Int J Thermophys (2009) 30:542–554
DOI 10.1007/s10765-009-0568-4

Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of Potassium Benzoate $C_7H_5O_2K(s)$

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Received: 5 September 2008 / Accepted: 4 February 2009 / Published online: 24 February 2009

Abstract Potassium benzoate $C_7H_5O_2K$ (CAS Registry No. 582-25-2) was synthesized by the method of liquid phase reaction. Chemical and elemental analyses, FTIR, and X-ray powder diffraction (XRD) techniques were applied to characterize the composition and structure of the compound. Low-temperature heat capacities of the compound were measured by a precision automated adiabatic calorimeter over the temperature range from 78 K to 398 K. A polynomial equation of the heat capacities as a function of temperature was fitted by the least-squares method. Smoothed heat capacities and thermodynamic functions of the compound were calculated based on the fitted polynomial. In accordance with Hess's law, a reasonable thermochemical cycle was designed, and 100 mL of 1 $\text{mol} \cdot \text{dm}^{-3}$ NaOH solution was chosen as the calorimetric solvent. The standard molar enthalpies of dissolution for the reactants and products of the supposed reaction in the selected solvent were measured by an isoperibol solution-reaction calorimeter. Finally, the standard molar enthalpy of formation of the title compound $C_7H_5O_2K$ (s) was derived to be $-(610.94 \pm 0.77)\, \text{kJ} \cdot \text{mol}^{-1}$.

Keywords Adiabatic calorimetry · Heat capacity · Isoperibol solution-reaction calorimeter · Potassium benzoate · Standard molar enthalpy of formation · Thermodynamic function

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1 Introduction

Potassium is an essential element and micronutrient in the upgrowth of humans and animals. It participates in the metabolism of sugar and protein of the cells in the biological body and helps to maintain the health of the nervous system. A shortage of potassium in body fluids may cause a potentially fatal symptom known as hypokalemia [1,2]. Benzoic acid has a prominent biological effect in the growth and development of humans and animals. Potassium benzoate is often used as an antiseptic and antimicrobial agent, and has wide application in the food industry. In addition, the compounds of benzoic acid with many biological metals can reduce or prevent the growth of microorganisms in biological bodies. Therefore, great attention has been focussed on the application of metallic compounds of benzoic acid in various fields such as food preservatives, feed additives, drugs, etc.

However, low-temperature heat capacities and the standard molar enthalpy of formation of potassium benzoate have not been found in the literature, which has restricted the progress of relevant theoretical study and application development of the title compound. The aim of the present work is to measure low-temperature heat capacities and the standard molar enthalpy of formation of the title compound.

2 Experimental

2.1 Synthesis and Characterization of the Compound $C_7H_5O_2K$ (s)

To a boiling solution of KOH (3.5020 g, 0.06 mol) in water (25 cm^3), benzoic acid (7.6225 g, 0.06 mol) dissolved in the water beforehand was slowly added. The resulting mixture was heated and condensed with continuous stirring on the electric furnace until a crystal membrane appeared. The product formed as a white solid when the solution was cooled naturally to room temperature, which was then filtered, and was subsequently washed with anhydrous ethanol three times. Recrystallization from the mixed solution of anhydrous ethanol and double-deionized water yielded white crystals of potassium benzoate. Finally, the sample was placed in a vacuum desiccator at 50 °C to dry for 6 h. The calculated contents of $C_7H_5O_2K$ were: K 24.40 %; C 52.48 %; H 3.15 %; and O 19.97 %. The measured contents were: K 24.42 %; C 52.46 %; and H 3.13 %. The content of K in the compound was determined with $Na[B(C_6H_5)_4]$ chemical titration. The contents of C, H, and N were determined by element analyses (Model PE-2400, Perkin Elmer, USA). This showed that the purity of the sample prepared was better than 99.1 mass%.

FTIR (Nicolet 5700 FT-IR, USA, KBr) was used to determine the bond mode of the potassium ion with benzoic acid; the range of the wavelength is 400 cm^{-1} to $4,000$ cm^{-1}. Vibration characteristic absorptions of main groups obtained from FTIR spectra of the compound and benzoic acid are listed in Table 1.

It can be seen from Table 1 that the organic component of the compound possesses distinctly different characteristic absorption peaks relative to that of benzoic acid. The strong absorption peak of the O–H stretching vibration (γ_{O-H}) which appeared at $3,600$ cm^{-1} in benzoic acid has disappeared in potassium benzoate. It showed that

Table 1 Characteristic vibration absorptions of main groups obtained from FTIR spectra of benzoic acid and potassium benzoate (cm^{-1})

Compound	$\nu_{\text{C=O}}$	$\nu_{-\text{OH}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C-H}}$	$\delta_{\text{C-H}}$	$\delta_{\text{C-O}}$
C_6H_5COOH	1690	3600	1575	3100 2925	710	1200
C_6H_5COOK	1650	–	1596 1550	3110 3080 2930	705	1068

the oxygen atom of the organic component in the title compound was directly linked with the potassium atom. The absorption peak of the C=O stretching vibration, $\gamma_{\text{C=O}}$, shifted to the low wave number in the title compound, $1,650\,\text{cm}^{-1}$, as a result of the formation of the delocalization π bond including the benzene ring and carboxylate ($–\text{COO}^{-}$), which lowered the density of the electron cloud around $–\text{COO}^{-}$. In addition, different shifts of other characteristic absorption peaks occurred, which were also ascribed to the replacement of the hydrogen atom in –COOH of benzoic acid with the potassium ion.

The X-ray powder diffraction (XRD) technique was used to determine whether the newly synthesized compound is novel. XRD spectra of benzoic acid and potassium benzoate have been plotted in Fig. 1. The step length of the powder diffraction angle is 0.01 rad, the wavelength is 0.154056 nm ($\text{CuK}_{\alpha}1$ radiation), the electric voltage is 36 kV, and the electric current is 20 mA. The scanning rate is $4\,\text{rad} \cdot \text{min}^{-1}$, and the graphite monochromator is used for filtering. It was found from Fig. 1, by comparison of two charts, that two obvious absorption peaks in the angle range of $2\theta = 16$ rad to 18 rad and seven other weak characteristic absorption peaks in the angle range of $2\theta = 24$ rad to 35 rad were seen in the chart of benzoic acid; three distinct absorption peaks appeared near $2\theta = 24$ rad, 30 rad, and 36 rad in the chart of potassium benzoate. Therefore, novel characteristic absorption peaks completely different from those of benzoic acid appeared in the diffraction spectrum of potassium benzoate. It was shown that a new substance was produced by the liquid phase reaction of benzoic acid with potassium hydroxide.

2.2 Adiabatic Calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \leq (T/K) \leq 400$. The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [3,4]. Briefly, the calorimeter comprised mainly a sample cell; a platinum resistance thermometer; an electric

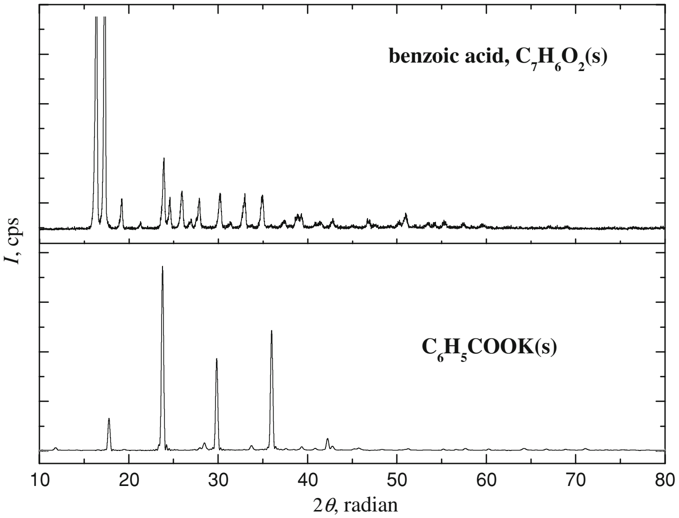

Fig. 1 XRD spectra of benzoic acid and potassium benzoate

heater; inner, middle, and outer adiabatic shields; three sets of six-junction chromel-constantan thermopiles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a data acquisition/switch unit (Model 34970A, Agilent, USA), and processed on-line by a computer.

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material ($\alpha - \mathrm{Al_2O_3}$) were measured over the temperature range $78 \leq (T/K) \leq 400$. The sample mass was 1.71431 g, which was equivalent to 0.0168 mol based on its molar mass, $M(\mathrm{Al_2O_3}) = 101.9613\ \mathrm{g \cdot mol^{-1}}$. Deviations of the experimental results from those of the smoothed curve lie within ±0.2 %, while the uncertainty is 0.3 %, as compared with the values given by the former National Bureau of Standards [5] over the whole temperature range.

Heat-capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at $0.1\ \mathrm{K \cdot min^{-1}}$ to $0.4\ \mathrm{K \cdot min^{-1}}$ and 1 K to 3 K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within $10^{-3}\ \mathrm{K \cdot min^{-1}}$ to $10^{-4}\ \mathrm{K \cdot min^{-1}}$ during the acquisition of all heat-capacity data. The data for heat capacities and corresponding equilibrium temperatures have been corrected for heat exchange of the sample cell with its surroundings [3]. The sample mass used for calorimetric measurements was 2.58455 g, which was equivalent to 1.61322×10^{-2} mol in terms of its molar mass, $M = 160.21036\,\text{g} \cdot \text{mol}^{-1}$.

2.3 Isoperibol Solution-Reaction Calorimetry

The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature control system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [6].

The reliability of the calorimeter was verified previously [6] by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17{,}547 \pm 13)\,\text{J} \cdot \text{mol}^{-1}$ for KCl, which compared with the corresponding published data, $(17{,}536 \pm 3.4)\,\text{J} \cdot \text{mol}^{-1}$ [7]. In all dissolution experiments of the sample, 100 mL of $1\,\text{mol} \cdot \text{dm}^{-3}$ NaOH was chosen as the calorimetric solvent.

Finally, UV/Vis spectra and data for the refractive indexes were used to confirm whether solution A was in the same thermodynamic state as that of solution B. These results have indicated that chemical components and physicochemical properties of solution A were consistent with those of solution B.

3 Results and Discussion

3.1 Low-Temperature Heat Capacities

All experimental results, listed in Table 2 and plotted in Fig. 2, showed that the structure of the potassium benzoate was stable over the temperature range between $T = 78$ K and 398 K; namely, no phase change, association, nor thermal decomposition occurred. By comparison of the two heat capacity curves of potassium benzoate and benzoic acid [8] in Fig. 2, it is shown that the heat capacity values of potassium benzoate are higher than those of benzoic acid. This is mainly due to the presence of the strong ionic bond O-K in potassium benzoate. The 90 experimental points in the temperature region were fitted by means of least squares, and a polynomial equation of experimental molar heat capacities ($C_{p,\text{m}}$) versus reduced temperature (X), $X = f(T) = \left[T - \frac{(T_1+T_2)}{2}\right] / \left[\frac{(T_1-T_2)}{2}\right]$ (where $T_1 = 398$ K and $T_2 = 78$ K), has been obtained:

$$C_{p,\text{m}}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 146.012 + 72.913X - 7.628X^2 + 0.062X^3 - 0.007X^4 \tag{1}$$

in which $X = (T - 238)/160$. This equation is valid between $T = 78$ K and $T = 398$ K. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ±0.3 % except

Table 2 Experimental molar heat capacities of potassium benzoate $C_7H_5O_2K$ (s) ($M = 160.2117\,\text{g} \cdot \text{mol}^{-1}$)

T (K)	$C_{p,\text{m}}$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	T (K)	$C_{p,\text{m}}$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	T (K)	$C_{p,\text{m}}$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
78.05	64.02	162.3	108.9	284.0	166.4
79.77	65.40	166.0	110.7	287.9	168.1
82.44	67.11	169.7	112.6	291.8	169.9
85.05	69.06	173.3	114.5	295.9	171.5
87.58	70.57	176.9	115.9	299.8	172.8
90.05	72.16	180.4	117.8	303.7	174.3
92.46	73.51	185.2	119.9	307.8	176.1
94.82	75.08	190.3	122.8	311.7	177.6
97.13	76.49	194.3	124.8	315.6	179.5
99.40	77.52	198.3	127.0	319.5	180.7
101.6	78.59	202.2	129.0	323.5	182.2
103.8	79.84	206.2	131.6	327.4	183.7
106.0	81.03	210.2	133.5	331.4	185.4
108.1	82.38	214.1	135.5	335.5	187.1
110.2	83.34	218.1	137.3	339.4	188.7
112.2	84.30	222.1	139.3	343.5	190.7
114.2	85.15	226.1	141.0	346.5	192.2
116.3	86.65	230.1	142.7	349.5	193.4
118.3	87.50	234.0	144.9	353.5	195.0
120.4	88.67	237.9	146.3	357.5	196.3
123.5	90.49	243.1	149.0	361.4	197.9
127.5	92.84	248.2	151.2	365.3	199.4
131.5	94.64	252.2	152.7	369.2	200.8
135.4	96.31	256.1	154.1	373.3	202.3
139.4	98.35	260.1	156.2	377.4	203.7
143.3	100.4	264.1	158.2	381.4	205.6
147.2	102.3	268.1	160.2	385.4	206.8
151.1	103.9	272.1	161.4	389.4	208.1
154.9	105.6	276.1	163.3	393.4	209.9
158.6	107.2	280.0	165.1	397.3	211.1

for several points around the lower and upper temperature limits. The coefficient of determination for fitting, R^2, is equal to 0.99995.

3.2 Thermodynamic Functions of the Compound

The smoothed molar heat capacities and thermodynamic functions were calculated based on the fitted polynomial of the heat capacities as a function of the reduced

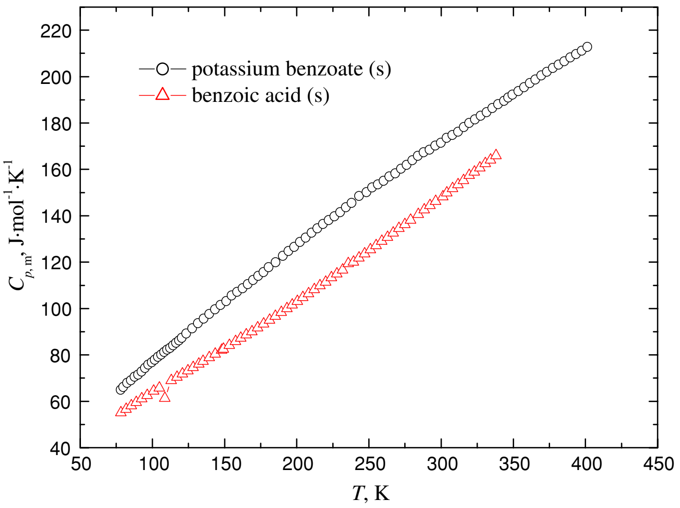

Fig. 2 Curves of experimental molar heat capacities of potassium benzoate $C_7H_5O_2K(s)$ and benzoic acid $C_7H_6O_2(s)$

temperature (X) according to the following thermodynamic equations,

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T \tag{2}$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p T^{-1} \mathrm{d}T \tag{3}$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T - T \int_{298.15}^{T} C_p T^{-1} \mathrm{d}T \tag{4}$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K were tabulated in Table 3 at 5 K intervals.

3.3 Determination of Enthalpy Change for the Solid-State Reaction of Potassium Acetate with Benzoic Acid

The solid-state reaction of anhydrous potassium acetate with benzoic acid is expressed as

$$C_7H_6O_2(s) + CH_3COOK(s) = C_7H_5O_2K(s) + CH_3COOH\ (l) \tag{5}$$

The enthalpy change of the reaction of Eq. 5 can be determined by respectively measuring the enthalpies of dissolution of benzoic acid and acetic acid in 1 mol · dm^{-3}

Table 3 Smoothed heat capacities and thermodynamic functions of potassium benzoate

T (K)	$C_{p,\mathrm{m}}$ $(\mathrm{J\cdot mol^{-1}\cdot K^{-1}})$	$H_T - H_{298.15\mathrm{K}}$ $(\mathrm{kJ\cdot mol^{-1}})$	$S_T - S_{298.15\mathrm{K}}$ $(\mathrm{J\cdot mol^{-1}\cdot K^{-1}})$	$G_T - G_{298.15\mathrm{K}}$ $(\mathrm{kJ\cdot mol^{-1}})$
80	66.51	−26.57	−145.3	−14.95
85	69.25	−26.23	−141.2	−14.23
90	71.99	−25.88	−137.1	−13.54
95	74.71	−25.51	−133.2	−12.86
100	77.41	−25.13	−129.3	−12.21
105	80.09	−24.74	−125.4	−11.57
110	82.77	−24.33	−121.6	−10.95
115	85.42	−23.91	−117.9	−10.36
120	88.06	−23.48	−114.2	−9.778
125	90.69	−23.03	−110.5	−9.217
130	93.30	−22.57	−106.9	−8.675
135	95.90	−22.10	−103.3	−8.150
140	98.48	−21.61	−99.79	−7.642
145	101.0	−21.11	−96.29	−7.152
150	103.6	−20.60	−92.82	−6.679
155	106.1	−20.08	−89.38	−6.223
160	108.6	−19.54	−85.98	−5.784
165	111.2	−18.99	−82.60	−5.361
170	113.6	−18.43	−79.25	−4.956
175	116.1	−17.85	−75.93	−4.566
180	118.6	−17.27	−72.63	−4.194
185	121.0	−16.67	−69.36	−3.838
190	123.5	−16.06	−66.11	−3.498
195	125.9	−15.43	−62.87	−3.174
200	128.3	−14.80	−59.66	−2.867
205	130.6	−14.15	−56.47	−2.575
210	133.0	−13.49	−53.30	−2.300
215	135.4	−12.82	−50.14	−2.041
220	137.7	−12.14	−47.01	−1.798
225	140.0	−11.44	−43.89	−1.570
230	142.3	−10.74	−40.78	−1.359
235	144.6	−10.02	−37.70	−1.163
240	146.9	−9.292	−34.62	−0.9823
245	149.2	−8.552	−31.57	−0.8175
250	151.4	−7.800	−28.53	−0.6682
255	153.7	−7.037	−25.50	−0.5342
260	155.9	−6.264	−22.49	−0.4155
265	158.1	−5.479	−19.50	−0.3119
270	160.3	−4.683	−16.52	−0.2233
275	162.5	−3.876	−13.55	−0.1497

Table 3 continued

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)	$H_T - H_{298.15\mathrm{K}}$ ($\mathrm{kJ \cdot mol^{-1}}$)	$S_T - S_{298.15\mathrm{K}}$ ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)	$G_T - G_{298.15\mathrm{K}}$ ($\mathrm{kJ \cdot mol^{-1}}$)
280	164.6	−3.058	−10.60	−0.09078
285	166.8	−2.229	−7.659	−0.04659
290	168.9	−1.390	−4.735	−0.01695
295	171.0	−0.5404	−1.826	−0.001752
298.15	172.3	0.000	0.000	0.000
300	173.1	0.3200	1.070	−0.01318
305	175.2	1.191	3.951	−0.01422
310	177.3	2.072	6.819	−0.04166
315	179.3	2.964	9.672	−0.08310
320	181.4	3.866	12.51	−0.1384
325	183.4	4.778	15.34	−0.2076
330	185.4	5.700	18.15	−0.2905
335	187.4	6.632	20.95	−0.3871
340	189.4	7.574	23.74	−0.4974
345	191.4	8.526	26.51	−0.6213
350	193.3	9.488	29.28	−0.7588
355	195.3	10.46	32.03	−0.9099
360	197.2	11.44	34.76	−1.075
365	199.1	12.43	37.49	−1.253
370	201.0	13.43	40.21	−1.446
375	202.9	14.44	42.92	−1.652
380	204.8	15.46	45.61	−1.873
385	206.6	16.49	48.30	−2.108
390	208.4	17.53	50.99	−2.358
395	210.3	18.57	53.66	−2.623

NaOH, $\mathrm{CH_3COOK(s)}$ in 1 $\mathrm{mol \cdot dm^{-3}}$ NaOH solution containing certain amounts of benzoic acid, and $\mathrm{C_7H_5O_2K(s)}$ in 1 $\mathrm{mol \cdot dm^{-3}}$ NaOH solution containing certain amounts of acetic acid at 298.15 K. The solid $\mathrm{CH_3COOK(s)}$ and benzoic acid were, respectively, ground within an agate mortar into a fine powder.

About 1×10^{-3} mol or 0.160 g of benzoic acid was dissolved in 100 mL of 1 $\mathrm{mol \cdot dm^{-3}}$ NaOH at 298.15 K. If "s" = calorimetric solvent, 1 $\mathrm{mol \cdot dm^{-3}}$ NaOH, then $\{\mathrm{C_7H_6O_2(s)}\} + $ "s" = solution A'. The results obtained from five dissolution experiments are listed in Table 4.

The stoichiometric number of $\mathrm{CH_3COOK(s)}$ in the reaction of Eq. 5 or [n(CH$_3$ COOK) / n(benzoic acid)] = 1:1] was regarded as a norm for sample weighing, about 1×10^{-3} mol or 0.098 g of $\mathrm{CH_3COOK(s)}$ were dissolved in the solution A′, i.e., $\mathrm{CH_3COOK(s)} +$ solution A′ = solution A. The results obtained from five dissolution experiments are listed in Table 4.

Table 4 Dissolution enthalpies of reactants and products of the reaction of Eq. 5 in the selected solvents [a]

System	Solvent	No.	$m_{C_6H_5NO_2}$ (g)	$\Delta E_s/\Delta E_e$	t_e(s)	$Q_s(J)$	$\Delta_s H_m^o$ (kJ · mol^{-1})
Benzoic acid	1 mol · dm^{-3} NaOH	1	0.12150	−0.7106	74.844	−25.846	−25.978
		2	0.12253	−0.8329	65.047	−26.328	−26.240
		3	0.12254	−0.8624	63.031	−26.416	−26.326
		4	0.12471	−0.8728	62.984	−26.715	−26.160
		5	0.12231	−0.8898	61.312	−26.512	−26.471
Avg. $\Delta_s H^o_{m,1} = -(26.23 \pm 0.08)$ kJ · mol^{-1}							
Potassium acetate	Solution A	1	0.10520	−0.2833	34.843	−4.7970	−4.4750
		2	0.10070	−0.5149	18.234	−4.5626	−4.4466
		3	0.10083	−0.9272	10.266	−4.6257	−4.5023
		4	0.09827	−0.8241	11.172	−4.4742	−4.4683
		5	0.09906	−0.8580	11.063	−4.6128	−4.5700
Avg. $\Delta_s H^o_{m,2} = -(4.49 \pm 0.02)$ kJ · mol^{-1}							
Acetate acid	1 mol · dm^{-3} NaOH	1	0.06066	−0.8939	123.985	−53.895	−53.317
		2	0.06045	−0.9320	123.672	−56.013	−55.642
		3	0.06073	−0.9069	123.718	−54.525	−53.914
		4	0.06088	−0.9109	123.749	−54.779	−54.032
		5	0.06058	−0.8902	123.578	−53.460	−52.992
Avg. $\Delta_s H^o_{m,3} = -(53.98 \pm 0.46)$ kJ · mol^{-1}							
Potassium benzoate	Solution B	1	0.16030	0.4720	33.000	7.5694	7.5652
		2	0.16070	1.2253	13.125	7.8153	7.7916
		3	0.16046	0.7054	23.094	7.9166	7.9044
		4	0.16033	0.8770	18.344	7.8180	7.8123
		5	0.16048	1.0411	15.329	7.7555	7.7425
Avg. $\Delta_s H^o_{m,4} = (7.76 \pm 0.06)$ kJ · mol^{-1}							

[a] m—mass of sample; t_e—heating period of electrical calibration; Q_s/J-heat effect during the sample dissolution; ΔE_s—voltage change during the sample dissolution; ΔE_e—voltage change during the electrical calibration; $\Delta s H_m^o = Q_s / n = (\Delta E_s/\Delta E_e)\, I^2 Rt(M/m)$, where R is the electro-resistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), I is the current ($I = 20.015$ mA), and M is the molar mass of the sample

About 1×10^{-3} mol of CH_3COOH (l) was dissolved in 1 mol · dm^{-3} NaOH at 298.15 K. Because of the volatilization of acetic acid, when the liquid was weighed, the room temperature must be controlled at 17 °C to 18 °C to reduce the rate of volatilization. The sample cell in which acetic acid was admitted should be covered with a plug made of polytetrafluoroethylene, then $\{CH_3COOH(l)\}$ + "s" = solution B'. The results obtained from five dissolution experiments are listed in Table 4.

The dissolution enthalpy of $C_7H_5O_2K$(s) in solution B′ was measured under the same condition as the above, $\{C_7H_5O_2K(s)\}$ + solution B′ = solution B. The results obtained from five dissolution experiments are listed in Table 4.

The enthalpy change of the solid-state reaction of Eq. 5 can be calculated in accordance with a thermochemical cycle and the experimental results as follows:

$$\begin{aligned}\Delta_r H_m^o &= \sum \Delta_{sol} H^o_{m(\text{Reactants})} - \sum \Delta_{sol} H^o_{m(\text{Products})}\\ &= \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4\\ &= [-26.2348 + (-4.4924)] - (-53.9790) - (7.7632)\\ &= (15.49 \pm 0.47)\ \text{kJ} \cdot \text{mol}^{-1}.\end{aligned}$$

3.4 Standard Molar Enthalpy of Formation of the Compound $C_7H_5O_2K$ (s)

A reaction scheme used to derive the standard molar enthalpy of formation of $C_7H_5O_2K$(s) is given in Table 5. The experimental values of the dissolution enthalpies of the reactants and products in the reactions of Eq. 5 were combined with some auxiliary thermodynamic data of $\Delta_f H_m^o$ ($C_7H_6O_2$, s) = $-(384.8 \pm 0.50)$ kJ · mol^{-1} [9], $\Delta_f H_m^o$(CH_3COOK, s) = -725.15 kJ · mol^{-1} [10], and $\Delta_f H_m^o$(CH_3COOH,l) = $-(483.52 \pm 0.36)$ kJ · mol^{-1} [11], to derive the standard molar enthalpy of formation of $C_7H_5CO_2K$ (s),

$$\begin{aligned}&\Delta_f H_m^o(C_7H_5O_2K, s)\\ &\quad = \Delta H_8\\ &\quad = \Delta_r H_m^o + \Delta_f H_m^o(C_7H_6O_2, s) + \Delta_f H_m^o(CH_3COOK, s) - \Delta_f H_m^o(CH_3COOH, l)\\ &\quad = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_7\\ &\quad = [-26.2348 + (-4.4924)] - (-53.9790 - (7.7632) + (-384.8)\\ &\qquad +(-725.15) - (-483.52)\\ &\quad = -(610.94 \pm 0.77)\ \text{kJ} \cdot \text{mol}^{-1}.\end{aligned}$$

Table 5 Reaction scheme used to determine the standard molar formation enthalpy of potassium benzoate

No.	Reactions	$\Delta_f H_m^o$ or $(\Delta_s H_m^o \pm \sigma_a)^*$(kJ · mol^{-1})
1	$C_7H_6O_2$(s) +“s”= solution A′	– (26.23 ± 0.08), ΔH_1
2	CH_3COOK(s)+ solution A′ = solution A	– (4.49 ± 0.02), ΔH_2
3	$CH_3COOH(l)$ +“s”= solution B′	– (53.98 ± 0.46), ΔH_3
4	$C_7H_5O_2K$(s)+ solution B′ = solution B	(7.76 ± 0.06), ΔH_4
5	7C(s) +3 H_2(g) +O_2(g) = $C_7H_6O_2$ (s)	– (384.8 ± 0.50), ΔH_5
6	2C(s) + $\frac{3}{2}H_2$(g) + O_2(g) + K(s) = CH_3COOK(s)	−725.15, ΔH_6
7	2C(s) +2H_2(g) +O_2(g) = CH_3COOH(l)	– (483.52 ± 0.36), ΔH_7
8	7C(s) + $\frac{5}{2}H_2$(g) +O_2(g) + K(s) = $C_7H_5O_2K$ (s)	– (610.94 ± 0.77), ΔH_8

$^*\ \sigma_a = \sqrt{\frac{\sum_{i=1}^{5}(x_i - \bar{x})^2}{n(n-1)}}$ in which n is the experimental number, x_i is a single value in a set of dissolution measurements, and $\bar{x}$ is the mean value of a set of measurement results

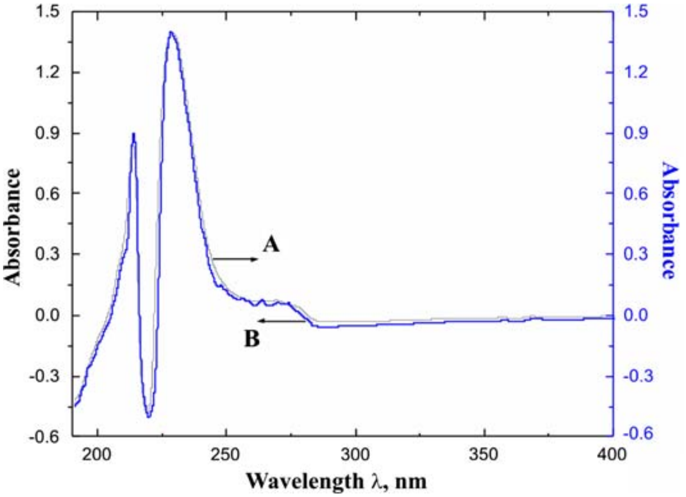

Fig. 3 UV/Vis spectra of solution A and solution B obtained from the dissolution of the [$C_7H_6O_2$(s) and CH_3COOK(s)] mixture and the [$C_7H_5O_2K$ (s) and CH_3COOH (l)] mixture in the supposed reaction of Eq. 5 in 100 cm^3 of 1 mol · dm^{-3} NaOH (diluted to 1:20)

in which ΔH_1 to ΔH_8 are the enthalpy changes of the reactions corresponding to the number of reactions in Table 5.

The results of UV/Vis spectra and refrangibility (refractive index) were both important information used to detect whether the differences of the structure and composition between two kinds of solutions existed. In this paper, all of the reactants and products of the reaction of Eq. 5 can be easily dissolved in the selected solvent. The measured values of the refractive indexes of solution A and solution B were 1.3421 ± 0.0004 and 1.3420 ± 0.0005, respectively. The results of UV/Vis spectroscopy are shown in Fig. 3. UV/Vis spectra and the data of the refractive indexes of solution A agreed with those of solution B; no difference in the structure and chemical composition existed between the two solutions. These results have demonstrated that solutions A and B were same; the designed Hess thermochemical cycle was reasonable and reliable, and can be used to derive the standard molar enthalpy of formation of the compound $C_7H_5O_2K$(s).

4 Conclusions

1. This paper reports low-temperature heat capacities of the solid-state compound C_6H_5COOK(s) measured by adiabatic calorimetry and the dissolution enthalpies of the reactants and the products of the designed solid-state reaction of anhydrous potassium acetate with benzoic acid by isoperibol solution calorimetry. Additionally, the thermodynamic functions and standard molar enthalpy of formation of the product C_6H_5COOK (s) were derived from these experimental results.
2. The enthalpy change of the solid phase reaction of Eq. 5 obtained by solution calorimetry was determined to be $\Delta_r H_m^o = (15.49 \pm 0.47)$ kJ · mol^{-1}, which was an endothermic reaction.

Acknowledgment This work was financially supported by the National Science Foundation of China under contract NSFC No. 20673050.

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