stability partial pressures of oxygen over NiO and Ni crystal phases at temperatures from 1373 to 1673 K. The oxygen pressures were controlled with CO_2 and H_2 gas mixtures. They obtained the formula

$$``\log P_{O_2} = 9.043 - 24\,730[1/T],\text{''}} \qquad (4.6)$$

where P_{O_2} was the pressure given in atm. Their result is dependent on properties of the gases, CO_2 and H_2, which were taken from material in 54COU.

68CAM/ROE performed much the same measurement as that described by 61HAH/MUA. They calculated the Gibbs energy change for $Ni(cr) + \frac{1}{2}O_2(g) = NiO(cr)$ to be $\{(-102.1, -92.5, \text{and} -83.3) \pm 0.4\}$ kJ·mol^{-1} at 1573, 1673, and 1773 K, respectively.

68KOD/KUS measured the decomposition pressure of NiO(cr) with a Knudsen gauge or McLeod gauge in a static system. They reported $``\log(pO_2) = -23810/T + 11.33,\text{''}}$ where p was the pressure in Torr for the reaction of Eq. (4.5). The equation was valid from 1400 to 1570 K.

87ONE measured the emf of cells of the type

$$Pt|Ni+NiO|CSZ|Cu+Cu_2O|Pt, \qquad (4.7)$$

$$Pt|Ni+NiO|CSZ|Fe+``FeO\text{''}|Pt, \qquad (4.8)$$
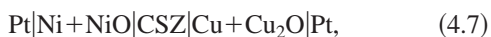
where CSZ is a calcia stabilized zirconia electrolyte that joins the cells of different oxygen potential. Measurements were made for temperatures from approximately 850 to 1420 K. The oxygen chemical potential, determined from the electrochemical measurements, was represented as

$$\mu_{O_2}/kJ\cdot mol^{-1} = -480.104 + 0.244\,700\,T/T^\circ - 9.167$$

$$\times 10^{-3}\,T/T^\circ \ln(T/T^\circ), \qquad (4.9)$$

where μ_{O_2} is the chemical potential in kJ·mol^{-1}. He gave an enthalpy of formation value for NiO at 298.15 K of -240.28 kJ·mol^{-1}.

93PRA/BIE measured the emf of cells of the type

$$Pt|Fe+Fe_xO|CSZ|air|Pt, \qquad (4.10)$$

$$Pt|Fe+Fe_xO|CSZ|Ni+NiO|Pt. \qquad (4.11)$$

They combined the emf's of the two cells and used the result to calculate the Gibbs energy of formation of NiO(cr) at temperatures of 950–1250 K, $\Delta_f G^\circ[NiO(cr)]/$ kJ·mol$^{-1} = -234.227 + 0.085\,678\,(T/T^\circ)$.

93ONE, using much the same methodology as that in 87ONE, reported

$$\mu_{O_2}/kJ\cdot mol^{-1} = -478.967 + 0.248\,514\,T/T^\circ - 9.7961$$

$$\times 10^{-3}\,T/T^\circ \ln(T/T^\circ) \qquad (4.12)$$

valid for temperatures from 700 to 1700 K.

67BLA measured the solubility of NiO(cr) in water at 293.15 K as 1.11×10^{-3} g NiO/ℓ of water.

80TRE/LEB measured the solubility of NiO(cr) in water as a function of pH for temperatures from 423 to 573 K in a flow apparatus.

93DIN/MAT measured the solubility of NiO(cr) in water from 373 to 523 K in an autoclave without control of the pH. Their measurements agreed approximately with those from 80TRE/LEB.

75MOS/FIT measured the emf of the cell,

$$Pt|Ni+NiO|CSZ|p_{O_2} = 0.21 \text{ atm}|Pt, \qquad (4.13)$$
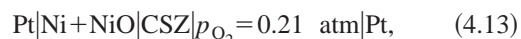
from 1023 to 1273 K. From their measured emf's they gave the Gibbs energy of formation of NiO(cr) as $\Delta_f G_m^\circ/$ kJ·mol$^{-1} = (-244.02 + 0.091\,96\,T/T^\circ)$ for 1023 K$<T <$1273 K.

77KEM/KAT measured the emf of the electrochemical cell given in Eq. (4.13) for temperatures from 1726 to 1823 K. They gave $\Delta_r G_m^\circ/kJ\cdot mol^{-1} = \{(-250.298 + 0.093\,97\,T/T^\circ) \pm 0.5\}$. (At these temperatures nickel is a liquid.)

78IWA/FUJ measured the emf of the cell of Eq. (4.13) and gave a representation of their measurements, $\Delta_r G_m^\circ/kJ\cdot mol^{-1} = -230.7 + 0.082\,84\,T/T^\circ$, valid from 973 to 1723 K.

68CHA/FLE measured the emf of a high-temperature cell of type

$$Pt|Ni+NiO|CSZ|p_{O_2} = 1 \text{ atm}|Pt \qquad (4.14)$$
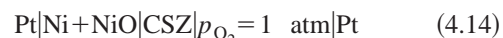
for temperatures from 911 to 1376 K. They gave $\Delta_r G_m^\circ/$ kJ·mol$^{-1} = (-233.651 + 0.084\,893\,T/T^\circ)$ for 911 K $<T <$1376 K.

70HUE/SAT measured the potential of electrochemical cells similar to those in Eq. (4.14) and also

$$Pt|Ni+NiO|CSZ|H_2O(g)+H_2(g)|Pt. \qquad (4.15)$$
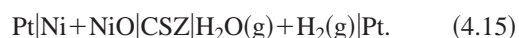
70HUE/SAT combined the measurements from the two types of cells and obtained $f_{O_2}(\pm 0.02) = 9.31 - 24810\,T^\circ/T$ and $\Delta_f G_m^\circ = (-237.442 + 0.089\,16\,T/T^\circ)$ kJ·mol^{-1} for 673 K$<T<$1273 K.

71MAR/MAT reported $\Delta_r G_m^\circ = (-244.107 + 0.093\,T/T^\circ)$ kJ·mol^{-1} for 1023 K$<T<$1373 K, based on emf's described in Studii si Cercetari Acad. R.S.R. (1970).

76ROG measured the emf of the cell given in Eq. (4.13) for temperatures from 873 to 1273 K. From his measured emf's he gave the Gibbs energy of formation of NiO(cr) as $\Delta_f G_m^\circ/kJ\cdot mol^{-1} = (-230.5 + 0.082\,26\,T/T^\circ)$ for 873 K$<T <$1273 K.

77SHA/WU measured the emf of the electrochemical cell described by Eq. (4.7). For the cell reaction $Ni(cr) + Cu_2O(cr) = NiO(cr) + 2Cu(cr)$, they reported $E/V = 0.350 - 7.13 \times 10^{-5}(T/T^\circ)$. Their equation was valid for the temperature range of 700–1100 K.

79KEM/KAT measured the emf of the cell given in Eq. (4.13). Their equation for the emf, $E/mV = (1204.4 \pm 1.3) - (0.4667 \pm 0.0009)(T/K)$, can be used to obtain the Gibbs energy of formation of NiO(cr), $\Delta_f G_m^\circ = (-232.42 + 0.083\,60\,T/T^\circ)$ kJ·mol^{-1} for 1191 K$<T<$1699 K.

84COM/PRA measured the emf of the cell given in Eq. (4.13) for temperatures from 873 to 1823 K and obtained $\Delta_f G_m° = (-232.45 + 0.083435\, T/T°)$ kJ·mol^{-1} for 1023 K $< T < 1273$ K.

86HOL/ONE measured the emf of the cell of Eq. (4.13). They gave

$$\Delta_f G_m°/\text{kJ·mol}^{-1} = -239.885 + 0.122350\, T/T° - 4.584$$

$$\times 10^{-3}\, T/T° \ln(T/T°), \qquad (4.16)$$

valid from 900 to 1600 K.

71BAB/TIK used a circulation method to determine the equilibrium constant of the reaction

$$NiO(cr) + H_2(g) = Ni(cr) + H_2O(g) \qquad (4.17)$$
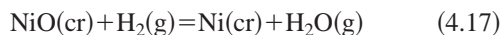
for temperatures from 973 to 1273 K. They obtained $\ln K = \{2966/(T/T°)\} - 2.288$. The equilibrium constant was calculated from the ratio of the pressures of water and hydrogen, and this ratio was taken to be equal to the ratio of the fugacities at the pressure of the measurement, ~ 1.3 Pa.

73RAU/GUE measured gas-phase compositions for the reaction

$$NiO(cr) + H_2(g) = Ni(cr) + H_2O(g) \qquad (4.18)$$
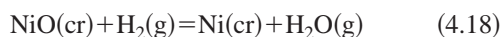
by means of a palladium-membrane apparatus for temperatures from 711 to 860 K. Using literature values for thermal properties of each of the substances of Eq. (4.18), they calculated $\Delta_f H_m° = (-239.53 \pm 1.0)$ kJ·mol^{-1} for the α phase of NiO for 298.15 K.

76BER measured the emf of oxygen concentration cells for temperatures from 825 to 1675 K. He calculated the Gibbs energy of formation for NiO(cr) to be $(-235.071 + 0.086\,20\, T/T°)$ kJ·mol^{-1}.

83LEV/NAR used an oxygen-sensing electrode to measure the oxygen pressure over NiO(cr) from 1043 to 1179 K. The pressures, calculated from the emf of the sensing electrode, were represented as

$$``\lg p(\pm 0.033) = -(24300 \pm 120)/T + (13.67 \pm 0.33).\text{''}$$
$$(4.19)$$

The unit of pressure in Eq. (4.19) was Pa.

80TRA/BRU measured the emf of oxygen concentration cells of the type

$$Pt(O_2)(\text{air})|Y_2O_3\text{–}ZrO_2|\text{glass melt}|$$

$$Y_2O_3\text{–}ZrO_2|Pt:O_2(Ni+NiO) \qquad (4.20)$$
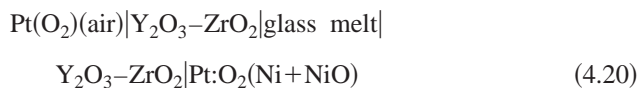
for temperatures from 923.15 to 1323.15 K and from 1373 to 1573 K. The electrodes were measured in air for the former range of temperatures and in glass melts for the latter. They used their measured values to calculate $\Delta_f G_m° = (-235.321 + 0.086\,755\, T/T°)$ kJ·mol^{-1} for 923 K$<$T <1573 K.

80VOL/NEU used an electrochemical cell similar to that of Eq. (4.13) with the CSZ electrolyte replaced with yttrium oxide-zirconium oxide for temperatures from 1073 to 1573 K. They calculated $\Delta_f G_m° = (-235.126 + 0.0920\, T/T°)$ kJ·mol^{-1} from their measurements.

72KLI/STE measured the emf of electrochemical cells of the type

$$Pt|CO(g),CO_2(g)|YDT|Ni,NiO|Ni|Pt, \qquad (4.21)$$

where YDT is yttria-doped thoria. They assumed knowledge of the Gibbs energy change for the CO–CO$_2$ reaction, the parameters of which were taken from 63WIC/BLO. They combined the Gibbs energy change for the CO–CO$_2$ reaction with their measured emf's for the cell in Eq. (4.21) to obtain the Gibbs energy of formation of NiO(cr) for temperatures from 923.15 to 1223.15 K. These values ranged from -155.27 kJ·mol^{-1} at 923 K to -130.08 kJ·mol^{-1} at 1223 K.

84RAY/PET measured the emf of the electrochemical cell

$$Pt|\text{air}|\text{zirconia}|Ni+NiO|Pt \qquad (4.22)$$

for elevated temperatures. They calculated two values of the enthalpy of formation of NiO(cr). These values were $\Delta_f H°[NiO(cr)] = (-232.88 \pm 0.33)$ kJ·mol^{-1} for $T>913$ K and $\Delta_f H°[NiO(cr)] = (-234.72 \pm 0.59)$ kJ·mol^{-1} for $T<913$ K. They indicated that the difference between the two results was indicative of a transition at 913 K.

74WHI measured the heat capacity of NiO(cr) from 3.2 to 18.75 K.

76COY/TOM measured the phonon dispersion of states for NiO(cr) and calculated the effective Debye temperature as a function of the temperature and calculated the heat capacity of the solid. The calculated results were smaller than those from 74WHI and from 79DUB/NAU for temperatures below about 40 K.

79DUB/NAU measured the heat capacity of NiO(cr) in an adiabatic calorimeter for temperatures from 14 to 280 K.

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5. NiOH$^+$(aq)

### A. Selected Values, NBS Tables

The Gibbs energy of formation for NiOH$^+$(aq) was calculated by averaging results from five hydrolysis studies; these follow.

56CUT/KSA measured the pH of NiClO$_4$(aq) solutions with NaOH added to obtain a ''1 μ'' (unit ionic strength) solution. They obtained $K = 1.15 \times 10^{-9}$ for

$$Ni^{2+}(aq) + H_2O = NiOH^+(aq) + H^+(aq) \qquad (5.1)$$

by using Debye-Hückel theory for extrapolation to infinite dilution of nickel. This value led to $\Delta_r G_m° = 51.0$ kJ·mol^{-1} (12.2 kcal·mol^{-1}). Subsequent combination with the Gibbs energies of formation of Ni^{2+}(aq) and H$_2$O(l); -45.6 kJ·mol^{-1} (-10.9 kcal·mol^{-1}) and -237.178 kJ·mol^{-1} (-56.687 kcal·mol^{-1}), respectively, led to $\Delta_f G_m°$ [NiOH$^+$(aq)] $= -231.7$ kJ·mol^{-1} (-55.4 kcal·mol^{-1}).

53SCH/POL titrated nickel solutions with hydroxide and obtained $K = 10^5$ for the reaction

$$Ni^{2+}(aq) + OH^-(aq) = NiOH^+(aq) \qquad (5.2)$$
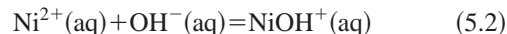
for 298.15 K which was used to calculate $\Delta_r G_m° = -28.4$ kJ·mol^{-1} (-6.8 kcal·mol^{-1}). Combination of this value with the Gibbs energies of formation of Ni^{2+}(aq) (given above) and OH$^-$(aq), -157.293 kJ·mol^{-1} (-37.594 kcal·mol^{-1}), gave $\Delta_f G_m°$[NiOH$^+$(aq)] $= -231.4$ kJ·mol^{-1} (-55.3 kcal·mol^{-1}).

63BOL/JAU determined $K = 1.74 \times 10^{-10}$ at 298.15 K for the reaction of Eq. (5.1) by means of a potentiometric titration at constant ionic strength in NaClO$_4$(aq) solutions and for temperatures from 298.15 to 323.15 K. The 298.15 K

equilibrium constant gave $\Delta_r G_m° = 55.7$ kJ·mol^{-1} (13.3 kcal·mol^{-1}) and $\Delta_f G_m°[\text{NiOH}^+(\text{aq})] = -227.1$ kJ·mol^{-1} (-54.3 kcal·mol^{-1}).

64PER used potentiometric titration of nickel in potassium nitrate solutions with ionic strengths ranging from 1.6×10^{-6} to 4.30×10^{-5} mol·m^{-3} for temperatures from 288.15 to 315.15 K. The equilibrium constant he determined for the reaction of Eq. (5.1) was 1.38×10^{-10}. The 298.15 K value of K was used to calculate $\Delta_r G_m° = 56.5$ kJ·mol^{-1} (13.5 kcal·mol^{-1}) and $\Delta_f G_m°[\text{NiOH}^+(\text{aq})] = -226.3$ kJ·mol^{-1} (-54.1 kcal·mol^{-1}).

52GAY/WOO measured the pH of nickel chloride solutions at 298.15 K. They obtained an equilibrium constant of 2.3×10^{-11} for the reaction of Eq. (5.1). This value of K yielded $\Delta_r G_m° = 60.7$ kJ·mol^{-1} (14.5 kcal·mol^{-1}) and $\Delta_f G_m°[\text{NiOH}^+(\text{aq})] = -222.2$ kJ·mol^{-1} (-53.1 kcal·mol^{-1}).

The average of these five values was taken to obtain the tabulated Gibbs energy of formation value, $\Delta_f G_m°[\text{NiOH}^+(\text{aq})] = -227.6$ kJ·mol^{-1} (-54.4 kcal·mol^{-1}).

The temperature dependence of the reaction of Eq. (5.1) from 64PER was used to determine $\Delta_r H_m° = 51.8$ kJ·mol^{-1} (12.4 kcal·mol^{-1}). This was combined with $\Delta_f H_m°[\text{Ni}^{2+}(\text{aq})] = -54.0$ kJ·mol^{-1} (-12.9 kcal·mol^{-1}) and $\Delta_f H_m°[\text{H}_2\text{O(l)}] = -285.830$ kJ·mol^{-1} (-68.315 kcal·mol^{-1}) to give $\Delta_f H_m°[\text{NiOH}^+(\text{aq})] = -287.9$ kJ·mol^{-1} (-68.8 kcal·mol^{-1}).

The entropy, $S_m°[\text{NiOH}^+(\text{aq})]$, was calculated from $S_m°[\text{NiOH}^+(\text{aq})] = -(\Delta_f G_m° - \Delta_f H_m°)/(298.15 \text{ K}) + S_m°(\text{Ni}) + 1/2\{S_m°[\text{H}_2(\text{g})] + S_m°[\text{O}_2(\text{g})]\} - 1/2 S_m°[\text{H}_2(\text{g})]$ and resulted in $S_m°[\text{NiOH}^+(\text{aq})] = -71$ J·K^{-1}·mol^{-1} (-17 cal·K^{-1}·mol^{-1}).

B. Comments

The NBS Tables staff used the temperature dependence of the equilibrium constant for the reaction of Eq. (5.1) from 64PER to calculate the standard-state enthalpy change of reaction (5.1). But 64PER was not the only study to report the temperature dependence of that reaction, for example, 63BOL/JAU determined $-\log K = (1692 \text{ K})/T + 4.09$ for the reaction in Eq. (5.1) determined from 298.15 to 323.15 K. The temperature dependence of the equilibrium constant given by 63BOL/JAU was not noted on the NBS Tables notes. The 63BOL/JAU value for $\Delta_r H_m°$, 32 kJ·mol^{-1}, independent of temperature, was significantly different than the 64PER value $\Delta_r H_m° = 52$ kJ·mol^{-1}, which had a significant dependence on temperature. These two values imply a minimum uncertainty of the enthalpy of formation of ± 20 kJ·mol^{-1}. No indication was given in the notes why the 64PER value was superior to that given by 63BOL/JAU. In both cases, the equilibrium constants used above were not truly thermodynamic equilibrium constants; no activity coefficients of the various species in the background electrolytes had been used in the calculations.

The values averaged for the Gibbs energy of formation

corresponded to a variation of an order of magnitude in the equilibrium constant for the reaction of Eq. (5.1). (There are some round-off effects in the calculations described above, however, they are trivial compared to the uncertainty that one estimates from the spread of the values.) Combination of a minimum uncertainty of 4 kJ·mol^{-1} for the Gibbs energy of formation and 20 kJ·mol^{-1} for the enthalpy of formation results in a minimum uncertainty in the entropy of $\text{NiOH}^+(\text{aq})$ of ± 80 J·K^{-1}·mol^{-1}.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f G_m°[\text{OH}^-(\text{aq})],$$
$$\Delta_f G_m°[\text{Ni}^{2+}(\text{aq})],$$
$$\Delta_f G_m°[\text{H}_2\text{O(l)}],$$
$$\Delta_f H_m°[\text{H}_2\text{O(l)}],$$
$$\Delta_f H_m°[\text{Ni}^{2+}(\text{aq})],$$
$$S_m°[\text{Ni(cr)}],$$
$$S_m°[\text{O}_2(\text{g})],$$
$$S_m°[\text{H}_2(\text{g})].$$

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties of NiOH$^+$(aq)

52GAY/WOO measured the pH of solutions of aqueous solutions of NiCl$_2$ at 298.15 K. An average of six values for the equilibrium constant for the reaction of Eq. (5.1) gave $K = (2.2 \pm 0.6) \times 10^{-11}$.

59ACH measured the hydrolysis of Ni(NO$_3$)$_2$ in KClO$_4$(aq) or K$_2$SO$_4$(aq) as functions of pH and ionic strength. They obtained $K = 2.3 \times 10^{-11}$ for the reaction of Eq. (5.1).

97MAT/RAI measured the solubility of nickel hydroxide in aqueous solutions with 1×10^{-5} mol·m^{-3} sodium perchlorate and pH's ranging from 7 to 14. Solutions were aged from 3–90 days. The measurements were represented by a model that incorporated speciation. They determined the $\log K$ to be 5.65 ± 0.1 for the reaction of Eq. (5.2).
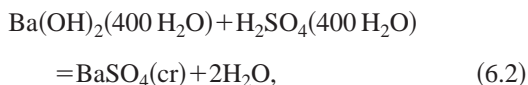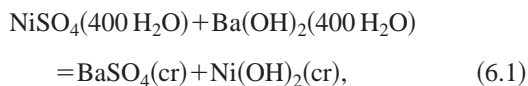
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6. $Ni(OH)_2(cr)$

A. Selected Values, NBS Tables

1882THO determined the enthalpy changes for the reactions,

$$NiSO_4(400\,H_2O) + Ba(OH)_2(400\,H_2O)$$
$$= BaSO_4(cr) + Ni(OH)_2(cr), \qquad (6.1)$$

$$Ba(OH)_2(400\,H_2O) + H_2SO_4(400\,H_2O)$$
$$= BaSO_4(cr) + 2H_2O, \qquad (6.2)$$

for $T = 291.15$ K. The two enthalpies of reaction, -44.48 kJ·mol^{-1} (-10.63 kcal·mol^{-1}) and -154.39 kJ·mol^{-1} (-36.90 kcal·mol^{-1}), respectively, were combined to give the enthalpy change of the reaction

$$NiSO_4(400\,H_2O) + 2H_2O(l)$$
$$= H_2SO_4(400\,H_2O) + Ni(OH)_2(cr), \qquad (6.3)$$
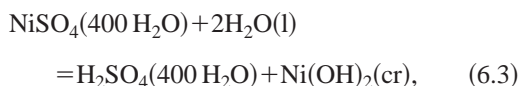
with $\Delta_r H_m = 109.91$ kJ·mol^{-1} (26.27 kcal·mol^{-1}) for 291.15 K. The heat capacity of the reaction was assumed to be 83.6 J·K^{-1}·mol^{-1} (20 cal·K^{-1}·mol^{-1}) in order to calculate the 298.15 K enthalpy of reaction, 110.50 kJ·mol^{-1} (26.41 kcal·mol^{-1}). This enthalpy of reaction was combined with the enthalpies of formation of $NiSO_4(400\,H_2O)$, $H_2O(l)$, and $H_2SO_4(400\,H_2O)$, -958.797 kJ·mol^{-1} (-229.158 kcal·mol^{-1}), -285.830 kJ·mol^{-1} (-68.315, kcal·mol^{-1}), and -889.974 kJ·mol^{-1} (-212.709 kcal·mol^{-1}), respectively, to obtain $\Delta_f H_m°[Ni(OH)_2(cr)] = -529.99$ kJ·mol^{-1} (-126.67 kcal·mol^{-1}).

1882THO also measured the enthalpy of the reaction

$$NiSO_4(400H_2O) + 2KOH(200H_2O)$$
$$= K_2SO_4(800H_2O) + Ni(OH)_2(cr) \qquad (6.4)$$
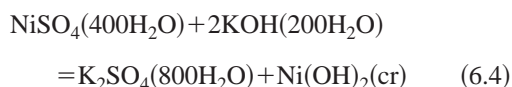
at 291.15 K as -22.30 kJ·mol^{-1} (-5.33 kcal·mol^{-1}). The NBS Tables staff assumed a value for the heat capacity of the reaction, 313.8 J·K^{-1}·mol^{-1} (75 cal·K^{-1}·mol^{-1}) and then calculated the enthalpy of the reaction to be -20.08 kJ·mol^{-1} (-4.80 kcal·mol^{-1}) for 298.15 K. Combination of this enthalpy of reaction with the enthalpies of formation of $K_2SO_4(800H_2O)$, -1413.23 kJ·mol^{-1} (-337.77 kcal·mol^{-1}), $KOH(200H_2O)$, -481.742 kJ·mol^{-1} (-115.139 kcal·mol^{-1}), and $NiSO_4(400H_2O)$, -958.797 kJ·mol^{-1} (-229.158 kcal·mol^{-1}) gave $\Delta_f H_m°[Ni(OH)_2(cr)] = -529.15$ kJ·mol^{-1} (-126.47 kcal·mol^{-1}).

The NBS Tables staff chose $\Delta_f H_m°[Ni(OH)_2(cr)] = -529.7$ kJ·mol^{-1} (-126.6 kcal·mol^{-1}), a value intermediate between the two above.

Two values of the solubility product for $Ni(OH)_2(cr)$ were indicated as having been chosen from three values tabulated in 64SIL/MAR. The two chosen were $\log K = -15.21$ and -15.5. These two values were used to calculate the Gibbs

energies of reaction of 86.78 kJ·mol^{-1} (20.74 kcal·mol^{-1}) and 88.45 kJ·mol^{-1} (21.14 kcal·mol^{-1}), which were then averaged to obtain 87.6 kJ·mol^{-1} (20.94 kcal·mol^{-1}). This value, when combined with $\Delta_f G_m°$ values for the aqueous nickel ion, -45.6 kJ·mol^{-1} (-10.9 kcal·mol^{-1}), and the aqueous hydroxide ion, -157.293 kJ·mol^{-1} (-37.594 kcal·mol^{-1}), resulted in $\Delta_f G_m° = -447.7$ kJ·mol^{-1} (-107.0 kcal·mol^{-1}). The value tabulated was $\Delta_f G_m° = -447.3$ kJ·mol^{-1} (-106.9 kcal·mol^{-1}); the reason for this change was not discernible from the notes.

Combination of $\Delta_f G_m°$ and $\Delta_f H_m°$ gave $\Delta_f S_m° = -275.06$ J·K^{-1}·mol^{-1} (-65.74 cal·K^{-1}·mol^{-1}), which, in turn, resulted in $S_m°[Ni(OH)_2(cr)] = 90.4$ J·K^{-1}·mol^{-1} (21.6 cal·K^{-1}·mol^{-1}) which was then changed to $S_m°[Ni(OH)_2(cr)] = 88$ J·K^{-1}·mol^{-1} (21 cal·K^{-1}·mol^{-1}); the reason for this change was also not discernible from the notes.

B. Comments

The heat capacity that was assumed for the reaction of Eq. (6.3) was significantly smaller than expected. An estimate of $\Delta_r C_{p,m}$ can be obtained from estimates of 90 J·K^{-1}·mol^{-1} for $Ni(OH)_2(cr)$, -175 J·K^{-1}·mol^{-1} for $NiSO_4(400\,H_2O)$, 50 J·K^{-1}·mol^{-1} for $H_2SO_4(400\,H_2O)$, and -75.3 J·K^{-1}·mol^{-1} for $H_2O(l)$. Combination of these values results in $\Delta_r C_{p,m} = 164$ J·K^{-1}·mol^{-1}, or about twice the value used for the calculation described in Sec. A. Using this estimate of the heat capacity of the reaction (164 J·K^{-1}·mol^{-1}), the resultant $\Delta_f H_m°[Ni(OH)_2(cr)]$ is -529.42 kJ·mol^{-1}, or 570 J·mol^{-1} different.

For the reaction of Eq. (6.4), the enthalpy of formation used for $K_2SO_4(800H_2O)$ namely, -1413.23 kJ·mol^{-1} (-337.77 kcal·mol^{-1}), did not match the value given in NBS 270-8. The difference was due most likely to a transcription error, the tabulated value being -337.707 rather than -337.77 kcal·mol^{-1}. Also, a better value of the heat capacity of the reaction is 267 J·K^{-1}·mol^{-1} obtained from the estimates for $Ni(OH)_2(cr)$ and $NiSO_4(400\,H_2O)$, given in the previous paragraph, and values of -106 J·K^{-1}·mol^{-1} for $KOH(200\,H_2O)$ and -210 J·K^{-1}·mol^{-1} for $K_2SO_4(800\,H_2O)$. Taking these two changes into account gives $\Delta_f H_m°[Ni(OH_2)(cr)] = -529.74$ kJ·mol^{-1}. The two enthalpies of formation corresponding to measurements of reactions (6.1)–(6.4) calculated in this section disagree by only 330 J·mol^{-1} (79 cal·mol^{-1}) compared to a difference of 840 J·mol^{-1} calculated in Sec. A, a significant improvement. The remaining difference, namely, 300 J·mol^{-1}, is small compared to the uncertainty expected from mathematical combination of three different measurements from Thomsen (1882THO) and the auxiliary values required for the calculation.

C. Auxiliary Values Required for Data Pathway

$$S_m°[O_2(g)],$$
$$S_m°[H_2(g)],$$

$$S_m°[\text{Ni(cr)}],$$

$$\Delta_f G_m°[\text{Ni}^{2+}(\text{aq})],$$

$$\Delta_f G_m°[\text{OH}^-(\text{aq})],$$

$$\Delta_f H_m°[\text{H}_2\text{O(l)}],$$

$$\Delta_f H_m°[\text{KOH(200 H}_2\text{O)}],$$

$$\Delta_f H_m°[\text{K}_2\text{SO}_4(800 \text{ H}_2\text{O)}],$$

$$\Delta_f H_m°[\text{H}_2\text{SO}_4(400 \text{ H}_2\text{O)}],$$

$$\Delta_f H_m°[\text{NiSO}_4(400 \text{ H}_2\text{O)}].$$

### D. Other Thermodynamic Measurements Considered

Another value was tabulated in 64SIL/MAR for the solubility product. This value, $\log K = -17.19$ was considered unacceptable because it led to an entropy of 125 $J \cdot K^{-1} \cdot mol^{-1}$ for $\text{Ni(OH)}_2(\text{cr})$. This value of $\log K$ was from 49GAY/GAR. Values of pH determined by 49GAY/GAR possess a systematic error, as has been noted in 56JEN/PRA and 97MAT/RAI. The solubility measurements given in 49GAY/GAR are in very good accord with those in 97MAT/RAI.

29GIO/MAT measured the enthalpy of dissolution of $\text{Ni(OH)}_2(\text{cr})$ in hydrochloric acid and obtained -20.65 $kcal \cdot mol^{-1}$ (average of two measurements) for the reaction

$$\text{Ni(OH)}_2(\text{cr}) + 2\text{HCl(20 H}_2\text{O)} = (\text{NiCl}_2 + 2\text{H}_2\text{O})[\text{HCl(aq)}]$$
(6.5)
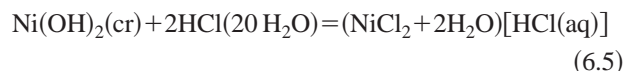
at 299.15 K. The NBS Tables staff combined this enthalpy of reaction with $\Delta_f H_m°$ values for $\text{H}_2\text{O(l)}$, -285.830 $kJ \cdot mol^{-1}$, $\text{HCl(20 H}_2\text{O)}$, -163.845 $kJ \cdot mol^{-1}$, and $\text{NiCl}_2(20 \text{ H}_2\text{O)}$, -376.14 $kJ \cdot mol^{-1}$ to obtain $\Delta_f H_m°$ $[\text{Ni(OH)}_2(\text{cr})] = -533.71$ $kJ \cdot mol^{-1}$. (Author's note: The composition of the final mixture was 78.9 moles H_2O, 3.7 moles HCl, and 0.1 moles Ni. Therefore, the enthalpy of formation value used in the calculation, which was for a composition ratio of 1 mole Ni to 20 moles H_2O, was not representative of the final state of the reaction.)

29GIO/MAT measured the enthalpy of the reaction

$$\text{Ni(OH)}_2(\text{cr}) + \text{SO}_3 \cdot 20 \text{ H}_2\text{O} = (\text{NiSO}_4 + 2\text{H}_2\text{O})[\text{HCl(aq)}]$$
(6.6)
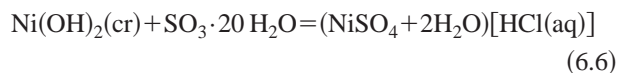
as -92.74 $kJ \cdot mol^{-1}$ at 301.15 K. The NBS Tables staff assumed the heat capacity of the reaction to be zero. They used $\Delta_f H_m°$ values for $\text{H}_2\text{O(l)}$, -285.830 $kJ \cdot mol^{-1}$, $\text{H}_2\text{SO}_4(20 \text{ H}_2\text{O)}$, -884.92 $kJ \cdot mol^{-1}$, and $\text{NiSO}_4(?)$, -958.1 $kJ \cdot mol^{-1}$ to obtain $\Delta_f H_m°[\text{Ni(OH)}_2(\text{cr})] = -548.10$ $kJ \cdot mol^{-1}$. (Author's note: The composition of the final mixture was 78.9 moles H_2O, 3.7 moles H_2SO_4, and 0.1 moles Ni. The source of the value $\Delta_f H_m° = -958.1$ $kJ \cdot mol^{-1}$ for NiSO_4 in the final state is unknown.)

E. More Recent Determinations of the Thermodynamic Properties of Ni(OH)₂(cr)

42NÄS measured the solubility of Ni(OH)_2 in $0.002-2$ $mol \cdot kg^{-1}$ KCl(aq).

56JEN/PRA measured the solubility of nickel hydroxide for pH's from 6.8 to 7.1 with pH controlled with HCl(aq). They obtained $K_{sp} = (1.8 \pm 0.6) \times 10^{-16}$. They also measured the solubility in a sodium acetate+acetic acid buffer and obtained $K_{sp} = 1 \times 10^{-16}$.

67BLA measured the solubility of $\text{Ni(OH)}_2(\text{cr})$ in water at 293.15 K. Methods for controlling pH and CO_2 content were not described. He reported a solubility of 1.38×10^{-3} g $\text{Ni(OH)}_2/\ell$ of solution.

In a short communication, 68SOR/KOS stated that they had measured the heat capacity from 1.5 to 300 K of samples of $\text{Ni(OH)}_2(\text{cr})$ with different particle sizes. They did not give the measured values and said that detailed results and discussions will be published in due course. The subsequent publication appears to be 69SOR/KOS, in which heat capacity values of $\text{Ni(OH)}_2(\text{cr})$ were reported.

69CHU/DOR determined the solubility product, K_{sp}, of Ni(OH)_2 by coprecipitation with Mg(OH)_2. They reported $K_{sp} = 4.38 \times 10^{-15}$.

73NOV/COS measured the solubility of Ni(OH)_2 in 0.55 M NaCl(aq) at 298.15 K. The concentration of nickel ranged from 0.2 to 5×10^{-6} M and the pH ranged from 2 to 8. They reported $K_{sp} = 6.31 \times 10^{-16}$.

78ENO/TSU measured the heat capacity of Ni(OH)_2 crystals from 4.2 to 35 K. They presented their measurements graphically. They reported a temperature of the magnetic transition that was approximately 1 K different than that reported by 69SOR/KOS.

80CHI/SAB measured the solubility of Ni(OH)_2 in water from 298.15 to 313.15 K. Neither the measured concentrations of nickel nor the pH were given, only the solubility products were given, and they appear to be erroneous (discordant with all other values) e.g., K_{sp} for 298.15 K given as 1.5×10^{-12}.

96POU/DRE measured the solubility of nickel hydroxide in aqueous solutions of NaNO_3. Solutions were aged 70 days and speciation was calculated using thermodynamic information from the MINTEQA2 database. The value they determined for pK_{sp} was 15.9 at 295.15 K.

97MAT/RAI also measured the solubility of nickel hydroxide in aqueous solutions with 0.01 M sodium perchlorate and with pH's ranging from 7 to 14. Solutions were aged from 3 to 90 days. The measurements were represented by a model that incorporated speciation. They determined pK_{sp} to be 16.1 ± 0.1. 97MAT/RAI also showed that their value of K_{sp} and nonideality model were in agreement with measured solubilities from 42NÄS, 56JEN/PRA, and 49GAY/GAR, the latter after correcting for pH measurement errors.

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7. NiCl$_2$(cr)

A. Selected Values, NBS Tables

The entropy, heat capacity, and enthalpy relative to 0 K were taken from 52BUS/GIA, who measured the heat capacity from 14 to 336 K; $S_m° = 97.65$ J·K^{-1}·mol^{-1}.

53BUS/GIA measured the equilibrium compositions of the gas phase for the reaction

$$NiCl_2(cr) + H_2(g) = Ni(cr) + 2HCl(g) \qquad (7.1)$$
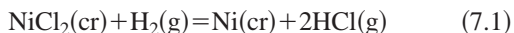
for temperatures from 661.7 to 737.9 K. The measured compositions were combined with thermal data to give the 298.15 K $\Delta_r H_m° = 120.717$ kJ·mol^{-1} (28.852 kcal·mol^{-1}). This was combined with $\Delta_f H_m°[HCl(g)] = -92.307$ kJ·mol^{-1} (-22.062 kcal·mol^{-1}) to obtain $\Delta_f H_m°[NiCl_2(cr)] = -305.332$ kJ·mol^{-1} (-72.976 kcal·mol^{-1}).

Combination of the enthalpy of formation and the entropies of NiCl$_2$(cr), Ni(cr), and Cl$_2$(g) gave $\Delta_f G_m° = -259.065$ kJ·mol^{-1} (-61.918 kcal·mol^{-1}).

B. Comments

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m°[HCl(g)],$$

$$S_m°[Cl_2(g)],$$

$$S_m°[Ni(cr)].$$

D. Other Thermodynamic Measurements Considered

37SAN measured gas phase compositions for the reaction of Eq. (7.1) for temperatures from 661 to 792 K. The 298.15 K $\Delta_f H_m°[NiCl_2(cr)]$ obtained from their results was -307.482 kJ·mol^{-1}.

56SMI/TIK measured gas phase compositions for the reaction

$$2NiCl_2(cr) + O_2(g) = 2NiO(cr) + 2Cl_2(g) \qquad (7.2)$$

for temperatures from 673 to 923 K. They gave the expression $\log\{(p_{Cl_2})^2/p_{O_2}\} = -8750$ K/$T + 8.32$. The NBS Tables staff calculated $\Delta_r H_m° = 167.53$ kJ·mol^{-1} for 525 K. The NBS Tables staff assumed $\Delta_r C_{p,m} = -25$ J·K^{-1}·mol^{-1} and obtained $\Delta_r H_m° = 179.9$ kJ·mol^{-1} for 298.15 K. This value, which is per mol of oxygen, was then combined with the enthalpy of formation of NiO(cr) to obtain $\Delta_f H_m° = -329.7$ kJ·mol^{-1}.

54SHC/TOL measured compositions for the reaction of Eq. (7.1) for temperatures of 573–823 K. Their results for approaching equilibrium from either direction did not agree well. Values of $\Delta_f H_m°$ calculated from these measurements ranged from -304.4 to -307.4 kJ·mol^{-1}, and one extremely small value was ignored.

E. More Recent Determinations of the Thermodynamic Properties of NiCl$_2$(cr)

68KOS/ZAR measured the heat capacity of NiCl$_2$(cr) from 2 to about 50 K. The measured values were not given.

70EFI/KUD measured the enthalpy of solution of NiCl$_2$(cr) in water at 298.15 K by means of an ''isothermal jacket calorimeter.'' They reported an enthalpy of solution of (-83.3 ± 0.4) kJ·mol^{-1} for a final composition of 0.0014–0.005 mol·kg^{-1}.

75BAR/MAS measured the enthalpy of solution of NiCl$_2$(cr) in 2 N HCl and obtained $\Delta_r H = (-74.43 \pm 0.17)$ kJ·mol^{-1}.

75WEE/KOE measured the enthalpy of solution of NiCl$_2$(cr) in 0.1 M HCl(aq) by means of an LKB calorimeter. They obtained $\Delta_r H = (-76.82 \pm 0.42)$ kJ·mol^{-1} for the solution process. The final concentration of nickel in the solution, as nickel chloride, was 0.046 mol [NiCl$_2$(aq)]·kg^{-1}.

75KOS measured the heat capacity of NiCl$_2$(cr) between 2 and 30 K.

76GEE/SHE measured the emf of cells of the type

$$Pt|M,MCl_2|electrolyte|Ni,NiCl_2|Pt \qquad (7.3)$$

for temperatures from 530 to 800 K where the electrolyte was either $PbCl_2$ or $BaCl_2$. The metals used in the cell opposite the nickel cell, M, were iron, manganese, chromium, or cobalt.

77KAS/SAK used gas analysis, a ''thermanobalance,'' and x-ray analysis to determine compositions for the reaction

$$NiO(cr) + 2HCl(g) = NiCl_2(cr) + H_2O(g) \qquad (7.4)$$

at temperatures from 298.15 to about 773 K at 0.101 325 MPa. 77KAS/SAK gave equilibrium constant values for 298.15 and 773 K of 3.14×10^{16} and 4.3×10^{2}, respectively. From the temperature dependence of the equilibrium constant, $\Delta_r H = -128.78$ kJ·mol^{-1} was determined.

84LAV/TIM measured the energy change for the reaction

$$Ni(cr) + Cl_2(g) = NiCl_2(cr) \qquad (7.5)$$
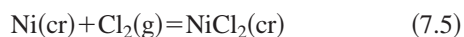
for 298.15 K in a calorimetric bomb. They obtained $\Delta U° = (-302.30 \pm 0.16)$ kJ·mol^{-1} and $\Delta_f H°(NiCl_2) = (-304.78 \pm 0.16)$ kJ·mol^{-1}.

88EFI/EVD reported determination of the enthalpy of formation of $NiCl_2(cr)$ by a calorimetric pathway. They measured the enthalpies of mixing of $Br_2(l)$, $Ni(cr)$, and $KCl(cr)$ into a calorimetric solution that had a composition of $KBr \cdot 0.4 Br_2 \cdot 0.12 HBr \cdot 50.87 H_2O$. They also measured the enthalpies of mixing of $NiCl_2(cr)$ and $KBr(cr)$ into the calorimetric solution. They combined these enthalpies of mixing to obtain an enthalpy change for the reaction

$$Br_2(l) + Ni(cr) + 2KCl(cr) = NiCl_2(cr) + 2KBr(cr). \qquad (7.6)$$
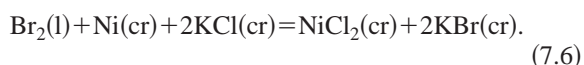
They reported their enthalpy of reaction for Eq. (7.6) as $\Delta_r H° = (-218.38 \pm 0.36)$ kJ·mol^{-1}. They then combined that result with other selected enthalpy of formation values to obtain $\Delta_f H°(NiCl_2) = (-304.46 \pm 0.53)$ kJ·mol^{-1}.

95MAN/KOR reported having measured the enthalpy of solution of $NiCl_2(cr)$ into water and into aqueous solutions of other electrolytes. The measurements were performed with an isoperibol calorimeter with a claimed accuracy of $\pm 0.6\%$. The values for the enthalpy of solution into water were given only graphically.

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76GEE/SHE Gee, R., and Shelton, R. A., J. Trans.-Inst. Min. Metall., Sec. C **85**, 208 (1976).

77KAS/SAK Kasaoka, S., Sakata, Y., and Shirata, M., Nippon Kagaku Kaishi 1728 (1977).

84LAV/TIM Lavut, E. G., Timofeyev, B. I., Yuldasheva, V. M., and Galchenko, G. L., J. Chem. Thermodyn. **16**, 519 (1984).

88EFI/EVD Efimov, M. E., Evdokimova, V. P., Medvedev, V. A., and Tsirel'nikov, V. I., Zh. Fiz. Khim. **62**, 1961 (1988).

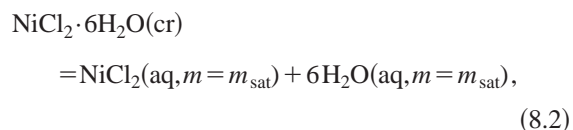95MAN/KOR Manin, N. G., and Koroloev, V. P., Zh. Neorg. Khim. **40**, 1042 (1995).

8. NiCl$_2$·6H$_2$O(cr)

A. Selected Values, NBS Tables

The solubility of $NiCl_2 \cdot 6H_2O$ was taken from 40SEI as 39.6 g $NiCl_2$/100 g saturated solution (5.058 mol·kg^{-1}). The Gibbs energy of solution is

$$\Delta_{sol} G_m° = -RT \ln(4 m_{sat} \gamma_{\pm, sat}/m°)^3 - 6RT \ln a_{w, sat}, \qquad (8.1)$$

for the reaction

$$NiCl_2 \cdot 6H_2O(cr)$$
$$= NiCl_2(aq, m = m_{sat}) + 6H_2O(aq, m = m_{sat}), \qquad (8.2)$$

where $m^0 = 1$ mol·kg^{-1}. An activity coefficient value for $NiCl_2(aq, sat)$, $\gamma_{\pm, sat} = 4.78$, extrapolated from values for other concentrations given in 59ROB/STO, and an unspecified value for the activity of water, $a_{w, sat}$, in the saturated solution were used to calculate $\Delta_{sol} G_m° = -17.544$ kJ·mol^{-1} (-4.193 kcal·mol^{-1}). Combination of $\Delta_{sol} G_m°$ with $\Delta_f G_m°$ values for $Ni^{2+}(aq)$, -45.6 kJ·mol^{-1} (-10.9 kcal·mol^{-1}), $Cl^-(aq)$, -131.260 kJ·mol^{-1} (-31.372 kcal·mol^{-1}), and $H_2O(l)$, -237.183 kJ·mol^{-1} (-56.688 kcal·mol^{-1}) gave $\Delta_f G_m°[NiCl_2 \cdot 6H_2O(cr)] = -1713.52$ kJ·mol^{-1} (-409.54 kcal·mol^{-1}).

The worksheet listed the entropy as 344.3 J·K^{-1}·mol^{-1} (82.3 cal·K^{-1}·mol^{-1}). This value was probably taken from 63KO/HEP.

B. Comments

63KO/HEP claimed that they had obtained a 298.15 K entropy for $NiCl_2 \cdot 6H_2O$ from ''unpublished heat capacity data'' of Friedberg; $S_m° = 344.3$ J·K^{-1}·mol^{-1}. A subsequent article containing the necessary heat capacity measurements was not found. Hence, this value may not be documented.

Backcalculating the osmotic coefficient from the material in Sec. A gave $\phi = 2.356$. This is a bit larger than what one might extrapolate from 59ROB/STO. Extrapolating an os-

motic coefficient from the table in the 2nd edition (1959) gave $\phi = 2.302$. This alters the Gibbs energies of solution and formation by about 200 $J \cdot mol^{-1}$. Other values of the 298.15 K solubility also existed, e.g., 37PEA/ECK reported the 298.15 K solubility as 4.9116 ± 0.0020 $mol \cdot kg^{-1}$. 33BOY reported 5.23 $mol \cdot kg^{-1}$.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f G_m °[Ni^{2+}(aq)],$$

$$\Delta_f G_m °[Cl^-(aq)],$$

$$\Delta_f G_m °[H_2O(l)].$$

D. Other Thermodynamic Measurements Considered

36JAH/JEL measured the emf of the electrochemical cell

$$Ni|NiCl_2 \cdot 6H_2O(cr)|NiCl_2(aq,sat)|AgCl(cr)|Ag(cr) \quad (8.3)$$

at 288.15 and 298.15 K and obtained 0.4021 and 0.3890 int. V, respectively. The 298.15 K emf was used to calculate $\Delta_r G_m ° = -75.06$ $kJ \cdot mol^{-1}$. To this value, a nonideality contribution due to water in saturated solution, -9.58 $kJ \cdot mol^{-1}$, was added to obtain $\Delta_r G_m ° = -65.48$ $kJ \cdot mol^{-1}$. This value was then combined with $\Delta_f G_m °[AgCl(cr)]$, -109.805 $kJ \cdot mol^{-1}$ (-26.244 $kcal \cdot mol^{-1}$) and $\Delta_f G_m °[H_2O(l)]$, -237.183 $kJ \cdot mol^{-1}$ (-56.688 $kcal \cdot mol^{-1}$), to obtain $\Delta_f G_m °[NiCl_2 \cdot 6H_2O(cr)]$, -1708.20 $kJ \cdot mol^{-1}$ (-408.27 $kcal \cdot mol^{-1}$). The emf for 288.15 K was not considered.

1882THO measured the enthalpy of solution of $NiCl_2 \cdot 6H_2O(cr)$ in water

$$NiCl_2 \cdot 6H_2O(cr) = NiCl_2(400\,H_2O) + 6H_2O(l) \quad (8.4)$$

at 291.65 K as 4.85 $kJ \cdot mol^{-1}$ (1.16 $kcal \cdot mol^{-1}$). The heat capacity change of the reaction was assumed to be -188 $J \cdot K^{-1} \cdot mol^{-1}$ (-45 $cal \cdot K^{-1} \cdot mol^{-1}$) and the 298.15 K $\Delta_{sol}H_m$ was calculated to be 3.64 $kJ \cdot mol^{-1}$ (0.87 $kcal \cdot mol^{-1}$). From this, L_ϕ for $NiCl_2(400\,H_2O)$, 3.502 $kJ \cdot mol^{-1}$ (0.837 $kcal \cdot mol^{-1}$) was subtracted to obtain $\Delta_{sol}H_m ° = 0.138$ $kJ \cdot mol^{-1}$ (0.033 $kcal \cdot mol^{-1}$). This calculation, if carried further than on the paper, would have been combined with $\Delta_f H_m °$ for $H_2O(l)$ and $NiCl_2(ai)$ to give $\Delta_f H_m °[NiCl_2 \cdot 6H_2O(cr)] = -2103.39$ $kJ \cdot mol^{-1}$ (-502.72 $kcal \cdot mol^{-1}$), which might appear to be in good agreement with the tabulated value. [Author's note: However, the value they used for L_ϕ does not match what one calculates from the tabulated values for $NiCl_2(aq)$. If one repeats the calculation using the values they actually tabulated, then one obtains $\Delta_f H_m °[NiCl_2 \cdot 6H_2O(cr)] = -2104.05$ $kJ \cdot mol^{-1}$, about 1 $kJ \cdot mol^{-1}$ different than the tabulated value.]

E. More Recent Determinations of the Thermodynamic Properties of NiCl₂·6H₂O(cr)

60ROB/FRI measured the heat capacity of $NiCl_2 \cdot 6H_2O(cr)$ from 1.4 to 20 K.

65DON/EDM measured the heat capacity of $NiCl_2 \cdot 6H_2O(cr)$ from 1 to 4.2 K.

69JOH measured the specific heat of $NiCl_2 \cdot 6H_2O(cr)$ in zero field and various strength applied fields at low temperatures.

76OKA/WAT measured the heat capacity of $NiCl_2 \cdot 6H_2O(cr)$ from 0.8 to 5.0 K. The results were given graphically.

70ASH reported measurement of the enthalpy of solution of $NiCl_2 \cdot 6H_2O(cr)$ in approximately 1 $mol \cdot kg^{-1}$ HCl(aq) at 298.15 K. Although the final composition of the solution was not stated explicitly, it appears to have been 0.012 $mol \cdot kg^{-1}$ $NiCl_2(aq) + 1.04$ $mol \cdot kg^{-1}$ HCl(aq). His value for the enthalpy for the solution process was $\Delta_{sol}H_m = (6.10 \pm 0.22) kJ \cdot mol^{-1}$ at 298.15 K.

73GUR/CAL measured the enthalpy of solution of $NiCl_2 \cdot 6H_2O(cr)$ in 1 M HCl(aq) at 298.15 K in a LKB calorimeter. They obtained $\Delta_{sol}H_m(7.00 \pm 0.13) kJ \cdot mol^{-1}$. The final solution contained approximately 0.025 $mol \cdot kg^{-1}$ $NiCl_2(aq)$ in addition to the HCl(aq).

75KAK/GIE reported measurement of the enthalpy of solution of $NiCl_2 \cdot 6H_2O(cr)$ in 4.36 M HCl(aq) to be (21.32 ± 0.13) $kJ \cdot mol^{-1}$.

77SOK/SAM reported measurement of the enthalpy of solution of $NiCl_2 \cdot 6H_2O(cr)$ in ''20% aqueous HCl'' at 298.15 K, and no other information about the composition of the final solution was given. They reported $\Delta_{sol}H_m = (26.07 \pm 0.13)$ $kJ \cdot mol^{-1}$.

87RAR determined the solubility of $NiCl_2 \cdot 6H_2O(cr)$ at 298.15 K to be 4.9208 ± 0.0038 $mol \cdot kg^{-1}$.

89BAL measured the solubility of $NiCl_2 \cdot 6H_2O(cr)$ for 288.15, 293.15, and 298.15 K as 4.437, 4.609, and 4.864 $mol \cdot kg^{-1}$.

89BAL/TEP reported the solubility of $NiCl_2 \cdot 6H_2O(cr)$ at 298.15 K to be 4.933 $mol \cdot kg^{-1}$.

92RAR determined the solubility of $NiCl_2 \cdot 6H_2O(cr)$ at 298.15 K to be 4.9172 ± 0.0049 $mol \cdot kg^{-1}$.

Other reported values of the 298.15 K solubility are 4.438, 4.89, 4.91, 4.93, 5.058, and 5.060 $mol \cdot kg^{-1}$ from 83KIM/IMA, 86FIL/CHA, 85FIL/CHA, 89LIL/TEP, 80PET/SHE, and 79OJK/MAK, respectively.

F. Bibliography

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33BOY Boye, E. Z., Anorg. Chem. **215**, 75 (1933).

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37PEA/ECK Pearce, J. N., and Eckstrom, H. C., J. Phys. Chem. **41**, 563 (1937).

40SEI Seidell, A., Solubilities of Inorganic and Metal Organic Compounds, 3rd ed. (Van Nostrand, New York, 1940).

59ROB/STO Robinson, R. A., and Stokes, R. H., Electrolyte Solutions, 2nd ed. (Butterworths Scientific, London, 1959).

60ROB/FRI Robinson, W. K., and Friedberg, S. A., Phys. Rev. **117**, 402 (1960).

63KO/HEP Ko, H. C., and Hepler, L. G., J. Chem. Eng. Data

8, 59 (1963).

65DON/EDM Donaldson, R. H., and Edmonds, D. T., Proc. Phys. Soc.. (London) **85**, 1209 (1965).

69JOH Johnson, W. L., US NTIS A. D. Rep. AD-704072 (1969).

70ASH Ashcroft, S. J., J. Chem. Soc. A 1020 (1970).

73GUR/CAL Gurrieri, S., Cali, R., and Siracusa, G., J. Chem. Eng. Data **18**, 22 (1973).

75KAK/GIE Kakolowicz, W., and Giera, E., Conf. Intern. Thermodyn. Chim. Quat. **1**, 73 (1975).

76OKA/WAT Okaji, M., and Watanabe, T., J. Phys. Soc. Jpn. **40**, 589 (1976).

77SOK/SAM Sokolov, Yu. N., Samplavsakya, K. K., and Karapet'yants, M. Kh., Zh. Fiz. Khim. **51**, 2367 (1977).

79OJK/MAK Ojkova, T., and Makarov, L. L., Z. Phys. Chem. (Leipzig) **260**, 609 (1979); Russ. J. Inorg. Chem. **24**, 122 (1979).

80PET/SHE Petrov, G. V., and Shevchuk, V. G., Russ. J. Inorg. Chem. **25**, 1715 (1980); **24**, 1274 (1979); **24**, 935 (1979).

83KIM/IMA Kim, T. P., Imanakunov, B. I., and Kazybaev, S. A., Russ. J. Inorg. Chem. **28**, 596 (1983).

85FIL/CHA Filippov, V. K., Charykov, N. A., and Solechnik, N. D., J. Appl. Chem. USSR **58**, 1811 (1985).

86FIL/CHA Filippov, V. K., Charykov, N. A., and Feodorov, Yu. A., Russ. J. Inorg. Chem. **31**, 1071 (1986).

87RAR Rard, J. A., J. Chem. Eng. Data **32**, 334 (1987).

89BAL Balej, J., Trans. Faraday Soc. **85**, 3327 (1989).

89BAL/TEP Balarew, Chr., Tepavitcharova, S., and Macicek, J., J. Solid State Chem. **82**, 225 (1989).

89LIL/TEP Lileev, A. S., Tepavicharova, S., Lyashchenko, A. K., and Balarev, Kh., Russ. J. Inorg. Chem. **34**, 281 (1989).

92RAR Rard, J. A., J. Chem. Eng. Data **37**, 433 (1992).

9. NiCl$_2\cdot$4H$_2$O(cr)

A. Selected Values, NBS Tables

16DER/YNG measured the vapor pressure of a mixture of the tetrahydrate in equilibrium with the hexahydrate for temperatures from 292.95 to 309.4 K. These measurements corresponded to the reaction

$$\text{NiCl}_2\cdot6\text{H}_2\text{O(cr)} = \text{NiCl}_2\cdot4\text{H}_2\text{O(cr)} + 2\text{H}_2\text{O(g)}. \quad (9.1)$$

The vapor pressure for 298.15 K was taken to be 10.5 Torr, resulting in $\Delta_r G_m° = 10.63$ kJ·mol^{-1} (2.54 kcal·mol^{-1}). The temperature dependence of the vapor pressure was used to calculate $\Delta_r H_m° = 51.17$ kJ·mol^{-1} (12.23 kcal·mol^{-1}).

40BEL also measured the vapor pressure of the reaction in Eq. (9.1) as a function of temperature. His measurements were used to calculate $\Delta_r G_m° = 10.63$ kJ·mol^{-1} (2.54 kcal·mol^{-1}). The temperature dependence of the vapor pressure was used to calculate $\Delta_r H_m° = 52.47$ kJ·mol^{-1} (12.54 kcal·mol^{-1}).

The $\Delta_r G_m°$ value was combined with the Gibbs energies of formation of the hexahydrate crystal, -1713.52 kJ·mol^{-1}

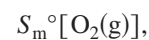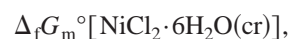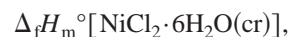(-409.54 kcal·mol^{-1}), and H$_2$O(g), -228.593 kJ·mol^{-1} (-54.635 kcal·mol^{-1}), to obtain $\Delta_f G_m° = -1235.1$ kJ·mol^{-1} (-295.2 kcal·mol^{-1}) for the tetrahydrate. The enthalpy of reaction was taken to be 51.5 kJ·mol^{-1} (12.3 kcal·mol^{-1}), based on the two values described above. Combination of $\Delta_r H_m°$ with the enthalpies of formation of the hexahydrate crystal, -2103.17 kJ·mol^{-1} (-502.67 kcal·mol^{-1}), and H$_2$O(g), -241.818 kJ·mol^{-1} (-57.796 kcal·mol^{-1}), to obtain $\Delta_f H_m° = -1516.7$ kJ·mol^{-1} (-362.5 kcal·mol^{-1}).

The entropy, $S_m°[\text{NiCl}_2\cdot4\text{H}_2\text{O(cr)}]$, was calculated from $-(\Delta_f G_m° - \Delta_f H_m°)/(298.15 \quad \text{K}) + S_m°(\text{Ni}) + 4S_m°[\text{H}_2(\text{g})] + 2S_m°[\text{O}_2(\text{g})] + S_m°[\text{Cl}_2(\text{g})]$. The result was $S_m°[\text{NiCl}_2\cdot4\text{H}_2\text{O(cr)}] = 243$ J·K^{-1}·mol^{-1} (58 cal·K^{-1}·mol^{-1}).

B. Comments

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m°[\text{NiCl}_2\cdot6\text{H}_2\text{O(cr)}],$$
$$\Delta_f G_m°[\text{NiCl}_2\cdot6\text{H}_2\text{O(cr)}],$$
$$\Delta_f H_m°[\text{H}_2\text{O(g)}],$$
$$\Delta_f G_m°[\text{H}_2\text{O(g)}],$$
$$S_m°[\text{H}_2(\text{g})],$$
$$S_m°[\text{O}_2(\text{g})],$$
$$S_m°[\text{Cl}_2(\text{g})],$$
$$S_m°[\text{Ni(cr)}].$$

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties of NiCl$_2\cdot$4H$_2$O(cr)

67VID/DRU measured the solubility of nickel chloride in water for temperatures of 303.15 and 323.15 K as 41.49 and 43.16 wt %, respectively.

89BAL/TEP reported the solubility of NiCl$_2\cdot$4H$_2$O(cr) at 323.15 K to be 5.872 mol·kg^{-1}.

93UVA/TIM measured the equilibrium vapor pressure for transformation of NiCl$_2\cdot$6H$_2$O to NiCl$_2\cdot$4H$_2$O as 1.191 kPa at 298.15 K and 2.607 kPa at 308.15 K.

F. Bibliography

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40BEL Bell, J., J. Chem. Soc. 72, (1940).

67VID/DRU Vidyakina, L. V., and Druzhinin, I. G., Zh. Fiz. Khim. **41**, 3142 (1967).

89BAL/TEP Balarew, Chr., Tepavitcharova, S., and Macicek, J., J. Solid State Chem. **82**, 225 (1989).

93UVA/TIM Uvaliev, Yu. K., Timofeeva, T. G., and Bold-amdaeva, O. K., Izv. Nats. Akad. Nauk Resp. Kaz., Ser. Khim. 23 (1993).
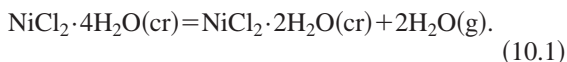
10. NiCl$_2\cdot$2H$_2$O(cr)

A. Selected Values, NBS Tables

16DER/YNG measured the vapor pressure of a mixture of the tetrahydrate in equilibrium with the diydrate for temperatures from 299 to 352.2 K. These measurements corresponded to the reaction

$$\text{NiCl}_2\cdot4\text{H}_2\text{O(cr)} = \text{NiCl}_2\cdot2\text{H}_2\text{O(cr)} + 2\text{H}_2\text{O(g)}. \tag{10.1}$$

The NBS Tables staff took the vapor pressure for 298.15 K to be 5.6 Torr, which was then used to obtain $\Delta_r G_m^\circ = 8.791$ kJ$\cdot$mol^{-1} (2.101 kcal$\cdot$mol^{-1}). The $\Delta_r G_m^\circ$ value was combined with the standard Gibbs energies of formation of the tetrahydrate crystal, -1235.1 kJ$\cdot$mol^{-1} (-295.2 kcal$\cdot$mol^{-1}), and H$_2$O(g), -228.593 kJ$\cdot$mol^{-1} (-54.635 kcal$\cdot$mol^{-1}) to obtain $\Delta_f G_m^\circ = -760.2$ kJ$\cdot$mol^{-1} (-181.7 kcal$\cdot$mol^{-1}).

The temperature dependence of the vapor pressure was used to calculate $\Delta_r H_m^\circ = 55.44$ kJ$\cdot$mol^{-1} (13.25 kcal$\cdot$mol^{-1}). Combination of $\Delta_r H_m^\circ$ with the enthalpies of formation of the tetrahydrate crystal, -1516.7 kJ$\cdot$mol^{-1} (-362.5 kcal$\cdot$mol^{-1}), and H$_2$O(g), -241.818 kJ$\cdot$mol^{-1} (-57.796 kcal$\cdot$mol^{-1}), gave $\Delta_f H_m^\circ = -922.2$ kJ$\cdot$mol^{-1} (-220.4 kcal$\cdot$mol^{-1}).

The entropy, $S_m^\circ[\text{NiCl}_2\cdot2\text{H}_2\text{O(cr)}]$, was calculated from $-(\Delta_f G_m^\circ - \Delta_f H_m^\circ)/(298.15 \text{ K}) + S_m^\circ(\text{Ni}) + 2 S_m^\circ[\text{H}_2(\text{g})] + S_m^\circ[\text{O}_2(\text{g})] + S_m^\circ[\text{Cl}_2(\text{g})]$. This resulted in $S_m^\circ[\text{NiCl}_2\cdot2\text{H}_2\text{O(cr)}] = 176$ J$\cdot$K$^{-1}\cdot$mol^{-1} (42 cal$\cdot$K$^{-1}\cdot$mol^{-1}).

B. Comments

An arithmetic error appears to have been made in the calculation of $\Delta_r G_m^\circ$. The worksheets gave ''log Pmm a 25° $=0.748$.'' This value should have given $\Delta_r G_m^\circ = 12.18$ kJ$\cdot$mol^{-1}, not 8.791 kJ$\cdot$mol^{-1} (2.910 vs 2.101 kcal$\cdot$mol^{-1}). The resulting Gibbs energy of formation should be -753.6 kJ$\cdot$mol^{-1}, 6.6 kJ$\cdot$mol^{-1} different from the value tabulated. The resulting entropy should have been 154 J$\cdot$K$^{-1}\cdot$mol^{-1}, 22 J$\cdot$K$^{-1}\cdot$mol^{-1} different.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m^\circ[\text{NiCl}_2\cdot4\text{H}_2\text{O(cr)}],$$
$$\Delta_f G_m^\circ[\text{NiCl}_2\cdot4\text{H}_2\text{O(cr)}],$$
$$\Delta_f H_m^\circ[\text{H}_2\text{O(g)}],$$
$$\Delta_f G_m^\circ[\text{H}_2\text{O(g)}],$$
$$S_m^\circ[\text{H}_2(\text{g})],$$
$$S_m^\circ[\text{O}_2(\text{g})],$$

$$S_m^\circ[\text{Cl}_2(\text{g})],$$
$$S_m^\circ[\text{Ni(cr)}].$$

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties of NiCl$_2\cdot$2H$_2$O(cr).

67VID/DRU measured the solubility of nickel chloride in water for 343.15 K as 45.37 wt %.

72POL/HER measured the heat capacity of NiCl$_2\cdot$2H$_2$O from 1.2 to 24.5 K. Measured values were shown in graphical form only.

89BAL/TEP reported the solubility of NiCl$_2\cdot$2H$_2$O(cr) at 348.15 K to be 6.900 mol$\cdot$kg^{-1}.

90JUR/DOM reported measurement of the heat capacity of NiCl$_2\cdot$2H$_2$O from about 80 to near 300 K. Values were given only in a graph. They reported that a first-order phase transition occurred at (220.0 ± 0.5) K.

93UVA/TIM measured the equilibrium vapor pressure for transformation of NiCl$_2\cdot$4H$_2$O to NiCl$_2\cdot$2H$_2$O as 0.998 kPa at 298.15 K and 1.702 kPa at 308.15 K.

F. Bibliography

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67VID/DRU Vidyakina, L. V., and Druzhinin, I. G., Zh. Fiz. Khim. **41**, 3142 (1967).

72POL/HER Polgar, L. G., Herweijer, A., and de Jonge, W. J. M., Phys. Rev. B **5**, 1957 (1972).

89BAL/TEP Balarew, Chr., Tepavitcharova, S., and Macicek, J., J. Solid State Chem. **82**, 225 (1989).

90JUR/DOM Juraitis, K. R., Domiciano, J. B., and Sano W., Phys. Rev. B Condens. Matter **42**, 2586 (1990).

93UVA/TIM Uvaliev, Yu. K., Timofeeva, T. G., and Bold-amdaeva, O. K., Izv. Nats. Akad. Nauk Resp. Kaz., Ser. Khim. 23 (1993).

11. NiSO$_4^0$(aq)

A. Selected Values, NBS Tables

One equilibrium constant and one enthalpy change for the reaction

$$\text{Ni}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) = \text{NiSO}_4^0(\text{aq}) \tag{11.1}$$
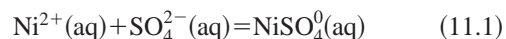
were selected from 64SIL/MAR; $\log K = 2.32$ and $\Delta_r H_m^\circ = 13.85$ kJ$\cdot$mol^{-1} (3.31 kcal$\cdot$mol^{-1}). From the equilibrium constant, $\Delta_r G_m^\circ = -13.22$ kJ$\cdot$mol^{-1} (-3.16 kcal$\cdot$mol^{-1}) was calculated. Combination with the $\Delta_f G_m^\circ$ values for Ni^{2+}(aq) and SO$_4^{2-}$(aq), -45.6 kJ$\cdot$mol^{-1} (-10.9 kcal$\cdot$mol^{-1}) and -744.63 kJ$\cdot$mol^{-1} (-177.97 kcal$\cdot$mol^{-1}), respectively, gave $\Delta_f G_m^\circ[\text{NiSO}_4^0(\text{aq})] = -803.3$ kJ$\cdot$mol^{-1} (-192.0 kcal$\cdot$mol^{-1}). The enthalpy of reaction was combined with $\Delta_f H_m^\circ$ values for Ni^{2+}(aq) and SO$_4^{2-}$(aq),

-54.0 kJ·mol^{-1} (-12.9 kcal·mol^{-1}) and -909.27 kJ·mol^{-1} (-217.32 kcal·mol^{-1}), respectively, to give $\Delta_f H_m°[\text{NiSO}_4^0(\text{aq})] = -949.34$ kJ·mol^{-1} (-226.9 kcal·mol^{-1}).

The entropy, $S_m°[\text{NiSO}_4^0(\text{aq})] = -18.0$ J·K^{-1}·mol^{-1} (-4.3 cal·K^{-1}·mol^{-1}) was calculated from the enthalpy and the Gibbs energy of formation.

B. Comments

The value chosen from 64SIL/MAR corresponded to $K = 209$ and was most likely that from 59NAI/NAN. Other values were given in 64SIL/MAR that ranged from $K = 114$ to 250. The value of an equilibrium constant of this magnitude is dependent on the assumptions used for the nonideality model of the assumed solute species. 55BRO/PRU demonstrated that changes in the assumed nonideality model and association constant pairs gave nearly equivalent representations of their freezing-point measurements with values of K ranging from 114 to 244. As such, giving any particular equilibrium constant, or Gibbs energy of formation, without giving the particular nonideality model used in its generation has no real value.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f G_m°[\text{Ni}^{2+}(\text{aq})],$$
$$\Delta_f G_m°[\text{SO}_4^{2-}(\text{aq})],$$
$$\Delta_f H_m°[\text{Ni}^{2+}(\text{aq})],$$
$$\Delta_f H_m°[\text{SO}_4^{2-}(\text{aq})],$$
$$S_m°[\text{Ni(cr)}],$$
$$S_m°[\text{S(cr)}],$$
$$S_m°[\text{O}_2(\text{g})].$$

D. Other Thermodynamic Measurements Considered

59NAI/NAN measured the electrochemical potential of the cell

$$\text{H}_2,\text{Pt}|\text{NiSO}_4,\text{HCl(aq)}|\text{AgCl},\text{Ag} \qquad (11.2)$$

from 273.15 to 318.15 K at various compositions. With assumption of a nonideality model, 59NAI/NAN calculated equilibrium constants at each temperature and an enthalpy of reaction $\Delta_r H_m° = (13.8 \pm 0.8)$ kJ·mol^{-1}.

E. More Recent Determinations of the Thermodynamic Properties of $\text{NiSO}_4^0(\text{aq})$.

69IZA/EAT reported values of the equilibrium constant, enthalpy, and entropy for the association reaction to form $\text{NiSO}_4(\text{aq})$, determined through titration calorimetry. Their values were $K = 646$, $\Delta_r H° = 1.72$ kJ·mol^{-1}, and $\Delta_r S° = 59.0$ J·K^{-1}·mol^{-1}.

71ISO measured freezing point depressions for $\text{NiSO}_4(\text{aq})$ for 0.02–0.2 mol·kg^{-1}. From his measurements he calcu-

lated values of the equilibrium constant assuming different values of the parameter a in the Debye-Hückel expression. For $a = 6$ Å, he calculated an association equilibrium constant, $K = 17 \pm 1.3$.

73KAT measured the electrical conductance of aqueous NiSO_4 solutions for temperatures from 273.15 to 318.15 K. Using an extended Debye-Hückel model for the activity coefficients of the ions, he determined an association constant, K, of 187 for 298.15 K and an enthalpy of association of 5.31 kJ·mol^{-1}, also for 298.15 K.

74MAK/MAS used conductimetric titration to determine the association constant for $\text{NiSO}_4^0(\text{aq})$ at 298.15 K. They reported $K = 500$.

76SHI/TSU measured the electrical conductance of aqueous NiSO_4 solutions for 288.15, 298.15, and 313.15 K. Using an extended Debye–Hückel model for the activity coefficients of the ions, they determined a molar-based association constant, K, of 204 for 298.15 K.

77KAT measured the electrical conductance of electrolyte solutions and deduced an association constant, K, of 165 and an enthalpy of association of 8.65 kJ·mol^{-1}, both for 298.15 K.

77SOL/VLA measured enthalpies of dilution of $\text{NiSO}_4(\text{aq})$ for compositions from 2.32 to 0.278 mol·kg^{-1}.

79FIS/FOX reported electrical conductivity measurements for $\text{NiSO}_4(\text{aq})$ as a function of pressure to 200 MPa and for temperatures of 288.15, 293.15, and 298.15 K. Their results yielded values of the association constant, K, of 145, 167, and 161, respectively, for the three temperatures.

80LIB/SAD measured isopiestic molalities of $\text{NiSO}_4(\text{aq})$ using KCl(aq) as the reference electrolyte.

83HOL/MES measured isopiestic molalities of $\text{NiSO}_4(\text{aq})$ with NaCl(aq) as the reference substance for temperatures of 383.14 and 413.22 K. For 383.14 K, the composition range was from 1.5 to 5.7 mol·kg^{-1}, and for 413.22 K it was 4.4–5.2 mol·kg^{-1}.

85DRA/MAD measured the heat capacities of aqueous solutions of nickel sulfate at temperatures 323.15, 343.15, and 363.15 K with an adiabatic calorimeter.

F. Bibliography

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76SHI/TSU Shimizu, K., Tsuchihashi, N., and Furumi, Y.,

Rev. Phys. Chem. Jpn. **46**, 30 (1976).

77KAT Katayama, S., Rikagaku Kenkyusho Hokoku **53**, 212 (1977).

77SOL/VLA Solov'eva, S. G., Vlasenko, K. K., and Karapet'yants, M. Kh., Zh. Fiz. Khim. **51**, 2991 (1977).

79FIS/FOX Fisher, F. H., and Fox, A. P., J. Solution Chem. **8**, 309 (1979).

80LIB/SAD Libus, W., Sadowska, T., and Libus, Z., J. Solution Chem. **9**, 341 (1980).

83HOL/MES Holmes, H. F., and Mesmer, R. E., J. Chem. Thermodyn. **15**, 709 (1983).

85DRA/MAD Drakin, S. I., Madanat, A. T., and Karlina, O., Tr. Inst. Mosk. Khim. Tekhnol. Inst. Mendeleeva **136**, 47 (1985).

12. NiSO$_4$(cr)

A. Selected Values, NBS Tables

65ADA/KIN determined calorimetrically the enthalpy changes for a set of reactions that, when combined, gave the enthalpy change for the reaction

$$Ni(cr) + H_2SO_4(7.068H_2O) = NiSO_4(cr) + H_2(g). \quad (12.1)$$
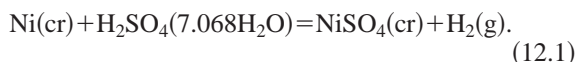
65ADA/KIN obtained $\Delta_r H_m = 3.60$ kJ·mol^{-1} (0.86 kcal·mol^{-1}) for the reaction of Eq. (12.1). This value was combined with the enthalpy of formation of H$_2$SO$_4$(7.068H$_2$O), -876.527 kJ·mol^{-1} (-209.495 kcal·mol^{-1}), to obtain $\Delta_f H_m°[NiSO_4(cr)] = -872.91$ kJ·mol^{-1} (-208.63 kcal·mol^{-1}).

The entropy of NiSO$_4$(cr) appeared to have been estimated. Values of $\{S_m°[MSO_4(cr)] - S_m°[MO(cr)]\}$ were calculated for M=Ba, Ca, Cd, Cu, Fe, Mg, Mn, and Sr. These values ranged from 50 J·K^{-1}·mol^{-1} (12 cal·K^{-1}·mol^{-1}) to 69.5 J·K^{-1}·mol^{-1} (16.6 cal·K^{-1}·mol^{-1}). The entropy of NiSO$_4$(cr) was assigned the value 92 J·K^{-1}·mol^{-1} (22 cal·K^{-1}·mol^{-1}). From this value the entropy of formation was calculated to be -379.5 J·K^{-1}·mol^{-1} (-90.7 cal·K^{-1}·mol^{-1}) and the Gibbs energy of formation was calculated to be -759.8 kJ·mol^{-1} (-181.6 kcal·mol^{-1}).

The heat capacity tabulated for NiSO$_4$(cr), 138 J·K^{-1}·mol^{-1} (33 cal·K^{-1}·mol^{-1}), was indicated as having been taken from 1863PAP.

B. Comments

Another estimated value of the entropy of NiSO$_4$(cr) was also listed on the worksheet as 104.6 J·K^{-1}·mol^{-1} (25 cal·K^{-1}·mol^{-1}) resulting in $\Delta_f G_m° = -763.6$ kJ·mol^{-1} (-182.5 kcal·mol^{-1}). No legible reason was available for the choice of $S_m° = 22$ over 25 cal·K^{-1}·mol^{-1} or over the measured values (see Sec. D below). Finally, the comparison method used to estimate the entropy value would not have taken into account an entropy contribution from electronic effects.

C. Auxiliary Values Required for Data Pathway

$\Delta_f H_m°[H_2SO_4(7.068\,H_2O)]$,

$S_m°[H_2(g)]$,

$S_m°[O_2(g)]$,

$S_m°[Ni(cr)]$,

$S_m°[S(cr)]$,

$S_m°[BaO(cr)]$,

$S_m°[BaSO_4(cr)]$,

$S_m°[CaO(cr)]$,

$S_m°[CaSO_4(cr)]$,

$S_m°[CdO(cr)]$,

$S_m°[CdSO_4(cr)]$,

$S_m°[CuO(cr)]$,

$S_m°[CuSO_4(cr)]$,

$S_m°[FeO(cr)]$,

$S_m°[FeSO_4(cr)]$,

$S_m°[MgO(cr)]$,

$S_m°[MgSO_4(cr)]$,

$S_m°[MnO(cr)]$,

$S_m°[MnSO_4(cr)]$,

$S_m°[SrO(cr)]$,

$S_m°[SrSO_4(cr)]$.

D. Other Thermodynamic Measurements Considered

A memorandum that described a value of the entropy of NiSO$_4$(cr) as 103.85 J·K^{-1}·mol^{-1} (24.82 cal·K^{-1}·mol^{-1}) was found in the files. That document indicated that the entropy value was obtained from E. G. King at the Bureau of Mines and was dated 2/14/66. King's communication undoubtedly regarded the work of 65WEL and described the contribution to the entropy that resulted from proper inclusion of the ordering of spin moments.

65WEL reported heat-capacity measurements from 52 to 296.3 K for NiSO$_4$(cr). He reported integration of his measured heat capacities, combination of that value with an extrapolation from 51 to 0 K, and the addition of a theoretical contribution for ordering of spin moments. The resultant value was $S_m° = 103.8$ J·K^{-1}·mol^{-1}. 65WEL also gave the 298.15 K $C_{p,\,m}° = 99.08$ J·K^{-1}·mol^{-1} (23.68 cal·K^{-1}·mol^{-1}).

There was a notation that ''Marchal's data'' (assumed by the present author to be 25MAR) were recalculated to yield $\Delta_f H_m° = -886.6$ kJ·mol^{-1} (-211.9 kcal·mol^{-1}) for 298.15 K. The data were for the reaction

$$2NiSO_4(cr) = 2NiO(cr) + 2SO_2(g) + O_2(g). \quad (12.2)$$
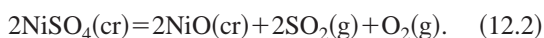
This value of $\Delta_f H_m°$ was about 14 kJ·mol^{-1} more exothermic than the value tabulated.

E. More Recent Determinations of the Thermodynamic Properties of NiSO$_4$(cr)

65ALC/SUD used a thermogravimetric method to determine decomposition and reformation temperatures of NiSO$_4$(cr) in a controlled atmosphere of SO$_2$, O$_2$, and N$_2$. The equilibrium composition of the gas phase was calculated by means of $\Delta_r G°/\text{kJ·mol}^{-1} = 189.117 - 0.1787(T/T°)$ for the reaction

$$2SO_3 = 2SO_2 + O_2, \quad (12.3)$$

where $T° = 1$ K. For the reaction

$$NiSO_4(cr) = NiO(cr) + SO_2(g) + \tfrac{1}{2}O_2(g), \quad (12.4)$$

65ALC/SUD obtained $\Delta_r G°/\text{kJ·mol}^{-1} = 354.217 - 0.2971(T/T°)$ for temperatures from 1110 to 1160 K.

64WAR measured the total pressure above a nickel sulfate+nickel oxide sample where the partial pressure of oxygen was controlled by a Pd+PdO couple in common with the nickel material. His measurements spanned the temperature range of 900–1100 K. For the reaction of Eq. (12,4) above, his measurements were adequately represented by $\Delta_r G°/\text{kJ·mol}^{-1} = 345.35 - 0.29109(T/T°)$.

66ING reported decomposition pressures over NiSO$_4$(cr) for temperatures from 999 to 1163 K. The equilibrium constant for the reaction of Eq. (12.3) above was taken to be

$$\log_{10} K = 8.857 - 5465.5 \ (T°/T) - 1.215\,72 \log_{10}(T/T°). \quad (12.5)$$

The measured vapor pressure measurements were adequately represented with the equation

$$\Delta_r G_m°/\text{kJ·mol}^{-1} = 235.35 + 0.012\,13(T/T°)\log_{10}(T/T°)$$
$$- 0.224\,54(T/T°) \quad (12.6)$$

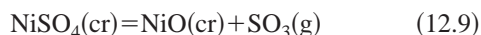for the reaction NiSO$_4$(cr) = NiO(cr) + SO$_3$(g). This equation is valid to 298.15 K.

72UME/TOZ measured the dissociation pressure of nickel sulfate at elevated temperatures using thermogravimetry. They gave the SO$_3$(g) pressure as

$$\log[p(SO_3(g))/p°] = -12\,476(T°/T) + 9.98. \quad (12.7)$$

This equation yields a Gibbs energy of reaction

$$\Delta_r G_m°/\text{kJ·mol}^{-1} = 238.848 - 0.1911(T/T°) \quad (12.8)$$

for the reaction

$$NiSO_4(cr) = NiO(cr) + SO_3(g) \quad (12.9)$$

where $p° = 1$ atm. Equation (12.7) was valid for temperatures of 988–1106 K.

73SKE/ESP measured the electromotive force of an electrochemical cell containing nickel sulfate+nickel oxide coupled to an oxygen reference cell, where the coupling was achieved with a CSZ electrolyte. The potential of the cell was measured at temperatures from 881 to 1128 K. They gave values of the enthalpy of reaction and entropy of reaction, valid for those temperatures, of (347.44 ± 2.0) and (293.21 ± 2.0) J·K^{-1}·mol^{-1}, respectively, for the reaction given in Eq. (12.4).

77SAD/KAW used electrochemical cells with a CSZ electrolyte at temperatures from 903 to 1069 K to determine the Gibbs energy of formation of NiSO$_4$(cr) at these temperatures. The equation they gave was

$$\Delta_f G°/\text{kJ·mol}^{-1} = (-905.00 \pm 3.35) + (0.4197 \pm 0.0079)$$
$$\times (T/T°), \quad (12.10)$$

which was valid for 903 K $< T <$ 1069 K. Generation of Eq. (12.10) required values of the Gibbs energies of formation of NiO(cr), SO$_2$(g), and SO$_3$(g) at those temperatures.

78KAR/MAL determined vapor pressures for the decomposition of nickel sulfate with a manometric device. They accepted thermodynamic properties for the SO$_2$(g)–SO$_3$(g) equilibrium and combined them with the measured pressures to calculate the Gibbs energy change for the reaction given in Eq. (12.9). They gave the Gibbs energy of reaction as

$$\Delta_r G_m°/\text{kJ·mol}^{-1} = 237.643 - 0.1855(T/T°). \quad (12.11)$$

78KAR/MAL used the same Gibbs energy change for the SO$_2$(g)–SO$_3$(g) reaction as did 65ALC/SUD.

78STU/FER reported measurements of the heat capacity of NiSO$_4$(cr) from 10 to 70 K. They combined their measurements with those of 65WEL and fitted these values piecewise with polynomials. They reported $S_m°(298.15 \ \text{K}) = 101.3$ J·K^{-1}·mol^{-1} and $\Delta_f G_m° = -762.41$ kJ·mol^{-1}, the latter value having been obtained from combination of their entropy value, values for the elements, and the 65ADA/KIN measurements.

83GAU/BAL used an electrochemical concentration cell, with K$_2$SO$_4$ as the cell junction, to determine partial pressures over a nickel sulfate+nickel oxide mixture for temperatures from 883 to 1028 K. The cell was

$$Pt|SO_3(pSO_3)NiSO_4,NiO|K_2SO_4|$$
$$SO_3'(pSO_3'),O_2'(pO_2')|Pt, \quad (12.12)$$
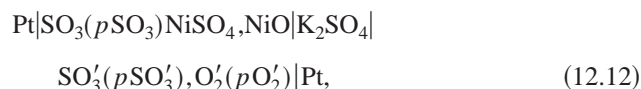
for which one can write Eq. (12.9) for the cell reaction. They took the equilibrium constant for the SO$_2$(g)–SO$_3$(g) reaction to be

$$\ln K = 22.289 - 23\,496/(T°/T) \quad (12.13)$$

for the reaction of Eq. (12.3). They gave the equation

$$\Delta_r G_m°/\text{kJ·mol}^{-1} = 247.99 - 0.300\,69(T/T°),$$
$$\sigma = 0.53 \ \text{kJ/mol}, \quad (12.14)$$

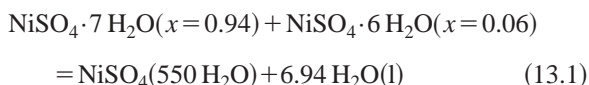as a representation of their measured partial pressures.

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65ALC/SUD Alcock, C. B., Sudo, K., and Zador, S., Trans. Metall. Soc. AIME **233**, 655 (1965).

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78STU/FER Stuve, J. M., Ferrante, M. J., and Ko H. C., Thermodynamic Properties of $NiBr_2$ and $NiSO_4$ from 10 to 1200 K, US Bureau of Mines, RI 8271, 1978.

83GAU/BAL Gauthier, M., and Bale, C. W., Metall. Trans. B **14B**, 117 (1983).

13. $NiSO_4 \cdot 7\,H_2O(cr)$

A. Selected Values, NBS Tables

The entropy, heat capacity, and enthalpy relative to 0 K were all taken from 66STO/ARC; $S_m° = 378.94$ $J \cdot K^{-1} \cdot mol^{-1}$ (90.57 $cal \cdot K^{-1} \cdot mol^{-1}$). 66STO/ARC also measured the enthalpy of solution of a mixture of $NiSO_4 \cdot 6\,H_2O$ and $NiSO_4 \cdot 7\,H_2O$ in water:

$$NiSO_4 \cdot 7\,H_2O(x=0.94) + NiSO_4 \cdot 6\,H_2O(x=0.06)$$
$$= NiSO_4(550\,H_2O) + 6.94\,H_2O(l) \qquad (13.1)$$

at 298.15 K, where x is the mole fraction. Compensation for the amount of hexahydrate in the mixture gave $\Delta_{sol}H_m$ $= 16.627$ $kJ \cdot mol^{-1}$ (3.974 $kcal \cdot mol^{-1}$). Combination of this value with $\Delta_f H_m°[NiSO_4(550\,H_2O)] = -958.906$ $kJ \cdot mol^{-1}$ (-229.184 $kcal \cdot mol^{-1}$) and $\Delta_f H_m°[H_2O(l)] = -285.830$ $kJ \cdot mol^{-1}$ (-68.315 $kcal \cdot mol^{-1}$) gave $\Delta_f H_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2976.34$ $kJ \cdot mol^{-1}$ (-711.36 $kcal \cdot mol^{-1}$).

The Gibbs energy of formation was calculated from the difference of the enthalpy of formation -2976.34 $kJ \cdot mol^{-1}$ (-711.36 $kcal \cdot mol^{-1}$) and the entropy of formation -1724.23 $J \cdot K^{-1} \cdot mol^{-1}$ (-412.10 $cal \cdot K^{-1} \cdot mol^{-1}$); $\Delta_f G_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2462.242$ $kJ \cdot mol^{-1}$ (-588.49 $kcal \cdot mol^{-1}$).

B. Comments

The enthalpy of formation used for $NiSO_4(550\,H_2O)$ was actually the value tabulated for $NiSO_4(500\,H_2O)$. Use of $\Delta_f H_m°[NiSO_4(550\,H_2O)] = -958.960$ $kJ \cdot mol^{-1}$ (-229.197 $kcal \cdot mol^{-1}$) gives $\Delta_f H_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2976.40$ $kJ \cdot mol^{-1}$.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m°[NiSO_4(550\,H_2O)],$$
$$\Delta_f H_m°[H_2O(l)],$$
$$S_m°[H_2(g)],$$
$$S_m°[O_2(g)],$$
$$S_m°[Ni(cr)],$$
$$S_m°[S(cr)].$$

D. Other Thermodynamic Measurements Considered

36PER measured the enthalpy change for

$$NiSO_4 \cdot 7\,H_2O = NiSO_4(n\,H_2O) + 7\,H_2O(l) \qquad (13.2)$$
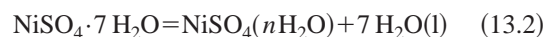
for temperatures of 287.15 and 290.15 K for different concentrations (i.e., different values of n). Two enthalpy of reaction values, one for each temperature, corresponding to $n = 84.97$, namely, 4.28 and 4.36 $kcal \cdot mol^{-1}$, were used to extrapolate to 298.15 K, resulting in $\Delta_{sol}H_m$ $= 19.58$ $kJ \cdot mol^{-1}$ (4.68 $kcal \cdot mol^{-1}$). This $\Delta_{sol}H_m$ value was then combined with an extrapolated value $\Delta_f H_m°[NiSO_4(84.97\,H_2O)] = -958.312$ $kJ \cdot mol^{-1}$ (-229.042 $kcal \cdot mol^{-1}$) and with $\Delta_f H_m°[H_2O]$ (given above) to give $\Delta_f H_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2978.70$ $kJ \cdot mol^{-1}$ (-711.93 $kcal \cdot mol^{-1}$).

1882THO measured the enthalpy change for

$$NiSO_4 \cdot 7\,H_2O(cr) = NiSO_4(800\,H_2O) + 7\,H_2O(l), \qquad (13.3)$$
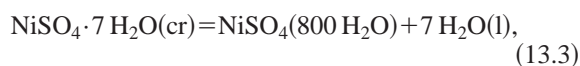
for 292.15 K as $\Delta_{sol}H_m = 17.78$ $kJ \cdot mol^{-1}$ (4.25 $kcal \cdot mol^{-1}$). The heat capacity of the reaction was assumed to be $\Delta_r C_{p,m} = 167$ $J \cdot K^{-1} \cdot mol^{-1}$ (40 $cal \cdot K^{-1} \cdot mol^{-1}$) and the 298.15 K $\Delta_{sol}H_m$ was calculated to be 18.79 $kJ \cdot mol^{-1}$ (4.48 $kcal \cdot mol^{-1}$). Combination of this enthalpy of solution with $\Delta_f H_m°[NiSO_4(800\,H_2O)] = -959.169$ $kJ \cdot mol^{-1}$ (-229.247 $kcal \cdot mol^{-1}$) and $\Delta_f H_m°[H_2O(l)]$ (given above) led to $\Delta_f H_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2978.80$ $kJ \cdot mol^{-1}$ (-711.95 $kcal \cdot mol^{-1}$).

The Gibbs energy of solution was calculated from the solubility, the activity coefficient of the solute, and a vapor pressure for water in the saturated solution. This calculation gave $\Delta_f G_m°[NiSO_4 \cdot 7\,H_2O(cr)] = -2480.3$ $kJ \cdot mol^{-1}$ (-592.8 $kcal \cdot mol^{-1}$), quite different from the tabulated value. [Author's note: On the worksheets the nonideality contributions for both water and the solute were miscalculated. Whereas the worksheets indicated that the Gibbs energy of solution was 25.56 $kJ \cdot mol^{-1}$ (6.11 $kcal \cdot mol^{-1}$), correction of the arithmetic errors gives $\Delta_{sol}G_m° = 12.80$

kJ·mol^{-1} (3.06 kcal·mol^{-1}) and $\Delta_f G_m°[\text{NiSO}_4 \cdot 7\,\text{H}_2\text{O(cr)}]$ $= -2467.60$ kJ·mol^{-1} (-589.77 kcal·mol^{-1}].

E. More Recent Determinations of the Thermodynamic Properties of NiSO$_4$·7 H$_2$O(cr)

93PRZ/WIS measured the enthalpy of solution of NiSO$_4$·7 H$_2$O in water at 298.15 K in a ''nonadiabatic-nonisothermic calorimeter.'' Measurements were made at a ''mass ratio of salt to water'' of 5×10^{-4}. The enthalpy of solution was reported to be 15.644 kJ·mol^{-1}; it was not clear whether this was for the concentration in the calorimeter or whether it had been reduced to infinite dilution by some means. Assuming this value corresponded to infinite dilution and combining it with tabulated values of $\Delta_f H_m°[\text{NiSO}_4(\text{ai})] = -963.2$ kJ·mol^{-1} and $\Delta_f H_m°(\text{H}_2\text{O})$ (given above) yields $\Delta_f H_m°[\text{NiSO}_4 \cdot 7\,\text{H}_2\text{O(cr)}] = -2979.65$ kJ·mol^{-1}.

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93PRZ/WIS Przepiera, A., Wisniewski, M., Dabrowski, W., and Jablonski, M., J. Therm. Anal. **40**, 1139 (1993).

14. α-NiSO$_4$·6 H$_2$O(cr)

A. Selected Values, NBS Tables

The entropy, heat capacity, and enthalpy relative to 0 K were all taken from 66STO/ARC; $S_m° = 334.47$ J·K^{-1}·mol^{-1} (79.94 cal·K^{-1}·mol^{-1}). 66STO/ARC also measured the enthalpy of solution of NiSO$_4$·6 H$_2$O in water:

$$\text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)} = \text{NiSO}_4(556.7\,\text{H}_2\text{O}) + 6\,\text{H}_2\text{O(l)}$$
$$(14.1)$$
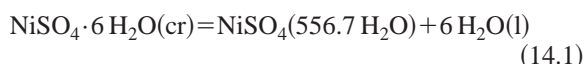
at 298.15 K and obtained $\Delta_{sol} H_m = 8.945$ kJ·mol^{-1} (2.138 kcal·mol^{-1}). Combination of this value with $\Delta_f H_m°[\text{NiSO}_4(556.7\,\text{H}_2\text{O})] = -958.906$ kJ·mol^{-1} (-229.184 kcal·mol^{-1}) and $\Delta_f H_m°[\text{H}_2\text{O(l)}] = -285.830$ kJ·mol^{-1} (-68.315 kcal·mol^{-1}) gave $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)}] = -2682.831$ kJ·mol^{-1} (-641.212 kcal·mol^{-1}).

The Gibbs energy of formation was calculated from the difference of the enthalpy of formation -2682.82 kJ·mol^{-1} (-641.21 kcal·mol^{-1}) and the entropy of formation -1535.645 J·K^{-1}·mol^{-1} (-367.028 cal·K^{-1}·mol^{-1}); $\Delta_f G_m°[\text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)}] = -2224.980$ kJ·mol^{-1} (-531.783 kcal·mol^{-1}).

B. Comments

The enthalpy of formation used for NiSO$_4$(557 H$_2$O) was actually the value tabulated for NiSO$_4$(500 H$_2$O). Use of $\Delta_f H_m°[\text{NiSO}_4(557\,\text{H}_2\text{O})] = -958.960$ kJ·mol^{-1} (-229.197 kcal·mol^{-1}) [this is the same value as that calculated for NiSO$_4$(550 H$_2$O); the tabulated values are no more accurate than this] gives $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)}] = -2682.885$ kJ·mol^{-1}.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m°[\text{NiSO}_4(557\,\text{H}_2\text{O})],$$
$$\Delta_f H_m°[\text{H}_2\text{O(l)}],$$
$$S_m°[\text{H}_2(\text{g})],$$
$$S_m°[\text{O}_2(\text{g})],$$
$$S_m°[\text{Ni(cr)}],$$
$$S_m°[\text{S(cr)}].$$

D. Other Thermodynamic Measurements Considered

65JAM/BRO measured the enthalpy of solution of NiSO$_4$·6 H$_2$O(cr) in water at 302.15 K. The NBS worksheet indicated the measured $\Delta_{sol} H_m$ was 6 kcal·mol^{-1}. The heat capacity for the reaction was assumed to be 40 cal·K^{-1}·mol^{-1} to calculate the 298.15 K value of $\Delta_{sol} H_m$ $= 5.8$ kcal·mol^{-1}. This value was combined with $\Delta_f H_m°[\text{NiSO}_4(\text{aq})] = -229.0$ kcal·mol^{-1}, and the enthalpy of formation of water (given above) to obtain $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)}] = -644.7$ kcal·mol^{-1}, which was significantly different than the tabulated value. However, 65JAM/BRO gave the enthalpy of reaction value as -6 cal·g^{-1}, not $+6$ kcal·mol^{-1}, in both a table and a figure. They also stated that the mass of the solute used was on the order of 0.2–0.5 g and that the amount of water was 1 kg. They stated that their uncertainty in the measurement of the temperature difference was 0.002 K which would yield a minimum uncertainty of 2.5 cal in the enthalpy of solution. Combination of all this information results in a 302.15 K enthalpy of solution of -1.6 kcal·mol^{-1} with a minimum uncertainty in the range of $\pm(1.3–3.2)$ kcal·mol^{-1}, as opposed to an enthalpy of solution of $+6$ kcal·mol^{-1}. Additionally, the enthalpy of formation used for aqueous nickel sulfate would correspond to a very high concentration, whereas 65JAM/BRO described a procedure that would have resulted in a solution concentration of about 0.001 mol·kg^{-1}. Combination of all these factors results in a 298.15 K enthalpy of formation of (-2671.5 ± 12) and (-638.5 ± 3) kcal·mol^{-1} for NiSO$_4$·6 H$_2$O(cr).

39SIM/KRO measured the vapor pressure of water over nickel sulfate hydrate and determined the enthalpy of the reaction

$$\text{NiSO}_4 \cdot 7\,\text{H}_2\text{O(cr)} = \text{NiSO}_4 \cdot 6\,\text{H}_2\text{O(cr)} + \text{H}_2\text{O(g)}$$
$$(14.2)$$
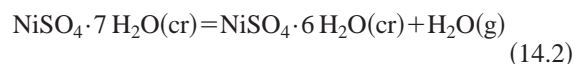
to be 43.9 kJ·mol^{-1}. This result was considered no further. It would have yielded $\Delta_f H_m° = -2690.6$ kJ·mol^{-1}.

64KOH/ZÄS measured the vapor pressure corresponding to the reaction of Eq. (14.2) for temperatures from 296.15 to 307.15 K and obtained

$$\log(p/\text{Torr}) = -2566(T°/T) + 9.92. \qquad (14.3)$$

Calculation of the enthalpy of reaction from Eq. (14.3) gave 49.12 kJ·mol^{-1} (11.74 kcal·mol^{-1}). An assumed heat capacity of the reaction of Eq. (14.2), $\Delta_r C_{p,m} = -6.3$ J·K^{-1}·mol^{-1} (-1.5 cal·K^{-1}·mol^{-1}), was used to obtain $\Delta_r H_m(298.15\ \text{K}) = 49.16$ kJ·mol^{-1} (11.75 kcal·mol^{-1}). This was combined with the enthalpies of formation of NiSO$_4$·7H$_2$O(cr) and H$_2$O(g) to obtain $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\text{H}_2\text{O(cr)}] = -2685.37$ kJ·mol^{-1} (-641.82 kcal·mol^{-1}).

35BON/BUR measured decomposition pressures for the reaction of Eq. (14.2) from 283.15 to 298.15 K. These measurements were apparently considered no further. If one uses the same method of treatment as that described in the previous paragraph, one obtains $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\text{H}_2\text{O(cr)}] = -2682.20$ kJ·mol^{-1} (-641.06 kcal·mol^{-1}).

40BEL measured the vapor pressure corresponding to the reaction of Eq. (14.2) and gave values for temperatures of 293.15, 298.15, and 303.15 K. The 298.15 K value was used to calculate $\Delta_r G_m° = 8.933$ kJ·mol^{-1} (2.135 kcal·mol^{-1}). Repeating the calculation described for 64KOH/ZÄS gave $\Delta_r H_m°(298.15\ \text{K}) = 52.22$ kJ·mol^{-1} (12.48 kcal·mol^{-1}). This was combined with the enthalpies of formation of NiSO$_4$·7H$_2$O(cr) and H$_2$O(g) to obtain $\Delta_f H_m°[\text{NiSO}_4 \cdot 6\text{H}_2\text{O(cr)}] = -2682.3$ kJ·mol^{-1} (-641.09 kcal·mol^{-1}).

23SCH also measured the vapor pressure for the reaction of Eq. (14.2) at 298.15 K and obtained 20.69 Torr. This led to $\Delta_r G_m° = 8.933$ kJ·mol^{-1} (2.135 kcal·mol^{-1}).

E. More Recent Determinations of the Thermodynamic Properties of α-NiSO$_4$·6H$_2$O(cr).

66GOL/RID measured enthalpies of solution of NiSO$_4$·6H$_2$O(cr) from 8.54 kJ·mol^{-1} for $m = \sim 0.05$ mol·kg^{-1} to 7.41 kJ·mol^{-1} for $m = 0.01$ mol·kg^{-1} at 298.15 K.

75RAB/WAN used differential scanning calorimetry and other methods to determine the enthalpy change for conversion of the α form of NiSO$_4$·6H$_2$O(cr) to the β form to be (6.53 ± 0.17) kJ·mol^{-1}.

F. Bibliography

23SCH Schwab, W. C., J. Am. Chem. Soc. **45**, 342 (1923).
35BON/BUR Bonnell, D. G. R., and Burridge, L. W., Trans. Faraday Soc. **31**, 473 (1935).
39SIM/KRO Simion, A., and Kroner, H., Z., Anorg. Chem. **242**, 375 (1939).
40BEL Bell, J., J. Chem. Soc. 72 (1940).
64KOH/ZÄS Kohler K., and Zäske, P., Z. Anorg. Allg. Chem. **331**, 1 (1964).
65JAM/BRO Jamieson, J. W. S., Brown, G. R., Gruener, D. W., Peiluck, R. V., and LaMontagne, R. A., Can. J. Chem. **43**, 2148 (1965).
66GOL/RID Goldberg, R. N., Riddell, R. G., Wingard, M. R., Hopkins, H. P., Wulff, C. A., and Hepler, L. G., J. Phys. Chem. **70**, 706 (1966).
66STO/ARC Stout, J. W., Archibald, R. C., Brodale, G. E.,

and Giauque, W. F., J. Chem. Phys. **44**, 405 (1966).
75RAB/WAN Rabberling, G., Wanrooy, J., and Schuijiff, A., Thermochim. Acta **12**, 57 (1975).

15. NiSO$_4$·4H$_2$O(cr)

A. Selected Values, NBS Tables

64KOH/ZÄS measured the vapor pressure for the reaction

$$\text{NiSO}_4 \cdot 6\text{H}_2\text{O(cr)} = \text{NiSO}_4 \cdot 4\text{H}_2\text{O(cr)} + 2\text{H}_2\text{O(g)} \tag{15.1}$$
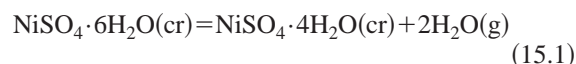
for temperatures from 313.15 to 327.15 K. The vapor pressure relation was reported to be

$$\log(p/\text{Torr}) = (-2478\ \text{K})/T + 9.34. \tag{15.2}$$

Calculation of the enthalpy of reaction from Eq. (15.2) gave 47.45 kJ·mol^{-1} (11.34 kcal·mol^{-1}). An assumed heat capacity of reaction (15.1) $\Delta_r C_{p,m}° = -6.3$ J·K^{-1}·mol^{-1} (-1.5 cal·K^{-1}·mol^{-1}) was used to obtain $\Delta_r H_m°(298.15\ \text{K}) = 47.57$ kJ·mol^{-1} (11.37 kcal·mol^{-1}). This was combined with the enthalpies of formation of NiSO$_4$·6H$_2$O(cr) and H$_2$O(g), -2682.83 kJ·mol^{-1} (-641.212 kcal·mol^{-1}) and -241.818 kJ·mol^{-1} (-57.796 kcal·mol^{-1}), respectively, to obtain $\Delta_f H_m°[\text{NiSO}_4 \cdot 4\text{H}_2\text{O(cr)}] = -2104.1$ kJ·mol^{-1} (-502.9 kcal·mol^{-1}).

B. Comments

A value of the Gibbs energy of formation could have been calculated from Eq. (15.2) but apparently was not. This value would have been $\Delta_f G_m°[\text{NiSO}_4 \cdot 4\text{H}_2\text{O(cr)}] = -1746.66$ kJ·mol^{-1} (-417.46 kcal·mol^{-1}) had it been calculated and tabulated.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f H_m°[\text{NiSO}_4 \cdot 6\text{H}_2\text{O(cr)}],$$

$$\Delta_f H_m°[\text{H}_2\text{O(g)}].$$

D. Other Thermodynamic Measurements Considered

None.

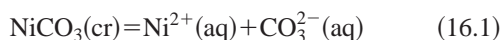### E. More Recent Determinations of the Thermodynamic Properties of NiSO$_4$·4H$_2$O(cr)

None.

F. Bibliography

64KOH/ZÄS Kohler K., and Zäske, P., Z. Anorg. Allg. Chem. **331**, 1 (1964).

16. NiCO$_3$(cr)

A. Selected Values, NBS Tables

A value of the solubility product, $\log K_{sp} = -6.87$, was taken from 64SIL/MAR for the reaction

$$NiCO_3(cr) = Ni^{2+}(aq) + CO_3^{2-}(aq) \qquad (16.1)$$

for 298.15 K. The Gibbs energy of reaction, 39.22 kJ·mol^{-1} (9.37 kcal·mol^{-1}), was calculated from that value and subsequently combined with the Gibbs energies of formation of Ni^{2+}(aq) and CO$_3^{2-}$(aq), −45.6 kJ·mol^{-1} (−10.9 kcal·mol^{-1}) and −527.90 kJ·mol^{-1} (−126.17 kcal·mol^{-1}), respectively, to obtain $\Delta_f G_m°[NiCO_3(cr)] = -612.5$ kJ·mol^{-1} (−146.4 kcal·mol^{-1}).

B. Comments

None.

C. Auxiliary Values Required for Data Pathway

$$\Delta_f G_m°[Ni^{2+}(aq)],$$

$$\Delta_f G_m°[CO_3^{2-}(aq)].$$

D. Other Thermodynamic Measurements Considered

None.

E. More Recent Determinations of the Thermodynamic Properties of NiCO$_3$(cr)

82GAM/REI measured the solubility of NiCO$_3$(cr) in aqueous perchlorate solution, with variation of pH, at temperatures of 348.15, 358.15, and 363.15 K. They extrapolated their results to $I = 0$ and to 298.15 K and combined them with other literature values of thermodynamic properties to obtain a range of possible Gibbs energies of formation. This range was (−634.4 to −640.2) kJ·mol^{-1}, or about 35 kJ·mol^{-1} more negative than the value described in Sec. A.

91TAR/FAZ measured the e uilibrium pressure for the reaction

$$NiCO_3(cr) = NiO(cr) + CO_2(g) \qquad (16.2)$$
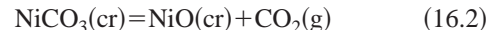
for temperatures from 573 to 673 K. From their measurements and auxiliary data, they calculated $\Delta_f G_m°[NiCO_3(cr)] = (-628.36 \pm 1.2)$ kJ·mol^{-1} and $\Delta_f H_m°[NiCO_3(cr)] = (-703.38 \pm 1.2)$ kJ·mol^{-1} for 298.15 K. Their Gibbs energy of formation was approximately 26 kJ·mol^{-1} more negative than that given in the NBS Tables.

62KAL measured the heat capacity of NiCO$_3$(cr) for temperatures from 1.6 K to 70 K.

64KOS/KAL measured the heat capacity of NiCO$_3$(cr) from 70 to 298 K, and the results were presented only graphically. They gave an entropy for 298.15 K, $S_m° = 85.4$ J·K^{-1}·mol^{-1}.

F. Bibliography

62KAL Kalinkina, N., Zh. Eksp. Teor. Fiz. **43**, 2028 (1962).

64KOS/KAL Kostryukov, V. N., and Kalinkina, I. N., Russ. J. Phys. Chem. **38**, 422 (1964).

64SIL/MAR Sillen, L. G., and Martell, A. E., Stability Constants of Metal-Ion Complexes (The Chemical Society, London, 1964).

82GAM/REI Gamsjäger, H., Reiterer, F., and Heindl, R., Ber. Bunsenges. Phys. Chem. **86**, 1046 (1982).

91TAR/FAZ Tareen, J. A. K., Fazelli, A. R., Basavalingu, and Bhandage, G. T., Eur. J. Mineral. **3**, 501 (1991).