Dec., 1995

MgB_4O_7 - $MgSO_4$ - $MgCl_2$ - H_2O 及次级体系 298.15K 时稀释热、热容和表观摩尔焓的研究

李积才* 王鲁英 曾忠民 翟宗玺

(中国科学院青海盐湖研究所, 西宁 810008)

本文研究了含硼四元水盐体系 MgB_4O_7 - $MgSO_4$ - $MgCl_2$ - H_2O 及次级体系 MgB_4O_7 - $MgSO_4$ - H_2O 和 MgB_4O_7 - $MgCl_2$ - H_2O 在 298.15K 时不同离子强度下的稀释热和热容,并将 Debye-Huckel 极限公式应用 到多元电解质稀溶液中,获得从高离子强度到低离子强度 I 为 19-0.0001 范围内的相对表观摩尔焓。

关键词: 含硼多元体系 稀释热 热容 相对表观摩尔焓

HEATS OF DILUTION, HEAT CAPACITIES AND APPARENT MOLAL ENTHALPIES OF MgB₄O₇-MgSO₄-MgCl₂-H₂O SYSTEMS AT 298.15K

Li Jicai Wang Luyin Zeng Zhongmin Zhai Zongxi (Qinghai Institute of Salt Lakes, Academia Sinica, Xining 810008)

The heats of dilution and heat capacities of MgB₄O₇-MgSO₄-MgCl₂-H₂O quaternary system and MgB₄O₇-MgSO₄-H₂O and MgB₄O₇-MgCl₂-H₂O subsystems were measured in the ionic strength range from 19 to 0.1 at 298.15K. The data of the heat of dilution were extrapolated to infinite dilution by use of the Debye-Huckel limiting law to obtain relative apparent molal enthalpies over the ionic strength *I* range from 19 to 0.0001.

Keywords: multi-component system containing boron heat of dilution heat capacity
apparent molal enthalpy

. INTRODUCTION

Most of the salt lakes on the Qinghai-Xizang plateau in China belong to the seawater system with aboundant boron and magnesium. In the late period of evaporation, because of depo-

收稿日期: 1995-01-11.

国家自然科学基金资助课题.

^{*} 通讯联系人

第一作者:李积才, 男, 28 岁, 助理研究员, 研究方向: 多元电解质溶液热化学。

sition of most salts of sodium and potassium and of high concentrating factors of boron and lithium, the brine becomes actually the Li⁺, Mg^{2+}/Cl^- , SO_4^{2-} , $B_4O_7^{2-}-H_2O$ system. The phase equilibra and properties of saturated solution in the Li⁺, Mg^{2+}/Cl^- , SO_4^{2-} , $B_4O_7^{2-}-H_2O$ systems have been studied $^{(1,2)}$.

This paper reports the heats of dilution, heat capacities and apparent molal enthalpies of MgB₄O₇-MgSO₄-MgCl₂-H₂O quaternary system and MgB₄O₇-MgSO₄-H₂O and MgB₄O₇-MgCl₂-H₂O ternary systems at 298.15K. The Debye-Huckel limiting law was used for the heats of dilution extrapolations in multi-component systems. This study is very valuable for understanding the thermochemical characteristics of brine in the late period of evaporation after deposition of salts of sodium and potassium, for extracting process of boron and magnesium from salt lakes, and for comprehensive utilization of brine.

EXPERIMENTAL

Magnesium sulfate and magnesium chloride used in the experiment were recrystallized from A. R. MgSO₄ • 7H₂O and MgCl₂ • 6H₂O. Magnesium tetraborate, MgB₄O₇ • 9H₂O was synthesized from analytical reagents. Its composition is (wt%) MgO 11.83, B₂O₃ 40.76, H₂O 47.43; B₂O₃ / MgO (mole ratio) 1.995 (theoretical values: 11.80, 40.75, 47.45, 2.000). X-ray diffraction analysis identifies it as the compound MgB₄O₇ • 9H₂O. The co-saturated point solution of MgB₄O₇-MgSO₄-MgCl₂-H₂O(MB₁) quaternary system and MgB₄O₇-MgCl₂-H₂O (MB₂) and MgB₄O₇-MgSO₄-H₂O(MB₃) subsystems were prepared by isothermal (25.00 \pm 0.03°C) method (3) . The components are given in Table 1. Redistilled water was used in the recrystallization of the reagents, the synthesis of the borate, and the preparation of equilibrium mixtures.

	Table 1 Component	ts of $MgB_4O_7-MgSO_7$	-MgCl,-H,O system	s
	MgB_4O_7	Mg_2SO_4	MgCl ₂	
systems	mol⋅kg ⁻¹	mol • kg ⁻¹	mol • kg ⁻¹	<i>i</i> * .
MB ₁	0.5909	0.2247	5.4251	19.5373
MB ₂	0.5420	_	5.4915	18.6425
MB ₃	0.07843	3.0438	_	12.4891

^aI is the molal ionic strength $(I=(1/2)\Sigma M_iZ_i^2)$, where M_i is the molality of ion i with charge Z_i).

A LKB-87001 precision calorimeter and a thermostatic bath $(25.00\pm0.01\text{°C})$ were used to measure the heat of dilution and the heat capacity. The accuracy of the calorimeter has been tested previously by measuring the heat effect of the standard reaction of trishydroxymethylaminomethane(THAM) with HCl at 298.15K. A weighed amount of the solution (titrate) was loaded in the glass reaction vessel. The vessel with its contents were laid to the thermostat at $25.00\pm0.01\text{°C}$ for 2h, then pre-fixed volumes of water (titrant) were titration-added by means of peristaltic pump. The titration rate was 3.1344 ± 0.0016 cm³ · min⁻¹. The temperature changes in the reaction vessel were measured in terms of an electrical

potential output from the thermistor with 2000Ω resistance R. The output was amplified by a microvolt amplifier and recorded. Heat capacity and leakage constant were measured with twice heating electrically for 500s using 200mW and 500mW power range, and once lowering the temperature experiment before and after each titration $^{(4,5)}$. The calorimetric measurements were processed by means of a computer program to obtain the heats of dilution and heat capacities according to the followign Eq. (1), (2):

$$C_i = W(t)^{-1} [C_1 + (dC_B / dt)t]$$
 (1)

$$\Delta H_{d} = -M^{-1} \{ C(t) [T(t) - T_{o}] + K t [T(t) - T_{a}] + t (dC_{B} / dt) [T_{o} - T_{B}] \}$$
(2)

where t [s] denotes time, $C_1[kJ \cdot K^{-1} \cdot kg^{-1}]$ is heat capacity of the solution of ionic strength I_t , $\Delta H_d[kJ \cdot mol^{-1}]$ is heat of dilution, W(t) [kg] is the weight of the solution in the reaction vessel at t, $C_1[kJ \cdot K^{-1}]$ is initial heat capacity of the solution before titration, $dC_B / dt[kJ \cdot K^{-1} \cdot s^{-1}]$ is the rise of heat capacity, M[mol] is the total molalities of all solutes in the titrate, $C(t)[kJ \cdot K^{-1}]$ is the total heat capacity of the reaction vessel plus titrate and titrant at t, $K[kJ \cdot K^{-1} \cdot s^{-1}]$ is leakage constant, T(t) [K] is the temperature of outer surface of the calorimeter at t, $T_o[K]$ is the initial temperature of the titrate, $T_a[K]$ is the final equilibrium temperature, $T_B[K]$ is the temperature of titrant.

RESULTS AND DISCUSSION

The heats of dilution and heat capacities of MgB_4O_7 - $MgSO_4$ - $MgCl_2$ - H_2O quaternary system and MgB_4O_7 - $MgSO_4$ - H_2O and MgB_4O_7 - $MgCl_2$ - H_2O subsystems were measured to cover a range from initial ionic strength I_0 to I_1 at 298.15K. The measured results are reported in Table 2, in which, M_1 (mol • kg⁻¹) are the molalities of the total solutes of the systems.

The apparent molal enthalpies ${}^{\Phi}L = -\Delta H_{\rm d}(I_{\rm i} \rightarrow 0)$ were determined with the extended limiting law equation (6-8)

$${}^{\Phi}L = S_{H}I^{1/2}[(1+I^{1/2})^{-1} - (\sigma/3)] + BI + CI^{3/2}$$
(1)

where S_H is the Debye-Hückel limiting law slope $(S_H = w \cdot A_H, w = (1/2)\Sigma V_i Z_i^2, V_i \text{ and } Z_i \text{ are the numbers and charge of ion } i$; and $A_H = 2.8786 \text{kJ} \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2} \text{ at } 298.15 \text{K}$;

$$\sigma = (3 / I^{3/2})[(1 + I^{1/2}) - (1 + I^{1/2})^{-1} - 2\ln(1 + I^{1/2})]$$
(2)

and B and C are adjustable parameters. The values of B and C have been determined from the experimentally measured enthalpies of dilution

$$\Delta H_{\mathsf{d}} = (I_{\mathsf{i}} \to I_{\mathsf{f}}) = -\Delta^{\Phi} L(I_{\mathsf{i}} \to I_{\mathsf{f}}) \tag{3}$$

using
$$(\Delta^{\Phi} L - S_H \Delta \{I^{1/2}[(1+I^{1/2})^{-1} - (\sigma/3)]\} / \Delta I = B + C(\Delta I^{3/2} / \Delta I)$$
 (4)

plots of the left side of Eq.(4) versus $\Delta I^{3/2}/\Delta I$ for the MgB₄O₇-MgSO₄-MgCl₂-H₂O systems are given in Fig.1. Equation(4) was originally suggested to be useful in extrapolating heat-of-dilution data to infinite dilution and was used in the molality range from 0 to 0.1 ⁽⁶⁾. However, it was found later ^(7,8) that this equation (4) would be valid for heat-of-dilution data of electrolytes as well as of seawater for the approximate molality and ionic strength range from 0.1 to 1.0. So that, Fig.1 was a plot from heat-of-dilution data of the MgB₄O₇-MgSO₄-MgCl₂-H₂O systems in molality and ionic strength less than 1.0.

Table 2 Heats of Dilution ΔH_d , Heat Capacities C and Apparent Molal Enthalpies $^{\Phi}L$ of MoB.O.-McSO.-McCl.-H.O Systems at 298.15K

19.5377		MgB ₄ O ₇ -		-H ₂ O Systems at 29		
19.5377	I_{o}	I_{i}	M_i mol • kg $^{-1}$	C kJ • kg ⁻¹ K ⁻¹	ΔH _d kJ•mol⁻¹	^Φ <i>L</i> kJ • mol ⁻¹
19.5377						
18.3221 3.8524 2.588 -0.836 16.049 17.3640 5.5464 2.641 -2.108 14.767 16.0168 5.1161 2.719 -3.707 13.168 15.014 4.9514 2.750 -4.288 12.587 14.4201 4.6660 2.818 -5.447 11.428 13.1322 3.667 2.026 -6.729 9.146 11.3853 3.6367 2.026 -8.341 8.534 10.1836 3.2528 3.117 -9.276 7.599 9.2555 2.9564 3.192 -10.174 6.701 8.2528 2.6361 3.276 -11.055 5.820 7.1101 2.2711 3.374 -11.055 5.820 7.1101 2.2711 3.374 -11.927 4.948 6.3319 2.0225 3.451 -12.440 4.435 5.0429 1.6108 3.578 -13.231 3.644 14.65 1.3245 3.673 -13.741 3.134 3.1159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.920 -14.632 2.243 1.0041 0.3207 4.048 -14.962 2.243 1.0041 0.3207 4.048 -14.962 2.243 1.0041 0.3207 4.048 -14.962 1.913 0.8163 0.2799 4.065 -15.020 1.853 0.01694 0.1979 4.009 -15.020 1.853 0.01024 0.0258 4.170 -15.181 1.064 18.6425 18.6425 6.0355 2.538 0.000 15.945 17.0231 3.5094 2.629 -1.465 14.480 1.00894 0.0286 4.172 -15.811 1.064 18.6425 18.6425 1.3094 2.629 -1.465 14.480 1.1044 0.0328 4.170 -15.157 1.124 0.0894 0.0286 4.172 -15.811 1.064 18.6425 18.6425 1.3094 2.629 -1.465 14.480 1.1044 2.9608 3.181 -9.060 3.364 1.191 3.327 1.1189 3.4915 2.744 -3.659 12.268 1.1043 3.3119 3.097 -6.533 2.759 -4.494 11.451 1.31429 4.2536 2.876 -5.827 10.118 1.31429 4.2536 2.876 -5.827 10.118 1.31429 4.2536 2.876 -5.827 10.118 1.31429 4.2536 2.876 -5.827 10.118 1.31429 4.2536 2.876 -1.064 3.901 1.1185 3.0810 3.097 -6.533 2.984 1.194 -1.581 1.064 18.6425 1.0660 3.0980 3.784 -1.3688 2.256 3.0080 4.1968 3.383 3.657 -1.3178 2.767 3.0080 4.1968 3.383 3.657 -1.3178 2.767 3.0080 4.1968 3.383 3.657 -1.3178 2.767 3.0080 4.1968 3.383 3.657 -1.3178 2.767 3.0080 5.0000 3.354 3.146 -0.422 4.111 3.11429 4.2536 3.364 -1.399 0.454 3.901 3.11465 3.364 3.364 -1.399 0.454 3.901 3.11465 3.364 3.364 -1.399 0.902 3.0000 4.1944 3.1999 3.366 -1.999 0.902 3.0000 4.1944 3.1999 3.366 -1.999 0.902 3.0000 4.1944 3.1999 -1.4690 3.374 3.1068 3.3000 -1.1099 3.423 3.1060 0.0000 4.154 4.1999 0.906 3.124891 3.1249 3.1223 3.000 -1.1099 3.423 3.1060 0.0000 3.135 3.146 0.000 4.532 3.1740 0.0000 3.375 3.146 0.	19.53 <i>77</i>	19.5377	6.2407	2.524	0.000	16.875
16.0168 5.1161 2.779 -3.707 13.168 15.5014 4.9514 2.750 -4.283 12.587 14.4201 4.6060 2.818 -5.447 11.428 12.0722 3.8561 2.976 -7.729 9.146 11.8563 3.2528 3.1016 -8.341 7.534 10.1856 3.2528 3.1016 -8.341 7.534 10.1856 3.2528 3.1012 -9.174 7.590 10.185 3.2528 3.1012 -9.174 7.590 10.185 3.2528 3.1012 -9.174 4.948 13.2528 2.6361 2.276 -1.1055 5.820 7.1101 2.2711 3.374 -11.927 4.948 4.1465 1.3245 3.673 3.788 -11.2440 4.455 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.115 0.9953 3.788 -14.188 2.686 2.0101 0.421 3.920 -4.632 2.243 1.0041 0.3207 4.048 -14.962 1.913 0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4014 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 -15.495 1.360 0.2042 0.0653 4.156 -15.495 1.360 0.0084 0.0286 4.172 -15.187 1.364 4.196 4.0918 3.5094 2.629 -1.465 1.4480 0.0894 0.0286 4.172 -15.187 1.064 4.192 4.2536 2.679 -1.465 1.4480 1.31429 4.2536 2.876 -5.837 10.118 1.3247 1.314 3.1419 3.1869 4.9151 2.741 -3.659 1.2286 1.6071 3.1419 3.1869 3.1819 3.018 -7.702 8.242 1.0118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.1829 4.2536 2.876 -5.837 10.118 3.0189 3.018 -7.702 8.242 3.044 3				2.588	0.8 26	
15,5014						
14,4201						
13,1393						
12,0722 33,8561 2.976 -7.729 9,146 11,3853 3.5367 3.026 -8.341 10,1836 3.2528 3.117 -9.276 7.599 9.2555 2.9564 3.192 -10.174 6.701 8.2528 2.6361 3.276 -11.055 5.820 7.1101 2.2711 3.374 -11.527 4.948 6.3319 2.0225 3.451 -12.440 4.455 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.134 3.1159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.3528 -14.632 2.243 1.0643 0.1799 4.048 -14.632 2.243 0.8163 0.1799 4.048 -14.632 2.243 0.8163 0.1799 4.099 -15.142 1.915 0.8163 0.1799 4.099 -15.142 1.915 0.0242 0.0653 4.156 -15.495 1.380 0.1024 0.0328 4.170 -15.157 1.124 0.0894 0.0286 4.172 -15.811 1.064 MB ₁ 18.6425 18.6425 6.0355 1.380 18.6425 18.6425 6.0355 1.380 18.6426 1.3496 2.629 -1.465 1.480 18.6427 1.3496 2.629 -1.465 1.480 18.6428 1.3496 2.629 -1.465 1.480 18.6429 1.3496 2.629 -1.465 1.480 18.6421 1.3496 2.2620 -1.465 1.480 18.6425 1.3496 2.2620 -1.465 1.480 18.6426 1.3496 2.2620 -1.465 1.480 18.6427 1.3496 2.2620 -1.465 1.480 18.6428 1.3496 2.2620 -1.465 1.480 18.6429 1.3496 2.2620 -1.465 1.480 18.6425 1.3496 2.2620 -1.465 1.480 18.6426 1.3496 2.2620 -1.465 1.480 18.6427 1.3496 2.2620 -1.465 1.480 18.6428 1.3496 2.2620 -1.465 1.480 18.6429 1.3496 2.2620 -1.465 1.480 18.6421 1.3496 2.2620 -1.465 1.480 18.6425 1.3496 2.2620 -1.465 1.480 18.6425 1.3496 2.2620 -1.465 1.480 18.6426 1.3496 2.2620 -1.465 1.480 18.6427 1.3496 2.2620 -1.465 1.480 18.6428 1.3496 2.2620 -1.465 1.480 18.6429 1.3496 2.2620 -1.465 1.480 18.6425 1.3696 2.3686 2.368 18.6426 2.2620 2.2620 2.2620 2.2620 18.6425 2.2620 2						
11.3853 3.6367 3.026 -8.341 8.534 10.1836 3.2528 3.117 -9.276 7.599 9.2555 2.9564 3.192 -10.174 6.701 8.2528 2.6361 3.276 -11.055 5.820 7.1101 2.2711 3.374 -11.927 4.948 6.3319 2.0225 3.451 -12.440 4.435 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.134 3.1159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.920 -14.632 2.243 1.0041 0.3207 4.048 -14.962 1.913 0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4034 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 -15.495 1.380 0.1024 0.0328 4.170 -15.157 1.24 0.0894 0.0228 4.170 -15.157 1.24 0.0894 0.0228 4.170 -15.157 1.24 18.6425 18.6425 6.0335 2.538 0.000 1.845 14.496 4.9151 2.241 -3.659 12.286 14.199 4.9951 2.741 -3.659 12.286 14.199 4.2536 2.279 -4.494 1.451 13.1429 4.2536 2.279 -4.494 1.451 13.1429 4.2536 2.279 -4.944 1.451 13.1429 4.2536 2.279 -4.944 1.451 13.1429 4.2536 2.371 -10.492 3.327 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.097 -8.564 3.293 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.997 -8.564 3.293 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.997 -8.564 3.200 3.0836 0.9980 3.784 -13.688 2.256 4.1968 1.3583 3.657 -13.178 3.694 5.0203 1.6248 3.369 -12.684 3.200 5.0203 1.6248 3.369 -12.684 3.200 0.0661 0.1962 4.099 -14.201 1.049 5.0203 1.6248 3.369 -12.684 3.200 0.0661 0.1962 4.099 -14.201 1.049 5.0203 1.6248 3.369 -12.684 3.200 6.0661 0.1962 4.099 -14.201 1.049 7.186 2.0099 3.361 -11.291 4.634 1.0168 2.2851 3.223 -0.888 2.266 1.0169 3.12542 3.464 -1.4501 1.049 1.0255 2.2814						
8,2558			3.6367	3.026		
8 2528 2.6361 3.276 -11.055 5.820 7.1101 2.2711 3.374 -11.927 4.948 6.3319 2.0225 3.451 -12.440 4.455 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.1344 3.1159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.920 -14.632 2.243 1.0041 0.3207 4.048 -14.962 2.1913 0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4044 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 0.15.495 1.380 0.0044 0.0284 4.172 -15.157 1.124 0.0894 0.0284 4.172 -15.157 1.124 0.0894 0.0284 4.172 -15.811 1.124 0.173 1.1041 1.124 0.1816 1.124 1						
7.1101 2.2711 3.374 -11.927 4.948 6.3319 2.0225 3.451 -12.440 4.435 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.134 3.1159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.920 -14.632 2.243 1.0041 0.3207 4.048 -14.962 1.913 0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4034 0.1288 4.128 -15.268 1.607 0.0024 0.0653 4.156 -15.409 1.5142 1.733 0.0094 0.0226 4.170 -15.157 1.124 0.0994 0.00286 4.172 -15.811 1.064 0.1024 0.0328 4.170 -15.157 1.124 0.0994 0.0226 4.172 -15.811 1.064 0.1024 0.0328 4.170 -15.157 1.124 0.131 0.104 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.1024 0.0328 0.170 0.15.157 1.124 0.181 0.104 0.1024 0.0328 0.170 0.15.157 1.124 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0328 0.1024 0.0024						
6.3319 2.0225 3.451 -12.440 4.455 5.0429 1.6108 3.578 -13.231 3.644 4.1465 1.3245 3.673 -13.741 3.134 3.159 0.9953 3.788 -14.188 2.686 2.0101 0.6421 3.920 -14.632 2.243 1.0041 0.3207 4.048 -14.962 1.913 0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4034 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 -15.495 0.0024 0.0328 4.170 -15.157 1.124 0.0824 0.0285 4.172 -15.811 1.064 1.0924 0.0285 4.172 -15.811 1.064 1.0924 0.0285 4.172 -15.811 1.064 1.0928 1.0023 1.5094 2.629 -1.465 14.480 1.60918 5.2080 2.685 -2.618 3.327 1.51869 4.9151 2.741 -3.659 12.286 1.4496 4.6659 2.790 -4.494 1.451 1.224 1.171 3.3189 4.2536 2.876 -5.827 10.118 1.244 1.11819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.097 -8.564 7.311 9.1484 2.2608 3.181 -9.509 6.435 8.1024 2.2023 3.271 -10.992 5.453 7.1186 2.2009 3.181 -9.509 6.436 8.1024 2.2023 3.271 -10.992 5.453 7.1186 2.2009 3.181 -9.509 6.436 8.1024 2.2023 3.271 -10.992 5.453 7.1186 2.2009 3.162 8.356 7.1284 3.200 4.1968 3.1583 3.0876 -12.684 3.260 4.1978 3.1						
1,000 1,00						
4,1465 1,3245 3,673 -13,741 3,134 3,1159 0,9953 3,788 -14,188 2,686 2,0101 0,6421 3,920 -14,632 2,243 1,0041 0,3207 4,048 -14,962 1,913 0,8163 0,2799 4,065 -15,020 1,855 0,6194 0,1979 4,099 -15,142 1,733 0,4034 0,1288 4,128 -15,268 1,607 0,2042 0,0653 4,156 -15,495 1,380 0,1024 0,0328 4,170 -15,157 1,124 1,1004 1,100						
3.1159						
1,0041 0,3207 4,048 -14,962 1,913 0,8163 0,2799 4,065 -15,020 1,835 0,6194 0,1979 4,099 -15,142 1,733 0,4034 0,1288 4,128 -15,288 1,607 0,2042 0,0653 4,156 -15,495 1,380 0,1024 0,0328 4,170 -15,157 1,124 0,0894 0,0226 4,170 -15,157 1,124 18,6425 18,6425 6,0335 2,538 0,000 15,945 17,0231 5,5094 2,629 -1,465 14,480 16,0918 5,2080 2,685 -2,618 13,327 15,1869 4,9151 2,741 -3,659 12,286 14,4196 4,6659 2,790 -4,494 11,451 13,1429 4,2536 2,876 -5,827 10,118 12,4171 4,0187 2,927 -6,553 9,392 11,1819 3,6189 3,018 -7,702 8,242 10,1753 3,2931 3,097 -8,564 7,381 9,1484 2,9608 3,181 -9,509 6,436 8,1024 2,6223 3,271 -10,492 5,453 7,1186 2,3039 3,361 -11,291 4,654 6,0122 1,9458 3,467 -12,044 3,901 5,0203 1,6248 3,569 -12,684 3,260 4,1968 1,3583 3,657 -13,178 2,767 3,0836 0,9980 3,784 -13,688 2,256 2,0056 0,6491 3,915 -14,060 1,884 1,0506 0,3400 4,039 -14,243 1,702 0,8026 0,2589 4,072 -14,316 1,629 0,6061 0,1962 4,099 -14,507 1,437 0,4022 0,1302 4,127 -14,729 1,216 0,2133 0,0690 4,154 -14,991 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0335 4,169 -14,979 0,966 0,1036 0,0315 0,2284 0,323 0,3384 -1,333 0,319 1,24891 1,24891 3,1223 0,364 0,000 0,323 1,24891 1,2562 0,2144				3.788		2.686
0.8163 0.2799 4.065 -15.020 1.855 0.6194 0.1979 4.099 -15.142 1.733 0.4034 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 -15.495 1.380 0.1024 0.0328 4.170 -15.157 1.124 0.0894 0.0286 4.170 -15.157 1.124 1.7021 5.0305 4.170 -15.157 1.124 1.8.6425 18.6425 6.0335 2.538 0.0000 1.5945 17.0231 5.5094 2.629 -1.465 14.480 16.0918 5.2080 2.685 -2.618 13.327 15.1869 4.9151 2.741 -3.659 12.286 14.4196 4.6659 2.790 -4.494 11.451 13.1429 4.2536 2.876 -5.827 10.118 12.4171 4.0187 2.927 -6.553 9.392 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.097 -8.564 7.381 9.1484 2.9608 3.181 -9.509 6.436 8.1024 2.6223 3.271 -10.492 5.453 7.1186 2.3039 3.361 -11.291 4.654 8.1024 2.6223 3.271 -10.492 5.453 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.569 -12.684 3.200 4.1968 1.3583 3.657 -13.178 2.767 3.0836 0.9980 3.784 -13.188 2.256 2.0056 0.6491 3.794 -14.060 1.884 1.0506 0.3400 4.039 -14.204 3.901 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.0921 0.0298 4.171 -15.012 0.933 12.4891 12.4891 3.1223 3.064 0.000 4.532 11.1658 2.5415 3.223 -0.808 3.724 11.1705 5 2.8164 3.140 -4.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.996 6.1998 1.5520 2.8811 3.203 -1.099 3.304 11.2652 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.996 6.1998 1.5520 3.538 -1.733 2.799 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.996 6.1998 1.5520 3.538 -1.733 2.799 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.996 6.1998 1.5520 3.538 -1.733 2.799 9.1325 2.2831 3.300 -1.109 3.423 9.1325 2.2831 3.300 -1.109 3.423 9.1325 2.2831 3.300 -1.109 3.299 9.1325 2.2831 3.300						
0.6194						
0.4034 0.1288 4.128 -15.268 1.607 0.2042 0.0653 4.156 -15.495 1.380 0.1024 0.0328 4.170 -15.157 1.124 0.0894 0.0286 4.172 -15.811 1.064						
0.2042 0.0653 4.156 -15.495 1.380 0.000 0.0286 4.172 -15.811 1.064 MB ₂ 1.172 -15.811 1.064 MB ₂ 1.18.6425 18.6425 6.0335 2.538 0.000 1.5.945 17.0231 5.5094 2.629 -1.465 14.480 16.0918 5.2080 2.685 -2.618 13.327 15.1869 4.9151 2.741 -3.659 12.286 14.4196 4.6659 2.790 -4.494 11.451 13.1429 4.2536 2.876 -5.827 10.118 12.4171 4.0187 2.927 -6.553 9.392 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.097 -8.564 7.381 9.1484 2.9608 3.181 -9.509 6.436 8.1024 2.6223 3.271 -10.492 5.453 7.1186 2.3039 3.361 -11.291 4.654 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.369 -12.684 3.260 4.1968 1.3583 3.657 -13.178 2.767 3.30836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.0021 0.0298 4.171 -15.012 0.933 1.223 1.223 0.0600 1.1540 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 4.169 -14.979 0.966 0.0335 1.254 1.177 -15.012 0.933 1.223 1.223 1.223 -0.808 3.724 1.104 1.01568 2.5415 3.223 -0.808 3.724 1.1056						
18.6425					-15.495	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						
18.6425				4.172		
17.0231 5.5094 2.629 -1.465 14.480 16.0918 5.2080 2.685 -2.618 13.327 15.1869 4.9151 2.741 -3.659 12.286 14.4196 4.6659 2.790 -4.494 11.451 13.1429 4.2536 2.876 -5.827 10.118 12.4171 4.0187 2.927 -6.553 9.392 11.1819 3.6189 3.018 -7.702 8.242 10.1753 3.2931 3.097 -8.564 7.381 9.1484 2.9608 3.181 -9.509 6.436 8.1024 2.6223 3.271 -10.492 5.453 7.1186 2.3039 3.361 -11.291 4.654 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.369 -12.684 3.260 4.1968 1.3583 3.657 -13.178 2.767 3.0836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.991 0.966 0.0921 0.0298 4.171 -15.012 0.933 12.4891 12.4891 3.1223 3.0640 -1.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.1036 0.0335 4.169 -14.979 0.966 0.921 0.0298 4.171 -15.012 0.933 12.4891 12.4891 3.1223 3.064 0.000 4.532 13.140 -0.422 4.111 -15.012 0.933 14.7055 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 3.3062 2.0766 3.364 -1.313 3.219 7.0455 1.7616 3.466 -1.570 2.962 6.1995 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.93 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.003 -2.768 1.765 0.4152				MB ₂		
16.0918	18.6425			2.538		
15.1869						
14,4196						
13,1429						
12.4171						
10.1753 3.2931 3.097 -8.564 7.381 9.1484 2.9608 3.181 -9.509 6.436 8.1024 2.6223 3.271 -10.492 5.453 7.1186 2.3039 3.361 -11.291 4.654 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.569 -12.684 3.260 4.1968 1.3583 3.657 -13.178 2.767 3.0836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 4.169 -14.979 0.966 0.9921 0.0298 4.171 -15.012 0.933 4.169 -14.979 0.966 0.9921 0.0298 4.171 -15.012 0.933 4.169 -14.979 0.966 0.9921 0.0298 4.171 -15.012 0.933 4.169 -14.979 0.966 0.9921 0.0298 4.171 -15.012 0.933 4.165 -1.466 0.422 4.111 0.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.465 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.355 1.177		12.4171	4.0187			
9.1484 2.9608 3.181 -9.509 6.436 8.1024 2.6223 3.271 -10.492 5.453 7.1186 2.3039 3.361 -11.291 4.654 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.569 -12.684 3.260 4.1968 1.3583 3.657 -13.178 2.767 3.0836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB3 12.4891 12.4891 3.1223 3.064 0.000 4.532 11.2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.355 1.177						
8,1024						
7.1186 2.3039 3.361 -11.291 4.654 6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.569 -12.684 3.260 4.1968 1.3583 3.657 -13.178 2.767 3.0836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 MB3 12.4891 12.4891 3.1223 3.064 0.000 4.532 11.2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.2847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0226 4.171 -3.355 1.177						
6.0122 1.9458 3.467 -12.044 3.901 5.0203 1.6248 3.569 -12.684 3.260 4.1968 1.3583 3.567 -13.178 2.767 3.0836 0.9980 3.784 -13.688 2.256 2.0056 0.6491 3.915 -14.060 1.884 1.0506 0.3400 4.039 -14.243 1.702 0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB ₃ 12.4891 12.4891 3.1223 MB ₃ 12.4891 12.4891 3.1223 3.064 0.000 4.532 11.2055 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
12.4891 12.4891 3.1223 3.064 0.000 4.532						
4.1968						
12.4891 12.4891 3.1223 3.064 0.000 4.532 11.2055 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -2.268 2.264 2.0621 0.1936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177					-13.178	
1.0506						
0.8026 0.2589 4.072 -14.316 1.629 0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB3 12.4891 3.1223 3.064 0.000 4.532 11.2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
0.6061 0.1962 4.099 -14.507 1.437 0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB3 12.4891 3.1223 3.064 0.000 4.532 11.2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 <						
0.4022 0.1302 4.127 -14.729 1.216 0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB ₃ 12.4891 12.4891 3.1223 3.064 0.000 4.532 11,2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177	•					
0.2133 0.0690 4.154 -14.901 1.044 0.1036 0.0335 4.169 -14.979 0.966 0.0921 0.0298 4.171 -15.012 0.933 MB ₃ 12.4891 3.1223 3.064 0.000 4.532 11,2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0455 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.268 2.0621 0.5155 3.944 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 <						
0.1036 0.0921 0.0298 4.171 -15.012 0.933 MB ₃ 12.4891 12.4891 3.1223 3.064 0.000 4.532 11.2055 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.555 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177		0.2133		4.154	-14.901	1.044
12.4891 12.4891 3.1223 3.064 0.000 4.532 11,2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177		0.1036				
12.4891 3.1223 3.064 0.000 4.532 11,2655 2.8164 3.146 -0.422 4.111 10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263		0.0921	0.0298		-15.012	0.933
11,2655 2.8164 3.146 -0.422 4.111 10,1658 2.5415 3.223 -0.808 3.724 9,1325 2.2831 3.300 -1.109 3.423 8,3062 2.0766 3.364 -1.313 3.219 7,0465 1.7616 3.466 -1.570 2.962 6,1998 1.5500 3.538 -1.733 2.799 5,0163 1.2542 3.645 -1.940 2.593 4,1652 1.0414 3.726 -2.064 2.468 3,1742 0.7936 3.826 -2.268 2.264 2,0621 0.5155 3.944 -2.420 2.112 1,0055 0.2514 4.063 -2.768 1.765 0,8519 0.2130 4.081 -2.847 1.686 0,6420 0.1605 4.106 -2.980 1.552 0,4152 0.1038 4.133 -3.158 1.375 0,2044 0.0511 4.159 -3.270 1.263 0,1023 0.0256 4.171 -3.355 1.177	12 4601	17 4001	3 1222	3 064	0.000	A 527
10.1658 2.5415 3.223 -0.808 3.724 9.1325 2.2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177	12.4891	12,4391				
9.1325 2 2831 3.300 -1.109 3.423 8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
8.3062 2.0766 3.364 -1.313 3.219 7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
7.0465 1.7616 3.466 -1.570 2.962 6.1998 1.5500 3.538 -1.733 2.799 5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
5.0163 1.2542 3.645 -1.940 2.593 4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177		7.0465	1.761 6	3.466	~1 .570	2,962
4.1652 1.0414 3.726 -2.064 2.468 3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
3.1742 0.7936 3.826 -2.268 2.264 2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
2.0621 0.5155 3.944 -2.420 2.112 1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
1.0055 0.2514 4.063 -2.768 1.765 0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
0.8519 0.2130 4.081 -2.847 1.686 0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177						
0.6420 0.1605 4.106 -2.980 1.552 0.4152 0.1038 4.133 -3.158 1.375 0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177					-2.847	1.686
0.2044 0.0511 4.159 -3.270 1.263 0.1023 0.0256 4.171 -3.355 1.177	•	0.6420	0.1605	4.106	-2.980	1.552
0.1023 0.0256 4.171 -3.355 1.177						
0.0737 0.0130 4.173 -3.371 1.101						
		U.U/39	V.V17U	4.113	J.J.1	1.101

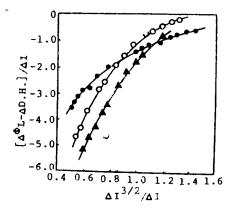


Fig. 1 Polts of $[\Delta^{\Phi}L - \Delta D.H.] / \Delta I$ versus $\Delta I^{3/2} / \Delta I$ for $MgB_4O_7 - MgSO_4 - MgCl_2 - H_2O$ systems at 298.15K \bullet , MB_1 ; \bigcirc , MB_2 ; \triangle , MB_3

The values of B and C determined by a least-square fit are given in Table 3, along with the sum of square errors R. The sum of square errors of the least-square fit for all the systems is less than $1.0 \text{kJ} \cdot \text{mol}^{-1}$.

Table 5 Values of B and C for the Extended Debve-Huckel Equation at 298 15K

 140103 741	des of D and C for the Date	dea Debye Hucker Dquar	1011 at 270.1512
	В	C	R
 MB ₁	-4,90955	3,48947	0.89
MB ₂	-7.12360	5.81439	0.68
MB ₃	-10.09040	8.17033	0.32

The apparent molal enthalpies ${}^{\Phi}L_{f}$ over an ionic strength range I_{f} 0.1–0.0001 were calculated from Eq.(1) using the coefficients B, C in Table 3, the results are given in Table 4.

Table 4 Apparent Molal Enthalpies of MgB₄O₇-MgSO₄-MgCl₂-H₂O Systems over the Ionic Strength Range 0.1-0.0001 at 298.15K

7		* L(kJ • mol ⁻¹)
I	MB ₁	MB ₂	MB ₃
0.1	1.095	0.947	1.216
0.09	1.066	0.929	1.197
0.08	1.032	0.908	1.173
0.07	0.994	0.882	1.143
0.06	0.950	0.851	1.106
0.05	0.898	0.813	1.059
0.04	0.834	0.764	0.998
0.03	0.754	0.700	0.918
0.02	0.648	0.610	0.803
0.01	0.490	0.470	0.622
0.005	0.363	0.353	0.468
0.001	0.170	0.168	0.223
0.0001	0.037	0.037	0.050

The apparent molal enthalpies ${}^{\Phi}L_i$ of MgB₄O₇-MgSO₄-MgCl₂-H₂O systems of the ionic strength range from 19 to 0.1 can be calculated from

$${}^{\Phi}L_{i} = {}^{\Phi}L_{f} - \Delta H_{d}(I_{i} - I_{f}) \tag{5}$$

using the heats of dilution ΔH_d and the apparent molal enthalpies ${}^{\Phi}L_f$ of the final ionic strength (MB₁ 0.0894; MB₂ 0.0921; MB₃ 0.0759). The results are given in Table 2.

summarize, the heats of dilution and the heat capacities the $MgB_4O_7-MgSO_4-MgCl_2-H_2O$ quaternary MgB₄O₇-MgSO₄-H₂O system and and MgB₄O₇-MgCl₂-H₂O subsystems have been measured over the ionic strength / range from 0.1 to 19 at 298.15K. The apparent molal enthalpies have been calculated by means of Debye-Huckel limiting law for the ionic strength range from 19 to 0.0001. The results give that the heats of dilution are negative, indicating exothermic dilution processes of various systems. With stronger ionic strength I or higher molalities, the values of heat capacities are smaller and the values of apparent molal enthalpies are greater. All these systems have shown similar heat behavior to a single electrolyte solution of alkaline-earth metal (9).

References

- [1] Song, P. S., Du, X. H., Kexue Tongbao, 19, 1338(1986).
- [2] Song, P. S., Du, X.H., Sun, B., Kexue Tongbao, 23, 1971(1988).
- [3] Du, X, H., Song, P.S., J. Salt Lake Science, 1, 9(1992).
- [4] Li Jicai, Zhai Zongxi ct al, Indian J. Chem., 34, 137(1995).
- [5] Wang, Y. D., Zhai, Z.X., Acta Chimica Sinica, 47, 465(1989).
- [6] Jongenberger, H. W., Wood, R. H., J. Phys. Chem., 69, 4231(1965).
- [7] Millero, F. J. et al, J. Mar. Res., 31, 21(1973).
- [8] Leung, W. H., Millero, F. J., J. Solution Chem., 4, 145(1975).
- [9] Li Jicai, Zhai Zongxi et al, Acta Phys. Chem., 10(8), 759(1994).