Thermodynamics of alkali alkanoates VII. Heat capacity and thermodynamic functions of potassium acetate from 4 to 585 K [a]

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The heat capacity of potassium acetate was measured by equilibrium adiabatic calorimetry from near 4 K up to 350 K and by d.s.c. from 325 K through melting (solid to isotropic liquid) to 585 K. No transition or anomaly was observed below 300 K in the heat-capacity curve but four anomalies were observed at super-ambient temperatures including a broad and diffuse hump extending from 300 to 375 K. A bifurcated peak was observed between 375 and 436.5 K with peak temperatures at 411 and 425 K and with enthalpy increments ($\Delta_{trs}H_m^\circ$) of 41.7 and 22.8$R \cdot K$ and entropy increments ($\Delta_{trs}S_m^\circ$) of 0.097R and 0.05R, respectively. A peak believed to be of first order (solid-to-solid transformation) was observed at 474 K having $\Delta_{trs}H_m^\circ$ and $\Delta_{trs}S_m^\circ$ of 194$R \cdot K$ and 0.407R. Finally, a solid-to-(isotropic) liquid transition occurred at 582 K having $\Delta_{trs}H_m^\circ$ and $\Delta_{trs}S_m^\circ$ of 920$R \cdot K$ and 1.58R.

1. Introduction

The thermophysical properties of potassium *n*-butanoate (K4C) were measured and established earlier.[1] Two close but separated solid-to-solid transformations were observed between 100 and 200 K thought at first to be overlapping by earlier d.s.c. studies.[2]

In this study we examine the thermophysics of potassium acetate (K2C). We considered the study of this compound to be very crucial in as much as (a) it is the first member of the even series of potassium *n*-alkanoates, (b) the odd-even effect seems to play a role in the thermodynamics of compounds with hydrocarbon tails,[1, 3, 4] and (c) it has been asserted that the lowest members always behave differently in that the increments per CH_2 groups are irregular.[1]

[a] The first paper in this series is reference 5.
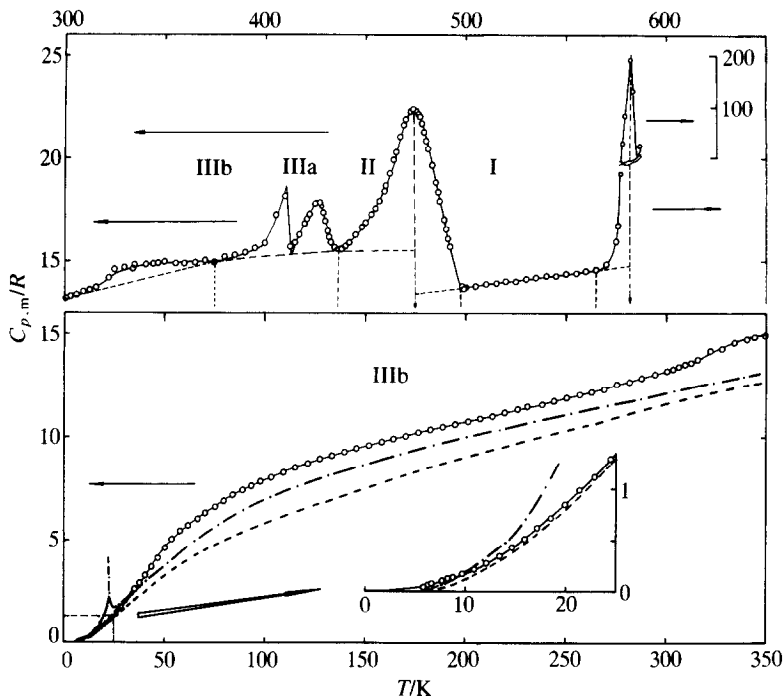[b] Work done while a student at the College of Wooster.

FIGURE 1. The heat-capacity curves of $\bigcirc$, potassium acetate; $-\cdot-$, sodium acetate; $---$, lithium acetate. The 21 K transition of sodium acetate[5] is noted. Designation IIIB refers only to potassium acetate.

The sample does not exhibit a mesomorphic phase.[1] Equilibrium adiabatic calorimetry confirmed the existence of the broad hump also observed by d.s.c. Good agreement between the two methods was obtained over the common temperature range of measurement. The heat-capacity morphology for this sample from near 4 K through melting is shown in figure 1. For comparison purposes the heat capacities of sodium and lithium acetates are also shown in this figure. The enthalpies and entropies of the hump and bifurcated peaks not considered to be of first order are also shown in tabular form.

The samples used in both types of measurements were from the same batch. No studies were made on premelted samples.

2. Experimental

The potassium acetate used in this sample was prepared by the method described previously.[1, 5] The purity was determined by using a DSC-4 purity software with the Dupont Thermal Analysis Data Station (TADS) program[6] which uses the van't Hoff equation as a basis for the analysis.[6, 7] The purity of this compound was determined as 99.95 moles per cent and considered satisfactory for thermodynamic studies.
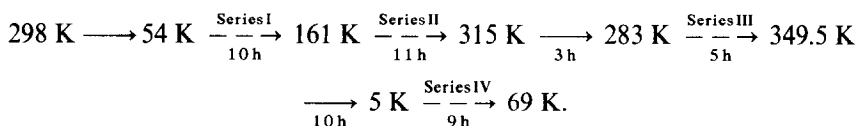
For d.s.c. measurements, the sample was removed from the vacuum line,[8] sealed into the sample pans by crimping, and then placed in the sample compartment of the d.s.c. over which a constant flow of inert gas was maintained to avoid sample oxidation before melting. The d.s.c. used in this study was a computerized DSC-4 version from Perkin-Elmer with adjustment System-4 micro-processor, a computer deck attached to a cathode ray tube, and a computer-controlled chart recorder. The d.s.c. proper also contained an inert atmosphere cover which made it possible to study the hygroscopic samples. Heat-capacity measurements were made using the "Specific Heat" software[9] which is capable of providing $C_p(T)$ values at various temperatures. The latter feature made it possible to delineate a true heat-capacity morphology—rather than a d.s.c. trace as with most other d.s.c. instruments—and hence was able to provide the appropriate integrals for thermodynamic properties.

The remaining salt was loaded into a gold-plated oxygen-free high-conductivity copper calorimeter (laboratory designation W-62) placed in the Mark X cryostat[8] provided with computer-assisted calorimetric data acquisition, logging, and programming.

After evacuation of the calorimeter, the sample was loaded and dry helium gas at a pressure of 6.2 kPa was added to promote thermal equilibrium during data acquisition. Leaks in the calorimeter were checked by a helium detector connected to the vacuum line. The mass of the potassium sample was 22.1246 g ($\hat{=}$ 0.225436 mol).

Buoyancy corrections were calculated for all masses using a density of $0.941 \mathrm{~g \cdot cm^{-3}}$ estimated from other members of the homologous series.

The thermal history of the sample is here presented:

$$298 \mathrm{~K} \longrightarrow 54 \mathrm{~K} \xrightarrow[10\,h]{Series\,I} 161 \mathrm{~K} \xrightarrow[11\,h]{Series\,II} 315 \mathrm{~K} \xrightarrow[3\,h]{} 283 \mathrm{~K} \xrightarrow[5\,h]{Series\,III} 349.5 \mathrm{~K}$$

$$\xrightarrow[10\,h]{} 5 \mathrm{~K} \xrightarrow[9\,h]{Series\,IV} 69 \mathrm{~K}.$$

3. Results and discussion

The experimental heat capacities are given in table 1 for both d.s.c. and adiabatic calorimetric determinations and are plotted in figure 1. The heat capacities were fitted to a series of orthogonal polynomials in regions where no heat capacity anomalies existed. Integration of these polynomials gave the thermodynamic properties listed in table 2.

By drawing the appropriate lattice heat-capacity curves in the transition regions, excess enthalpies and entropies associated with each transition were calculated and are provided in table 3.

Although potassium acetate has been widely studied[10] by various thermal methods, such as thermal analysis, differential thermal analysis, dilatometry, and visual-polythermal methods, only a few authors[11,12] report excess heat capacity, presumably related to the hump observed by us between 300 and 375 K with $\Delta_{trs}H_m^\circ$ of about $30.1R \cdot K$ and a $\Delta_{trs}S_m^\circ = 0.08R$. For the bifurcated peaks between 375 and 436 K, the total $\Delta_{III}^{II}H_m^\circ = 64.5R \cdot K$ and $\Delta_{III}^{II}S_m^\circ = 0.147R$. These values are in excellent

TABLE 1. Experimental heat capacity of potassium acetate ($KC_2H_3O_2$) ($R = 8.1345 \; \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		Series III		DSC	Data	465	20.27
54.67	5.681	286.49	12.835	325	14.64	467	21.01
57.10	5.401	294.71	13.059	330	14.71	469	21.59
61.72	5.704	303.45	13.328	335	14.85	470	21.91
66.15	6.028	309.62	13.545	340	14.89	472	22.26
70.61	6.338	313.80	13.765	345	14.85	474	22.36
75.11	6.634	321.96	14.221	350	14.98	475	22.23
79.63	6.920	328.02	14.308	355	14.84	476	22.20
84.18	7.212	334.10	14.631	360	14.88	477	21.96
88.76	7.467	340.27	14.780	365	14.95	479	21.28
93.37	7.658	346.46	14.883	370	15.05	480	20.88
98.00	7.844	Series IV		375	14.95	481	20.45
103.33	8.063	5.80	0.053	380	15.24	483	19.66
109.37	8.304	6.19	0.069	385	15.29	485	18.84
115.41	8.521	6.55	0.085	390	15.41	487	17.89
121.48	8.722	6.77	0.131	395	15.61	489	17.01
127.55	8.950	7.02	0.089	400	15.84	490	16.54
133.66	9.122	7.69	0.107	405	17.23	491	16.06
139.77	9.271	8.21	0.131	410	18.12	492	15.69
145.89	9.465	8.76	0.138	415	17.15	498	13.78
152.02	9.599	9.68	0.170	417	16.27	499	13.68
158.16	9.751	10.91	0.220	420	16.83	500	13.73
Series II		12.13	0.276	421	17.04	505	13.81
164.25	9.922	13.37	0.344	425	17.81	510	13.92
170.35	10.058	14.62	0.430	427	17.86	515	13.94
176.52	10.244	15.89	0.518	428	17.68	520	14.02
182.67	10.369	17.17	0.620	429	17.36	525	14.02
188.83	10.492	18.48	0.721	430	16.94	530	14.16
195.01	10.622	19.89	0.849	431	16.46	535	14.18
201.18	10.757	21.38	0.991	432	16.17	540	14.29
207.35	10.904	22.89	1.133	433	15.90	545	14.31
213.52	11.024	24.41	1.294	435	15.64	550	14.39
219.69	11.182	26.32	1.505	436	15.56	555	14.42
225.86	11.353	27.48	1.623	437	15.53	560	14.53
232.04	11.511	28.67	1.777	438	15.56	565	14.58
238.22	11.573	30.96	2.048	439	15.64	570	14.85
244.41	11.788	33.18	2.339	440	15.72	575	15.91
250.59	11.923	35.44	2.631	442	15.90	576	16.72
256.77	12.074	37.74	2.922	445	16.27	577	19.21
262.96	12.198	40.53	3.290	448	16.64	578	29.03
269.14	12.355	43.80	3.700	450	16.88	579	83.22
275.32	12.579	47.08	4.138	453	17.25	580	187.4
281.51	12.703	50.41	4.633	455	17.52	581	191.6
287.70	12.861	53.77	5.043	457	17.89	582	192.4
293.87	13.095	57.64	5.449	459	18.36	583	130.2
305.05	13.210	62.04	5.723	460	18.63	584	37.36
306.23	13.419	66.48	6.042	462	19.24	585	21.83
312.40	13.609			464	19.90	587	24.71

accord with the d.s.c. 422 K (onset) transition values of Ferloni et al.[2] (50$R \cdot$K, 0.12R). From crystallographic data,[13] $\Delta_{\mathrm{III}}^{\mathrm{II}} V_m$ is about 2.1 per cent and agrees acceptably with the $\Delta_{\mathrm{trs}} H_m^\circ$ value of Jenkins and O'Brien.[14] The presumed association is from one monoclinic phase to another with an eight-fold enhancement

TABLE 2. Smoothed thermodynamic functions at selected temperatures for potassium acetate $(KC_2H_3O_2)$ $(R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

T/K	$C_{p,m}/R$	$\Delta_0^T S_m°/R$	$\Delta_0^T H_m°/(R \cdot K)$	$\Phi_m°/R$
0	(0)	(0)	(0)	(0)
5	(0.040)	(0.013)	(0.050)	(−0.003)
10	0.180	0.143	0.664	0.077
15	0.453	0.262	2.183	0.116
20	0.860	0.446	5.482	0.175
25	1.355	0.690	10.927	0.253
30	1.934	0.987	19.115	0.350
35	2.571	1.332	30.363	0.464
40	3.220	1.718	44.841	0.597
45	3.853	2.134	62.52	0.745
50	4.546	2.576	83.56	0.905
60	5.551	3.496	134.15	1.260
70	6.311	4.411	193.63	1.645
80	6.929	5.295	259.91	2.046
100	7.938	6.955	409.05	2.865
120	8.685	8.472	575.7	3.675
140	9.289	9.857	755.6	4.460
160	9.818	11.133	946.7	5.216
180	10.283	12.316	1147.8	5.939
200	10.734	13.423	1358.0	6.633
220	11.202	14.468	1577.3	7.298
240	11.669	15.46	1806.0	7.935
260	12.143	16.41	2044.1	8.548
280	12.657	17.33	2292.0	9.144
298.15	13.155	18.14	2526.2	9.667
300	13.210	18.22	2550.6	9.718
325	13.2	(19.32)	(2892.4)	(10.42)
	[13.2]	[19.30]	[2887.5]	[10.42]
350	(15.0)	(20.42)	(3260.9)	(11.10)
	[14.3]	[20.35]	[3238.1]	[11.09]
		Phase II		
375[a]	15.0	21.45	3633.8	11.760
	[15.0]	[21.37]	[3603.7]	[11.760]
411[b]	(18.7)	(22.84)	(4179.2)	(12.67)
	[15.3]	[22.76]	[4149.1]	[12.66]
		Phase IIIa		
411[b]	(18.7)	(22.94)	(4220.9)	(12.67)
	[15.3]	[22.76]	[4149.1]	[12.66]
417.5[a]	(16.3)	(23.17)	(4320.4)	(12.82)
	[15.3]	[22.99]	[4248.6]	[12.81]
425[b]	(17.8)	(23.44)	(4435.5)	(13.00)
	[15.4]	[23.26]	[4363.7]	[12.99]
		Phase II		
425[b]	(17.08)	(23.49)	(4458.3)	(13.00)
	[15.4]	[23.26]	[4363.7]	[12.99]
436.5[a]	15.5	(23.90)	(4635.1)	(13.28)
	[15.5]	[23.67]	[4540.5]	[13.27]
474[b]	(22.5)	(25.23)	(5214.5)	(14.23)
	[15.5]	[25.00]	[5119.9]	[14.20]

TABLE 2—*continued*

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot K)$	Φ_m°/R
		Phase I		
474[b]	(22.5)	(25.64)	(5408.4)	(14.23)
	[15.5]	[25.00]	[5119.9]	[14.20]
497.5[a]	13.7	26.29	5727.4	14.78
	[13.7]	[25.65]	[5438.9]	[14.72]
500	13.8	26.39	5761.7	14.87
510	13.9	26.69	5899.8	15.12
520	14.0	26.99	6039.3	15.38
530	14.1	27.29	6180.1	15.63
540	14.3	27.59	6322.1	15.88
550	14.4	27.89	6465.1	16.14
560	14.5	28.19	6609.4	16.39
565[a]	14.6	28.49	6682.0	16.66
	[14.6]	[27.85]	[6393.5]	[16.53]
582[b]	≈ 200	(28.92)	(6931.5)	(17.01)
	[14.8]	[28.28]	[6643.0]	[16.87]
		Isotropic liquid		
582[b]	≈ 200	(30.50)	(7851.2)	(17.01)
	[14.8]	[28.28]	[6643.0]	[16.87]
585[a]	21.8	30.60	7915.7	17.07
	[21.8]	[28.38]	[6707.5]	[16.91]

[a] These are the (minimum) points on the heat-capacity curve for a given transition or pair of transitions from which extrapolation of the "lattice" heat capacity was made for the calculation of transition (excess) values of the thermodynamic functions.

[b] The values of the thermodynamics of transition are given at the transition temperatures on the assumption that the transitions are strictly isothermal at these temperatures.

of the unit cell volume. The II-to-I solid-to-solid transition is at 474 K and fusion is at 582 K. When account is taken of the differences between the usual practice of listing d.s.c. transitions by the first deviation from the "lattice" curve on heating, the II-to-I transition at 474 K;[12-14] the bifurcated peaks between 375 and 436 K;[12]

TABLE 3. Transitional thermodynamic properties of potassium acetate ($R = 8.3145$ J·K^{-1}·mol^{-1})

Transition (phases)	T_{trs}/K [b]	$\Delta_{trs}H_m/(R \cdot K)$ [a]	$\Delta_{trs}S_m^\circ/R$
Hump	300 to 375[c]	27.6 ± 0.3	0.080 ± 0.001
IIIb-to-IIIa[d]	≈ 411	41.7 ± 0.5	0.097 ± 0.001
IIIa-to-II	≈ 425	22.8 ± 0.1	0.050 ± 0.001
II-to-I	≈ 474	194 ± 2	0.407 ± 0.009
I-to-Isotropic liquid (*i.e.* melting)	≈ 582	920 ± 9	1.58 ± 0.02

[a] By d.s.c. The uncertainties are estimated standard deviations.

[b] These are peak temperatures.

[c] A broad and diffuse transformation extending from approximately 300 to 375 K.

[d] We cannot ascertain whether phases IIIa and IIIb and II are distinct phases or a single phase with thermal transformations, but have adopted a "phase" notation. (Compare reference 16.)

as well as fusion near 582 K[12] are in reasonable accord with the literature.

A complete description of the methods used and the transition temperatures therefrom can be found elsewhere.[10] Neither the purity of their samples nor their heat-capacity values are provided in any of the references quoted. Comparison of the excess enthalpies and entropies is difficult as the method of drawing lattice curves affects the calculated excess values and the lattice curves can be drawn only when heat-capacity morphology is known precisely. This may account for the lack of enthalpies of transition[11] and the complete absence of entropies of transitions.

Only three phase transformations—monoclinic (IIIa or IIIb)-to-monoclinic (III)-to-orthorhombic (I)-to-isotropic liquid—have been considered probable in potassium acetate as the other transformations appear to be non-isothermal and apparently do not involve phase changes.

Hatibarua and Parry[13] and Hatibarua[15] studied the transitions in K2C by crystallographic and thermal-expansion methods, respectively. The former investigators grew single crystals of the salt from the melt using dried polycrystalline commercial materials. They reported that K2C has three polymorphs; the form existing from room temperature to a temperature of about 348 K was found to be monoclinic (Phase III) with either superlattice or an eight-fold increase in volume over the monoclinic polymorph between 348 and 428 K (Phase II); that above 428 K was observed to be orthorhombic (Phase I).

Hatibarua[15] found the transition from Phase I to Phase II (i.e. orthorhombic to monoclinic) to be characterized by a change in the structural symmetry and termination of the rapid expansion in the cell constant a'. From the structural studies, he observed that the unit cell of Phase I consists of ionic double layers parallel to (100) of potassium and carboxylate ions firmly bound by ionic forces. Sandwiched between such double layers are the methyl groups in contact and bonded by much weaker van der Waals forces. He also observed a void in the unit cell of Phase I extending through the entire crystal along (100) and suggested that these two peculiarities seem to account for the thermal behavior of K2C.

Hatibarua,[16] using crystallographic methods, found that as the transition temperature 428 K is approached, the acetate ions begin to librate between two equivalent sites. As a result, twin orientations of the low-temperature monoclinic phase occur. As the temperature increases, increasingly more acetate ions switch between the two sites until both orientations have statistically equal populations. The reflections corresponding to the twin orientations move towards each other as the temperature increases and coalesce at 428 K. A dielectric study by the same author revealed no evidence for a ferro-to-para-electric transition (503 K) as hinted by Hazlewood et al.,[12] who suggested that Phase III could be a modulated structure obtained from the Phase II structure.

From our calorimetric studies, we found scant thermodynamic evidence for the existence of Phase III as the hump between 300 and 375 K and the bifurcated transition seem not to be phase transitions.

Jenkins and O'Brien[14] found the entropy change associated with the transition at 349 K (onset) to be of the order $R \cdot \ln 2$ and attributed this transition to orientational (order-disorder) effects. They used d.s.c., d.t.a., and Raman spectroscopy, and found

only two transitions; the one at 349 K (onset) presumably corresponding to ours at 375 and the other at 413 K (onset) corresponding to our transition at 474 K. Despite its prominence, the peak at 474 K has seldom been unambiguously identified as being within 85 K of our peak temperature.[14,17,18]

Thermal transformations were not detected in rubidium and cesium acetates between room temperature and the melting temperature.[13] Two transitions were observed between 100 and 200 K in potassium butanoate, K4C,[1] whereas in potassium acetate a similar pair appear at much higher temperature (375 to 500 K). Upon increasing the temperature, the longer hydrocarbon tail in K4C may possibly acquire freedom at lower temperatures than does the much shorter tail in K2C.

Sodium acetate exhibits a transition at 21 K,[5] while K2C and Li2C[19] do not show a similar transition. The heat-capacity curves lie in the expected order. As already noted[13] sodium and potassium acetates are not isostructural near 300 K. The presence of the 21 K transition in sodium acetate[5] was held responsible for the overall larger heat capacity of this salt compared to that of sodium propanoate but the nature of the transition is still unknown. After studying several compounds of lithium and potassium[4] by the same method, we found that the odd-even effect observed in compounds with hydrocarbon tails at ambient temperatures is also a low-temperature phenomenon and that the heat-capacity curves increase above the transition monotonically in the N_C sequence $6 \rightarrow 4 \rightarrow 3 \rightarrow 5 \rightarrow 7$.

REFERENCES

1. Westrum, E. F., Jr.; Ngeyi, S. P.; Franzosini, P. *J. Chem. Thermodynamics* **1987**, 219, 113.
2. Ferloni, P.; Sanesi, M.; Franzosini, P. *Z. Naturforsch.* **1975**, 30a, 1447.
3. Skoda, W. *Kolloid-Z. Polym.* **1969**, 234, 1128.
4. Ngeyi, S. P. Ph.D. Thesis, *Thermodynamic Properties of Lithium, Potassium, and Thallium(I) Alkanoates*, The University of Michigan, Ann Arbor, MI, 1985.
5. Franzosini, P.; Plautz, W. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1983**, 15, 445.
6. Blaine, R. L. *Thermal Analysis.* Dupont, Analytical Instruments Division: Delaware.
7. Wendlandt, W. *Thermal Methods of Analysis.* Wiley: New York. **1974.**
8. Westrum, E. F., Jr. *Proceedings of NATO Advanced Study, Institute on Thermochemistry at Viana do Castello, Portugal.* Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984**, p. 745.
9. Instructions for the Specific Heat Software Kit, Perkin Elmer, Norwalk, CT, **1983.**
10. Franzosini, P.; Sanesi, M. *Thermodynamic and Transport Properties of Organic Salts.* Pergamon: New York. **1980.**
11. Sokolov, N. M. *Tezisy Dokl. X Nauch. Konf. S-M 1.* **1956.**
12. Hazlewood, F. J.; Rhodes, E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1966**, 62, 3101.
13. Hatibarua, J.; Parry, G. S. *Acta Cryst.* **1972**, B28, 3099.
14. Jenkins, T. E.; O'Brien, P. *J. Phys. Chem. Solids* **1983**, 44, 565.
15. Hatibarua, J. *Current Science* **1978**, 47, 719.
16. Hatibarua, J. Ph.D. Thesis, London University, 1968.
17. Diogenov, G. G.; Erlykov, A. N. *Nauchn. Dokl. Vysshej Shkoly Khim. i Khim. Technol.* **1958**, 3, 413.
18. Diogenov, G. G.; Nurminsk, N. N.; Gimelshtein, V. G. *Russ. J. Inorg. Chem.* **1957**, 2, 237.
19. Ferloni, P.; Kenesey, C. K.; Westrum, E. F., Jr. Personal communication, **1989.**