Enthalpies of Dilution and Relative Apparent Molar Enthalpies of Aqueous Cobalt and Nickel Perchlorates

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Enthalpies of dilution at 298.15K for cobalt and nickel perchlorates and for the mixture $Ni(ClO_4)_2 \cdot 0.0693HClO_4$ were measured directly by solution calorimetry. Values of ϕ_L, the relative apparent molar enthalpy, were obtained over the range 0.0015–4m. For the mixture $Ni(ClO_4)_2 \cdot 0.0693HClO_4$, values of ϕ_L can be represented to within 3 cal mol^{-1} up to 0.5m and to 11 cal mol^{-1} at 1.1m by additivity of ϕ_L values for the components $Ni(ClO_4)_2$ and $HClO_4$ at the ionic strength of the mixture. Values of ϕ_L for $Ni(ClO_4)_2 \cdot xHClO_4$, where x = 0.00469, 0.0105, 0.0325, and 0.110, were also obtained at 298.15K from 1.5 to 4m.

This study is part of a continuing series on the relative apparent molar enthalpies, ϕ_L, of perchlorate salts. Shchukarev et al. (14) measured the enthalpies of solution for $Co(ClO_4)_2 \cdot 6H_2O(s)$ and $Ni(ClO_4)_2 \cdot 6H_2O(s)$ to form solutions from 0.06m to near saturation, with stated uncertainties of ± 40 cal mol^{-1}. Latysheva and Karavan (8, 9) reported enthalpies of solution and of dilution of the saturated solution of nickel perchlorate at 25°, 35°, and 45°C with somewhat higher precision. Their results form a curve of ϕ_L against $m^{1/2}$ which agrees closely, after adjusting reference points, with that found in this work. The results reported by Shchukarev et al. (14) do not agree within the stated uncertainties. The values of ϕ_L obtained in our work allow calculation of the standard enthalpies of solution of $Co(ClO_4)_2 \cdot 6H_2O(s)$ and $Ni(ClO_4)_2 \cdot 6H_2O(s)$ from the published work (8, 14, 19).

Another part of this study concerns the influence of small amounts of excess $HClO_4$ in the nickel perchlorate solution upon the relative apparent molar enthalpies per mole of nickel salt. The results reveal that for H^+/Ni^{2+} ratios of 0.11 and lower, the effects below 1.1m are small and fairly predictable, but at 1.8m and above, the excess acid causes appreciable increases in ϕ_L.

Experimental

Materials and analyses. $Co(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith Chemical Co.) was dissolved in twice distilled water, and the solution was brought to saturation by evaporation of water from the warmed solution (80°C), aided by a stream of $N_2(g)$ across the surface. The solution was cooled to 25°C, and enough water added to dissolve all of the solid. The acidity of the stock solution was adjusted until a portion, diluted 1:100 with twice distilled water, had a pH of 5.5.

A solution of $Ni(NO_3)_2$ (Mallinckrodt AR) was treated with a slight excess of Na_2CO_3 (Mallinckrodt AR), and the resulting precipitate was washed and digested, with mechanical stirring for extended periods, followed by decantation of the wash water, until the solid was free of sodium and nitrate ions. Most of the solid was then dissolved with 60% perchloric acid, and the solution was filtered and concentrated to near saturation by evaporation of solvent, as for the cobalt perchlorate. Adjustment of the acidity resulted in a pH of 3.5–3.7 for portions diluted

1:100 with twice distilled water. This was more acidic than desired, but a set of dilution measurements was made with this solution. The pattern of ϕ_L values so obtained raised questions concerning the degree of perturbation possibly produced by excess $HClO_4$ in the solution, so further analyses of the solution were made to confirm the Ni(II) molality and to determine the H^+/Ni^{2+} ratio in the solution. The perchloric acid content was determined by titration with a dilute (ca. 0.008m) NaOH solution. Gran's method (3) was used to locate the equivalence point. The composition of this solution was $Ni(ClO_4)_2 \cdot 0.0693HClO_4$, somewhat higher than the pH measurements indicated.

Another nickel perchlorate solution was prepared by dissolving Matheson, Coleman nickel carbonate (AR) in perchloric acid solution. Excess nickel carbonate was removed by filtration. The solution was warmed to 100–110°C and concentrated by evaporation of solvent, as for the previous preparation. Portions of this stock solution, diluted 1:100 with twice distilled water, had a pH of 7. A second solution prepared in the same way, with the same pH behavior, was used to prepare mixtures, $Ni(ClO_4)_2 \cdot xHClO_4$, where x = 0.00469, 0.0105, 0.0325, and 0.110, from measured amounts of standard stock solution and standard perchloric acid, to be used in dilutions to explore the effects of excess acid in the solution.

The presence of a slight amount of excess $HClO_4$ in the salt solutions, at the level used for the cobalt perchlorate solution, was considered prudent to guard against thermal effects from hydrolysis (1, 15). Although the cobalt and nickel salts undergo only weak hydrolysis (15), the enthalpy of hydrolysis may run from 7 to 10 kcal mol^{-1} (1), so even a small degree of hydrolysis should be avoided. To this end, a solution of $1 \times 10^{-4}m$ $HClO_4$ in twice distilled water was used as diluent. Dilution corrections for this amount of acid were considered negligible.

The cobalt and nickel perchlorate stock solutions were analyzed by titration with EDTA with murexide as indicator, by use of established procedures (21). The molality of the $Co(ClO_4)_2$ was $(4.061_5 \pm 0.006)m$ (mean and standard deviation for five determinations), and that of the $Ni(ClO_4)_2 \cdot 0.0693HClO_4$ was $(3.773 \pm 0.002)m$ (three determinations). The neutral $Ni(ClO_4)_2$ solutions were (4.011 ± 0.006) and $(4.120 \pm 0.004)m$ for triplicate determinations. From each stock solution, other solutions were prepared by dilution on a mass basis to facilitate the calorimetric operations.

The molalities were confirmed by analysis of stock solutions and some of the final calorimetric solutions, with a different EDTA solution, after the calorimetric work was completed. The EDTA was standardized as recommended by Welcher (21), both by preparation as a primary standard and by confirmatory titration of primary standard calcium carbonate (99.9+%) with murexide as indicator. The two procedures agreed within ±0.2%. Based upon the precision of analyses, purity of standard substances, and residual errors from indicator behavior at the equivalence point, the overall uncertainty in the molality of the $Co(ClO_4)_2$ solution was judged to be ±0.3%. For the

nickel analyses, the indicator behavior is more critically dependent upon buffer control in the solution during titration, and although we estimate the overall uncertainty to be ±0.3% for these also, this may be an underestimate.

Stock solutions of NaOH and $HClO_4$ were prepared from AR grade materials and twice distilled water with usual precautions against carbonates and CO_2. They were intercompared and standardized against primary standard potassium hydrogen phthalate (99.993%) with electrometric determination of the equivalence points.

All of the above analyses and subsequent manipulations of solutions in the calorimetric operations were car-

ried out on a mass basis. All weights were appropriately reduced to mass by use of reported densities (10) or from densities measured as needed.

Calorimetric equipment and procedures. The basic configuration of the calorimeter has been described elsewhere (16–19). Temperatures were measured with a Hewlett-Packard HP-M40-2801A quartz thermometer, operated at a resolution of 10^{-5} K with minimum time between readings. The temperature scale was checked against a calibrated platinum resistance thermometer with a G-1 Mueller bridge.

The thermostat was controlled to ±0.0005K by a thermistor bridge and a Leeds and Northrup 9834-2 null detector, followed by a Series 60 CAT control unit and a magnetic amplifier. Performance checks on the calorimeter by measuring the enthalpy of solution of TRIS in 0.1M HCl, following procedures and conditions recommended by the Standards Committee of the U.S. Calorimetry Conference, gave $\Delta H = -(7104 \pm 6)$ cal mol^{-1}, in close agreement with other values for the test reactions (4, 6, 7, 17).

The calorimeter used was normally charged with a measured mass, approximately 1 kg, of twice distilled water to which 1 cm^3 of 0.1M $HClO_4$ was added to suppress effects of hydrolysis in dilute solutions. Enthalpy contributions from this amount of $HClO_4$ were judged to be negligible. Dilution measurements followed one of two procedures. The first is a pulse-titration procedure, described elsewhere (16, 19), in which portions of a stock solution are delivered into the calorimeter from a calibrated buret through capillary plastic tubing and a platinum capillary in the lid of the calorimeter. This procedure gives relative enthalpies for a series of solutions in the range 0.0015–0.25m, all referred to a common stock solution. The other procedure involves a series of single batch dilutions with the concentrated salt solutions dispensed from 10-cm^3 cylindrical glass ampuls mounted in the calorimeter. The filling tube on the ampul was sealed with a Teflon plug and an outer paraffin seal. The ampuls are mounted in a carriage within the calorimeter with a breaking device to rupture the ends of the cylinder at the selected time. Batch-type operations were used to cover the range 0.25–4.12m.

For the pulse-titration procedure, electrical calibrations were run on the initial and final calorimeter solutions for a series. Previous studies showed that the electrical energy equivalents were linear with respect to the mass of solution added to the calorimeter, so the energy equivalents for intermediate points in the titration series were obtainable by interpolation. For the batch mode of operation, electrical calibrations were carried out on the final state of the system, and dilutions were initiated within ±0.04K of the desired reference temperature, 298.15K. All enthalpies of reaction reported in this paper are calculated for the isothermal dilution process at that reference temperature.

Dickinson's method (2, 5) was used to evaluate the corrected temperature changes for the pulse-titration procedure and for batch operations when the temperature change was less than 0.00250K. For larger changes, integration of the temperature-time curves was employed (2). The latter method could be used for the smaller temperature changes in the batch procedure, provided the temperature curves were screened for anomalous points as in the Dickinson procedure. Normally, the two procedures agreed to ±2 × 10^{-5} K or better.

All computations were performed by digital computer at the University of Nebraska Computing Center. Foreperiod and after-period data were fitted by linear least

Table I. Debye-Hückel and Curve-Fitting Parameters[a]

	$Co(ClO_4)_2$	$Ni(ClO_4)_2$	$Ni(ClO_4)\cdot$ 0.0693$HClO_4$
$\phi°$, cal mol^{-1}	−1.2	−1.4	−6.3
a, Å	5.8	5.9	5.9
$(d \ln a/dt)_p$, K^{-1}	-5.8×10^{-5}	-1.2×10^{-4}	-9.0×10^{-5}
K_H, cal l. mol^{-1}	−636	−528	−610
J_H, cal l.^{2} mol^{-3}	276	194	209
Range of fit	0–2M	0–1.5M	0–1.5
σ, cal mol^{-1}	3.4	5.3	3.5

[a] The above parameters are for the tabulated range of fit. Slightly different values with somewhat better precision of fit (σ) were obtained for the range of 0–1M, and the calculated values of ϕ_L varied by as much as σ from one range of fit to the other. The tabulated values are given to illustrate the quality of representation obtainable.

Table II. Relative Apparent Molar Enthalpies for $Co(ClO_4)_2$ at Experimental Molalities

	ϕ_L, cal mol^{-1}			ϕ_L, cal mol^{-1}	
m, mol kg^{-1}	Obsd	Calcd	m, mol kg^{-1}	Obsd	Calcd
Titration run 1			Titration run 2		
0.00596	151	151	0.02766	260	258
0.01425	213	210	0.06018	319	319
0.02448	243	243	0.0907	353	353
0.03856	281	283	0.1212	375	375
0.05446	309	310	0.1496	391	390
0.07015	333	332	0.1796	406	406
0.0927	354	355	0.2011	414	413
0.1224	376	376	1.9395	906	905
0.1507	390	391			
0.1760	405	405			
1.9395	900	905			
Batch measurements					
0.002277	104	102	0.2629	427	429
0.003145	113	115	0.3547	448	446
0.003891	123	126	0.4849	465	464
0.005709	148	149	0.6691	486	487
0.006525	155	157	0.7717	504	502
0.006658	162	160	0.2011	412	413
0.007456	166	165	0.9354	531	534
0.00999	183	185	1.208	605	603
0.01124	193	193	1.447	684	685
0.01269	203	202	1.634	759	759
0.01426	208	210	1.9395	905	905
0.01474	212	213	2.207	1058	1057
0.01561	218	218	2.333	1138	1139
0.01854	229	229	2.676	1385	1385
0.01908	231	231	2.779	1463	1464
0.02024	235	235	3.121	1741	1743
0.02227	241	243	2.945	1600	1598
0.02246	243	243	3.393	1984	1984
0.02408	247	247	4.062	2627	2630
0.02437	248	248	3.422	2010	2010
0.02585	251	251	4.062	2632	2630

squares. Accuracy of the corrected temperature changes approached the resolution of the thermometer, 10^{-5} K, and accuracy in the electrical energy inputs, based on calibration and certificate factors, is ±0.02%.

Treatment of experimental data. The enthalpy of dilution process can be represented by the equation

$$n_0 X(m_0) + n_1 X(m_1) = n_2 X(m_2) \qquad (1)$$

for each particular step in the dilution process. For this study, X refers to the substance being investigated, and m_0 is the concentration of X added to a solution containing n_1 moles of X at a concentration of m_1 to form a solution containing n_2 moles at a concentration of m_2. In the above equation, $n_2 = n_1 + n_0$.

The enthalpy change for the above process can be written in terms of the apparent molar enthalpies, ϕ_0, ϕ_1, and ϕ_2, by

$$\Delta H = n_2 (\phi_2 - \phi_0) - n_1 (\phi_1 - \phi_0) \qquad (2)$$

and one obtains the relative apparent molar enthalpy ϕ_L by assigning the appropriate value to ϕ_0 for a particular dilution process.

The pulse titration results yield a group of values, ϕ_1, ϕ_2, ϕ_3, etc., referred to a reference value ϕ_0, and define a segment of the ϕ vs. $m^{1/2}$ curve in the region 0.0015–0.25m. The titration operations were run in duplicate, and the two segments were blended into a single curve by appropriate assignment of the respective ϕ_0 values. A provisional extrapolation to infinite dilution was then made from this curve segment, by use of the results from Mg(ClO$_4$)$_2$, Sr(ClO$_4$)$_2$, and Ba(ClO$_4$)$_2$ to form model curves for guidance (20, 22), to yield provisional values of the relative apparent molal enthalpy, ϕ_L', defined by $\phi_L' = \phi - \phi^{\circ \prime}$ where $\phi^{\circ \prime}$ is the intercept at infinite dilution for the provisional curve. The rest of the curve for ϕ_L' was constructed from the data obtained by batch operations by appropriate location of ϕ_L' for the final solutions from the segment already constructed. Once a complete curve was outlined, errors for pairs of values obtained in a batch process were equally distributed between the two points to obtain a smoothed curve. Visual examination of the results in this manner is effective in searching for operational or computational errors.

For final smoothing and extrapolation, the completed curve of ϕ_L' vs. $m^{1/2}$ was fitted to the Debye-Hückel equation used by Vanderzee and Swanson (20), but with an additional term, $J_H C^2$, where J_H is an arbitrary constant and C is concentration. Fitting involved a least-squares procedure carried out by digital computer. The ion size parameter a was taken from data on the activity coefficients of Co(ClO$_4$)$_2$ and Ni(ClO$_4$)$_2$ (11), and molalities m were converted to concentrations C by means of density values from the literature (10).

The data were fitted with four adjustable parameters: ϕ°, the intercept at infinite dilution; $(d \ln a / dT)_p$, the temperature coefficient of the ion size parameter; 0.5 K_H, the linear concentration coefficient added by Owen and Brinkley (12); and J_H, as defined above. Table I gives the parameters, range of fit, and standard deviation σ, from the smoothed curve. The quantity ϕ° refines the extrapolation of the provisional values from graphical treatment to give relative apparent molal enthalpy $\phi_L = \phi_L' - \phi^{\circ}$ referred to the reference state of infinite dilution.

The results obtained for the mixture Ni(ClO$_4$)$_2$·0.0693HClO$_4$ were fitted in a similar manner. For this composition, the ionic strength $I = 3.0693m$. The appropriate changes were made in the valence factors for the Debye-Hückel equation. In particular, the limiting slope is 3.49% greater than for neutral solutions. For this

amount, the intercept ϕ° for the mixture was shifted about 5 cal mol^{-1} as compared to the fitting function for neutral solution applied to the mixture data.

Results and Discussion

In Tables II–V are given the experimental values of ϕ_L at operational molalities, together with values of ϕ_L based on the fitted curves up to 1.4m and on graphical fitting above 1.4m. Table VI presents selected values of ϕ_L for Co(ClO$_4$)$_2$ and Ni(ClO$_4$)$_2$ and also for the mixture Ni(ClO$_4$)$_2$·0.0693HClO$_4$ at selected molalities and mole ratios. The accuracy of the values is estimated to be ±2%, with a limit of ±30 cal mol^{-1} at the higher molalities, based on consideration of random errors as revealed by the fitting procedure and by replicate runs, together with consideration of multiple contributions from analytical errors. At the higher molalities, where $d\phi_L / dm$ is large, and where the effects of analytical errors are already magnified in computing m, the displacement from a ϕ_L vs. m curve owing to error in m may be larger than the influence of analytical error on ϕ_L directly.

The primary experimental data from which the above values were derived are given in Tables VII–X (deposited with the ACS Microfilm Depository Service) and reveal the patterns of operations related to Equation 1.

The range of fit, up to 1.4m, for the Debye-Hückel equation (Table I), is considerably larger than that obtainable without the squared term $J_H C^2$. Constraining ϕ° to a zero value does little to change the fit, but it seems prudent to use ϕ° as an adjustable parameter to correct for graphical errors of extrapolation. The temperature coefficients have little significance at present, other than

Table III. Relative Apparent Molar Enthalpies for Ni(ClO$_4$)$_2$·0.0693HClO$_4$ at Experimental Molalities

m, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd	m, mol kg^{-1}	ϕ_L, cal mol^{-1} Obsd	ϕ_L, cal mol^{-1} Calcd
Titration run 1			Titration run 2		
0.001485	77	88	0.02945	274	275
0.004433	135	139	0.05847	328	333
0.007364	169	170	0.08711	361	364
0.01309	213	209	0.1153	388	388
0.01878	244	238	0.1430	402	404
0.02702	270	268	0.1567	408	410
0.03766	294	296	0.1703	414	416
0.05295	323	325	0.1838	422	420
0.6183	471	477	0.1972	426	425
			0.2237	432	432
			0.2500	438	438
			3.773	2694	2692
Batch measurements					
0.001880	84	97	0.2500	446	438
0.003031	119	119	0.3687	451	455
0.003968	127	133	0.5661	473	473
0.005205	148	148	0.6506	480	480
0.006290	159	159	0.7695	493	491
0.007661	170	172	0.9350	517	511
0.007044	171	167	0.7884	491	493
0.008435	181	178	1.139	548	544
0.01174	205	201	1.409	599	603
0.01688	331	229	1.951	818	822
0.01698	331	229	2.234	981	979
0.01953	244	241	2.328	1036	1037
0.01918	242	239	2.936	1553	1554
0.01915	242	238	3.214	1941	1942
0.02123	251	247	2.724	1314	1339
0.02152	252	250	3.566	2428	2427
0.02392	259	257	3.773	2691	2692

Table IV. Relative Apparent Molar Enthalpies for Ni(ClO₄)₂ at Experimental Molalities

m, mol kg⁻¹	ϕ_L, cal mol⁻¹ Obsd	ϕ_L, cal mol⁻¹ Calcd	m, mol kg⁻¹	ϕ_L, cal mol⁻¹ Obsd	ϕ_L, cal mol⁻¹ Calcd
Titration run 1			Titration run 2		
0.003917	136	128	0.007520	157	166
0.01309	205	204	0.01750	211	226
0.02223	239	246	0.04449	291	304
0.04038	284	296	0.07086	341	344
0.05792	322	328	0.1128	384	383
0.1006	374	374	0.1618	412	410
0.1494	406	405	0.2078	428	427
0.1960	425	423	2.031	893	904
0.2545	440	440			
2.031	893	904			
Batch measurements					
0.008512	172	174	0.2545	446	440
0.01035	188	188	0.3115	455	451
0.01240	204	200	0.3775	462	461
0.01703	224	225	0.5256	484	479
0.02177	247	245	0.6799	498	497
0.007009	172	162	0.8709	514	521
0.008689	177	175	0.9888	532	539
0.009338	183	181	1.242	585	587
0.01100	195	192	1.405	630	624
0.01241	204	200	1.468	648	650
0.01368	211	208	1.789	779	779
0.01621	223	221	1.849	812	809
0.01478	217	214	2.031	904	904
0.01728	227	226	2.165	981	981
0.01711	227	225	2.318	1101	1078
0.02041	241	239	2.838	1450	1443
0.02301	251	249	3.384	1891	1889
0.02563	259	258	4.120	2581	2580

being small and negative. Alterations in the *a* parameter were made, with little discernible difference in the quality of fit, but with substantial changes in the other parameters, except $\phi°$. Inasmuch as *a* can be determined independently from activity coefficient data, we elected to use these values.

Comparison of final results for Co(ClO₄)₂ and Ni(ClO₄)₂ solutions (Table V) reveals that the values of ϕ_L for the nickel salt run slightly higher, as much as 14 cal mol⁻¹, than those for the cobalt salt up to 1*m*, above which the cobalt values run increasingly larger, up to about 85 cal mol⁻¹ at 4*m*. The differences below 1.5*m* are not outside the combined limits from analytical errors and systematic errors in data manipulation and experimental operations.

Values of ϕ_L obtainable from the enthalpies of solution measured by Shchukarev et al. (*14*) do not conform to the curves obtainable from Table V, with some differences considerably in excess of their stated uncertainty of ±40 cal mol⁻¹. From their results, we obtain for the standard enthalpies of solution: Co(ClO₄)₂·6H₂O(s), $\Delta H_s° = (1.45 \pm 0.20)$ kcal mol⁻¹; Ni(ClO₄)₂·6H₂O(s), $\Delta H_s° = (1.70 \pm 0.20)$ kcal mol⁻¹, at 298.15K based on their measurements in the concentration ranges from 0.1 to 1*m* where their results are probably most accurate.

Recent measurements by Latysheva and Karavan (*9*) on ΔH_{diln} for Ni(ClO₄)₂ solution give values of ϕ_L agreeing with ours to within ±30 cal mol⁻¹ over the range 0.03–4.1*m*. The average difference is ±13 cal mol⁻¹, with their values 10–20 cal mol⁻¹ above ours from 3.4 to 4.1*m*. The congruence of the ϕ_L curves over most of the molality range suggests that systematic errors are small rather than being fortuitously coincident. From measurements of ΔH_{soln} for Ni(ClO₄)₂·6H₂O(s) by Latysheva and Karavan (*8, 9*), we calculate for the standard enthal-

Table V. Relative Apparent Molal Enthalpies of Ni (ClO₄)₂·xHClO₄

m, mol kg⁻¹	$\phi(x = 0.00469)$, cal mol⁻¹	m, mol kg⁻¹	$\phi(x = 0.0105)$, cal mol⁻¹	m, mol kg⁻¹	$\phi(x = 0.0325)$, cal mol⁻¹	m, mol kg⁻¹	$\phi(x = 0.110)$, cal mol⁻¹
1.531	729	2.075	928	1.777	781	1.593	684
1.940	900	2.426	1141	2.240	1007	2.263	1089
2.616	1302	2.965	1547	2.793	1419	2.642	1408
3.429	1964	3.158	1720	3.642	2200	3.158	1898
4.107	2601	4.090	2594	4.028	2599	3.635	2443

Table VI. Selected Values of Relative Apparent Molar Enthalpies for Co(ClO₄)₂·n-H₂O and Ni(ClO₄)₂·n-H₂O Solutions

n, mol H₂O	ϕ_L, cal mol⁻¹ Co(ClO₄)₂	ϕ_L, cal mol⁻¹ Ni(ClO₄)₂	ϕ_L, cal mol⁻¹ Ni(ClO₄)₂·0.0693HClO₄	n, mol H₂O	ϕ_L, cal mol⁻¹ Co(ClO₄)₂	ϕ_L, cal mol⁻¹ Ni(ClO₄)₂	ϕ_L, cal mol⁻¹ Ni(ClO₄)₂·0.0693HClO₄
∞	0	0	0	300	405	420	421
100000	54	54	55	200	432	445	443
50000	74	74	76	150	445	461	455
20000	110	110	114	100	474	483	472
10000	147	147	152	75	497	504	489
7000	170	170	174	55.5	549	544	525
5000	192	193	198	50	576	561	540
4000	209	209	214	40	662	621	598
3000	229	231	237	37	703	659	630
2000	257	265	270	30	857	813	770
1500	280	289	295	27.75	936	893	844
1000	311	324	329	25	1067	1013	972
900	321	333	338	22.2	1255	1199	1159
800	331	343	348	20	1462	1402	1386
700	342	355	359	18.5	1642	1581	1639
600	354	367	372	15	2270	2188	2604
500	368	382	386	13.88	2557	2470	...
400	386	399	402				

Table XI. Deviations from ϕ_L Additivity Rule for Mixtures Ni(ClO₄)₂·xHClO₄

$m(Ni^{2+})$, mol kg⁻¹	I, mol kg⁻¹	$\phi(Ni(ClO_4)_2)$, cal mol⁻¹	$\phi(HClO_4)$, cal mol⁻¹	ϕ_L(calc), cal mol⁻¹	$\Delta\phi_L$(obs-calc), cal mol⁻¹
		$x = 0.0693$			
0.002775	0.00852	111	36	113	1
0.01388	0.04263	210	59	214	0
0.03700	0.1137	291	64	295	0
0.1110	0.3408	384	40	387	−1
0.2775	0.8518	446	−28	444	−1
0.5551	1.704	484	−123	475	−3
1.1102	3.408	566	−194	553	−13
1.850	5.679	833	−108	826	−55
2.220	6.814	1048	−10	1047	−75
2.500	7.673	1232	99	1239	−80
2.775	8.518	1444	226	1459	−73
3.00	9.208	1638	341	1662	−23
3.308	9.923	1889	467	1921	150
3.566	10.945	2137	694	2185	242
3.700	11.357	2270	816	2327	277
		$x = 0.0047$			
1.531	4.600	676	−171	675	54
1.940	5.829	858	−100	900	42
2.616	7.860	1290	117	1302	11
3.429	10.303	1936	547	1939	25
4.107	12.340	2575	1145	2580	21
		$x = 0.0105$			
2.075	6.247	993	−65	932	−3
2.426	7.303	1157	49	1157	−16
2.965	8.926	1555	294	1558	−11
3.158	9.507	1725	393	1729	−9
4.090	12.313	2566	1137	2578	+16
		$x = 0.0325$			
1.777	5.389	783	−127	779	2
2.240	6.793	1044	−12	1044	−37
2.793	8.470	1432	218	1439	−20
3.642	11.044	2168	717	2191	9
4.028	12.215	2535	1104	2571	28
		$x = 0.110$			
1.593	4.954	722	−152	707	−23
2.263	7.038	1100	16	1102	−13
2.642	8.217	1374	179	1394	14
3.158	9.821	1800	449	1849	49
3.635	11.305	2250	798	2338	105

py of solution, $\Delta H_{soln}° = (1.74 \pm 0.02)$ kcal mol⁻¹ at 25°C, close to that calculated in the preceding paragraph from the work of Shchukarev et al. (14).

Values of ϕ_L for the mixture Ni(ClO₄)₂·0.0693HClO₄ are close to those for the neutral nickel and cobalt perchlorates up to about $1m$, above which they lie below those of Ni(ClO₄)₂ up to about $2.8m$. At higher molalities the values for this mixture run much larger. The Debye-Hückel equation used for curve-fitting requires that in the low molality region ϕ_L for mixtures should be representable by the sum $\{\phi_L[Ni(ClO_4)_2] + x\phi_L[HClO_4]\}$, wherein ϕ_L values for the components are taken at the ionic strength of the mixture.

Table XI illustrates how closely the additivity condition applies to the above mixture ($x = 0.0693$), together with results of dilutions of other mixtures of Ni(ClO₄)₂+HClO₄ from the high molality region, with $x = 0.0047, 0.0105, 0.0325$, and 0.110. The deviations from additivity represented by the last column in Table XI are larger for $x = 0.0693$ than for the $x = 0.110$, and the general pattern of behavior for $x = 0.0693$ leads us to suspect the influence

of analytical errors for this solution larger than the $\pm 0.3\%$ estimate given in the experimental section, and which distort the curve from the patterns established by the other dilutions, especially above $3.2m$ and in the region around $2.5m$. Special care was taken with the analyses of subsequent nickel solutions with respect to proper buffering in the solutions during titration, and the concordance of our ϕ_L values for the neutral Ni(ClO₄)₂ solution with those obtainable from Latysheva and Karavan's work (9) reinforces our confidence in our later analyses on the nickel solutions.

The results summarized in Table XI indicate that small amounts of excess HClO₄ in the Ni(ClO₄)₂ solutions make only small contributions beyond the additivity rule, and the most significant contributions are above $I = 8$ mol kg⁻¹, even for $x = 0.11$. The pattern of differences for $x = 0.0047$ is not outside the combined influence of analytical errors.

Further mixing studies are planned for other systems with more reliable analytical behavior, but it does not appear likely that small amounts of excess HClO₄, such as $x = 0.01$, used to suppress hydrolysis would contribute significant errors to resultant ϕ_L values. The present results are reported so that users of the data and other experimentalists may have some measure of possible perturbations in such mixtures.

Acknowledgment

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