Journal of Thermal Analysis, Vol. 45 (1995) 53-58

STUDY ON THE CAPACITIES, HEATS OF DILUTION AND PROPERTIES OF CONCENTRATED POTASSIUM CARNALLITE SOLUTIONS AT 298.15 K

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Abstract

The heats of dilution of the infinitesimally dilute potassium carnallite solutions at 298.15 K have been studied by continuous titration from 1.8942 to 0.01044 mol·kg^{-1}, and an equation for the curve of heats of dilution has been fitted. It was shown that the enthalpy of dilution for the same concentration of the carnallite solution is equal to the sum of those of KCl and $MgCl_2$ solutions. The equation for the curve of enthalpy of dilution corresponds to that of natural carnallite.

Keywords: dilute heat, heat capacity, potassium carnallite

Introduction

There are salts of potassium, sodium and magnesium chlorides in Chaerham Salt Lakes, Qinghai, P.R.C.. The potassium carnallite ($KCl\cdot MgCl_2\cdot 6H_2O$) is a double salt used as raw material for the manufacture of potassium fertilizer. Xia Shuping *et al.* [1, 2] studied the processes of dissolution and crystallisation kinetics and the properties of $KCl\cdot MgCl_2\cdot 6H_2O$. In this paper, the heats of dilution from 1.8984 to 0.01061 mol·kg^{-1} of potassium carnallite solutions at 298.15 K have been determined in a continuous titration calorimeter and the heat capacities of synthesized concentrated potassium carnallite solutions from 1.8942 to 0.01044 mol·kg^{-1} have been calculated. Equations have been set up. They are identical with that for the curve of heats of dilution a single salt the KCl and $MgCl_2$ at the same concentration. The square sum of calculated deviation is not more than 1.0.

Experimental

1. 2.1087 mol·kg^{-1} KCl solution: KCl (extra pure) 29.5278 g was dissolved to make 200.00 ml of solution.

2. 1.8828 mol·kg^{-1} $MgCl_2$ solution: a given amount of $MgCl_2\cdot 6H_2O$ (analytically pure) was dissolved to make a supersaturated solution. The concentration was determined at 25°C and then diluted to 1.8828 mol·kg^{-1}.

0368–4466/95/ $ 4.00

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3. The natural and synthetic potassium carnallite solution: The maximum concentration of 1.8984 mol·kg^{-1} potassium carnallite is found in the K^+, Mg^{2+}, Cl^-//H_2O ternary system phase diagram at 25°C. At this point, the molar ratio of KCl and $MgCl_2$ is 1:1, and no crystal appears. Natural carnallite was dissolved. In addition, synthesized potassium carnallite solution was made. These two solutions were analyzed, and the exact concentrations are listed in Table 1.

Table 1 The analytical results of natural and synthetic potassium carnallite solutions

Solution properties	KCl:$MgCl_2$ molar ratio	KCl / mol·kg^{-1}	$MgCl_2$ / mol·kg^{-1}
Potassium carnallite synthetic	1:1	1.8986	1.8990
Potassium carnallite	1:1	1.8942	1.8942
KCl solution	–	2.1087	–
$MgCl_2$	–	–	1.8828

Instrument

Sweden LKB 8710 Precise Calorimeter; 100 ml glass calorimeter bottle; thermister resistance: R_D=2000Ω. The relationship between thermister resistance and temperature was calibrated with 1/10 standard thermometer and Beckmann thermometer. The precision of the calorimeter has been checked with data in literatures [3, 4]. The dilution range of solution concentration of the synthetical solution is from m_i=1.8942 mol·kg^{-1} to m_e=0.01044 mol·kg^{-1}; natural solution, from m_i=1.8984 to m_e=0.01061 mol·kg^{-1}.

Operation

Step by step continuous dilution method was used: At first, an initial solution of 50.00 ml was precisely weighed and put into the 100 ml calorimeter bottle. Then the bottle was sealed with a filled metalseal and thermostated at 25.000±0.001°C for 4 h. Next, redistilled water was added into the calorimeter bottle at constant speed by a peristaltic pump and the heat was measured. At the same time, two time different electric heating and one time cooling were used to determine the total capacities of the initial and the final solution C_1 and C_2 and the Newton cooling constant K. Then the capacities and heats of dilution ΔHd [5, 6] at different concentrations m_1 in the dilution systems were calculated:

$$C = W_{(t)}^{-1}\,[C_1 - C_o + (\mathrm{d}C_B / \mathrm{d}t)] \qquad (1)$$

$$\Delta Hd = -M^{-1}\{C_{(t)}[T_{(t)} - T_o] + K[T_{(t)} - T_o] + t(\mathrm{d}C_B / \mathrm{d}t)[T_o - T_B]\} \quad (2)$$

In above Eqs (1) and (2), $W(t)$ is the total weight (kg) of dilution system at t; M is the total molarity of solute in solution; $C(t)$ is the total capacity (kg·K^{-1}) at t; C_o is a constant (kg·K^{-1}) obtained in experiment; $T(t)$ is the solution temperature at t; T_o is the initial temperature; Ts is equilibrium temperature; T_B is dilute temperature; $\mathrm{d}C_B/\mathrm{d}t$ is the rate of change of heat capacities in the dilution process (kg·K^{-1}, S^{-1}), $C_B = C_2 - C_1$.

After the first dilute, 50.00 ml solution was weighted and the second dilution was begun. The procedure was repeated until the solution concentration was less than 0.1 mol·kg^{-1}.

In Table 2, M_i is the concentration of carnallite, C is the capacity of carnallite, ΔH_1 is the heat of dilution of carnallite, ΔH_2 is the heat of dilution of synthesized solution, ΔHy is the value of synthesized solution, ΔHk is the heat of dilution of KCl, ΔHm is the heat of dilution of $MgCl_2$, ΔHh is the sum of heat of dilution of KCl and $MgCl_2$.

Results and discussion

1. The heats of dilution of natural and synthetical potassium carnallite solutions and KCl and $MgCl_2$ single solution at different concentrations were measured. The heats of dilution from m_i to m_e ΔHd (kJ/mol), molar heat capacities C (kJ·kg^{-1}·K^{-1}) are listed in Table 2.

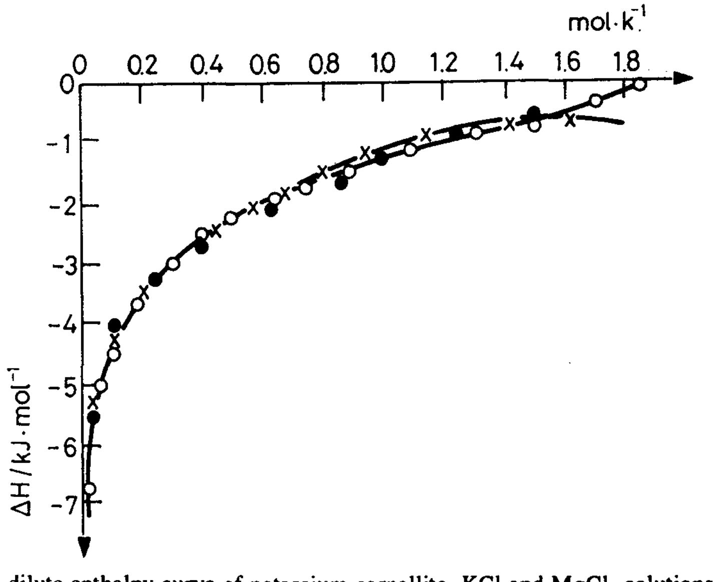

Fig. 1 The dilute enthalpy curve of potassium carnallite, KCl and $MgCl_2$ solutions
o: the dilute enthalpy curve of potassium carnallite; ×: stimulating curve;
•: the curve of sum dilution heat of KCl and $MgCl_2$ solution

Table 2 The dilute heats, capacities and simulating values of potassium carnallite solution and single component solution at 298.15 K

Carnallite solution			Synthetical solution				KCl	$MgCl_2$	KCl+$MgCl_2$	sti.
Mi/ mol·kg^{-1}	C/ kJ(k·mol)$^{-1}$	ΔH_2/ kJ·mol^{-1}	Mi/ mol·kg^{-1}	C/ kJ(k·mol)$^{-1}$	ΔH_2/ kJ·mol^{-1}	ΔHy/ kJ·mol^{-1}	ΔHk/ kJ·mol^{-1}	ΔHm/ kJ·mol^{-1}	ΔHh/ kJ·mol^{-1}	ΔHy/ kJ·mol^{-1}
1.8984	2.9633	0	1.3942	2.9727	0	0	0	0	0	0
1.7167	3.0538	–0.3515	1.7011	3.0685	–0.3631	–0.5218	0.1208	–0.4376	–0.3168	–0.5115
1.8081	3.1099	–0.5642	1.6331	3.1034	–0.4912	–0.5703	0.1562	–0.5911	–0.4349	–0.5604
1.5174	3.1582	–0.7252	1.5176	3.1642	–0.6916	–0.6633	0.2164	–0.8515	–0.6351	–0.6544
1.4606	3.1889	–0.8153	1.4377	3.2074	–0.8168	–0.7364	0.2580	–1.0316	–0.7736	–0.7285
1.3923	3.2267	–0.9158	1.3835	3.2372	–0.8943	–0.7905	0.2863	–1.1541	–0.8678	–0.7835
1.2989	3.2792	–1.0350	1.2989	3.2846	–1.0021	–0.8830	0.3303	–1.3417	–1.0114	–0.8778
1.1274	3.3796	–1.2019	1.1413	3.2846	–1.1679	–1.0852	0.4125	–1.7064	–1.2940	–1.0846
1.0601	3.4203	–1.2441	1.0972	3.9287	–1.2242	–1.1497	0.4354	–1.8086	–1.3732	–1.1508
0.9767	3.4718	–1.3947	0.9628	3.9555	–1.4730	–1.3707	0.5055	–2.1251	–1.6197	–1.3784
0.8848	3.5301	–1.5798	0.8966	3.9692	–1.5964	–1.4947	0.5399	–2.2847	–1.7448	–1.5065
0.8089	3.5794	–1.7429	0.8195	3.9854	–1.7450	–1.6533	0.5801	–2.6128	–1.8946	–1.6708
0.7574	3.6136	–1.8618	0.7508	4.0002	–1.8845	–1.8087	0.6159	–2.7565	–2.0327	–1.8322
0.7142	3.6426	–1.9693	0.6989	4.0115	–1.9986	–1.9358	0.6430	–2.8844	–2.1406	–1.9644
0.6517	3.6852	–2.1394	0.6520	4.0219	–2.1098	–2.0583	0.6777	–2.9191	–2.2414	–2.0921
0.5101	3.7850	–2.6058	0.5938	4.0351	–2.2647	–2.2211	0.6977	–3.0691	–2.3714	–2.2621
0.4683	3.8153	–2.6853	0.5062	4.0553	–2.5419	–2.4909	0.7434	–3.3237	–2.5803	–2.5445
0.4078	3.8598	–2.8184	0.4537	4.0677	–2.6206	–2.6679	0.7707	–3.4863	–2.7156	–2.7303
0.3503	3.9030	–2.9783	0.4013	4.0803	–2.7396	–2.8572	0.7980	–3.6584	–2.8604	–2.9293

Table 2 Continued

Carnellite solution			Synthetical solution				KCl	$MgCl_2$	KCl+$MgCl_2$	sti.
Mi/ $mol\cdot kg^{-1}$	*C*/ $kJ(k\cdot mol)^{-1}$	ΔH_2/ $kJ\cdot mol^{-1}$	*Mi*/ $mol\cdot kg^{-1}$	*C*/ $kJ(k\cdot mol)^{-1}$	ΔH_2/ $kJ\cdot mol^{-1}$	ΔHy/ $kJ\cdot mol^{-1}$	ΔHk/ $kJ\cdot mol^{-1}$	ΔHm/ $kJ\cdot mol^{-1}$	ΔHh/ $kJ\cdot mol^{-1}$	ΔHy/ $kJ\cdot mol^{-1}$
0.3119	3.9323	–3.1118	0.3592	4.0905	–2.8585	–3.0190	0.8199	–3.8056	–2.9857	–3.0996
0.2588	3.9733	–3.3536	0.3054	4.1038	–3.0533	–3.2392	0.8479	–4.0090	–3.1610	–3.3318
0.2041	4.0164	–3.6259	0.2549	4.1165	–3.3028	–3.4604	0.8743	–4.2205	–3.3484	–3.5656
0.1978	4.0213	–3.6561	0.2045	4.1298	–3.5761	–3.6962	0.9006	–4.4608	–3.5602	–3.8152
0.1834	4.0329	–3.7338	0.1996	4.1310	–3.5993	–3.7199	0.9031	–4.4861	–3.5830	–3.8404
0.1763	4.0385	–3.7763	0.1899	4.1335	–3.6488	–3.7675	0.9082	–4.5377	–3.6295	–3.8907
0.1682	4.0450	–3.8294	0.1801	4.1360	–3.7035	–3.8161	0.9133	–4.5916	–3.6783	–3.9422
0.1419	4.0662	–4.0432	0.1752	4.1373	–3.7331	–3.8407	0.9158	–4.6192	–3.7034	–3.9682
0.1302	4.0758	–4.1667	0.1702	4.1386	–3.7646	–3.8659	0.9184	–4.6471	–3.7297	–3.9949
0.1061	4.0954	–4.5009	0.1037	4.1560	–4.4525	–4.2172	0.9531	–5.1070	–4.1539	–4.3681
0.05117	4.1409	–5.1030	0.05158	4.1699	–5.0530	–5.1023	0.9802	–5.6599	–4.6797	
0.01061	4.1750	–6.7810	0.01044	4.1811	–6.7819	–6.7801	1.0017	–6.5844	–5.5827	

2. The curves and equations the enthalpy of dilution of natural and synthetic potassium carnallite solutions have been obtained:

In Table 2, it is shown that the dilution processes from m_i to m_e of natural and synthetic potassium carnallite solutions are endothermic processes, and their capacities are similar at identical concentrations and will decrease with increase of concentration. A diagram of ΔHd *vs.* concentration was made, with a smooth curve obtained as calculated by a NEC-8001 computer. The obtained equation is as follows:

$$\Delta Hd = A_{\exp}(bm_i)$$

where A, b are parameters, having values $A=$ 4.8300, $b=$ −1.3080.

3. The curve and equation of enthalpy of dilution of KCl and $MgCl_2$ solutions:

The sum of enthalpies of dilution of KCl and $MgCl_2$ solutions was diagrammed against concentrations as in Fig. 1, the calculated results are given in Table 2. The fitting equation is:

$$\Delta Hd = A_{\exp}(bm_i)$$

where $A=$ 5.021, $b=$ −1.343. It is shown that in the same concentration range the enthalpy of dilution of potassium carnallite solution is equal to the sum of those of KCl and $MgCl_2$ solutions'.

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Zusammenfassung — Die Verdünnungswärmen unendlich verdünnter Kaliumkarnallitlösungen bei 298.15 K wurden mittels kontinuierlicher Titration von 1.8942 bis 0.01044 mol/kg untersucht und der Kurve der Verdünnungswärmen eine Gleichung angepaßt. Man zeigte, daß die Verdünnungsenthalpie für die gleiche Konzentration der Karnallitlösung gleich der Summe derer der Lösungen von KCl und $MgCl_2$ ist.Die Gleichung für die Kurve der Verdünnungsenthalpie korrespondiert mit der Kurve für natürliches Karnallit.