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Fig. 1

Figure 1: Fig. 1

Abstract

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EXCHANGE DECOMPOSITION AND THE CHANGE IN ISOBARIC POTENTIAL IN MELTS

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To determine the direction of an exchange reaction in melts, there exist a number of empirical rules; among them the most widely used is the Beketov—Kablukov rule ([1,2]). According to this rule, the exchange reaction proceeds in the direction of a positive thermal effect of the reaction, calculated at 20–25°C, which A. G. Bergman ([3]) called the "conditional thermal effect of the reaction of exchange of reciprocal pairs of salts." The numerous diagrams of ternary reciprocal systems that have been studied, with some exceptions, confirm this rule. It has also been theoretically substantiated for a number of reciprocal systems by N. K. Voskresenskaya ([4]). I. N. Belyaev ([5]) based the theory of exchange decomposition on polarity, which characterizes the type of chemical bond of the compounds participating in the reactions.

Of interest is not only the finding of methods for determining the direction of an exchange reaction, but also the possibility of a preliminary judgment about the degree of its irreversibility, as well as about the chemical interaction of the components (complex formation). In determining the direction of an exchange reaction, the best indicator should be the change in isobaric potential, calculated at the corresponding reaction temperature. The isobaric potential is closely related to the constant of chemical equilibrium, from whose magnitude one can judge the degree of irreversibility of an exchange reaction. In addition, it has turned out that the equilibrium constant is closely related to the topological diagrams of reciprocal systems. This relation makes it possible to solve a number of questions in the theory of these systems.

Fig. 1

In the present work, ternary reciprocal systems are considered, based on the exchange reaction expressed by the following equation

$$\mathrm{AX} + \mathrm{BY} \rightarrow \mathrm{AY} + \mathrm{BX}, \qquad (1)$$

where A, B are cations, and X, Y are anions.

The calculation of the change in isobaric potential of the exchange reaction (ΔZ) in reciprocal systems was carried out using the Gibbs–Helmholtz equation:

$$\Delta Z = \Delta H - T\Delta S, \qquad (2)$$

where ΔH and ΔS are, respectively, the change in enthalpy and entropy during the reaction, and T is the absolute temperature.

On the basis of Kirchhoff' s equation, and also taking into account the processes of melting and crystallization that occur during the exchange reaction, equation (2) may be written as follows:

$$\Delta Z = \Delta H_{298} + \Delta H_{\text{melt}} - T\Delta S_{298} - T\Delta S_{\text{melt}} + \int_{298}^{T} \Delta C_p \, dT - T\int_{298}^{T} \frac{\Delta C_p}{T} \, dT, \qquad (3)$$

where ΔH_{298} and ΔS_{298} are the changes in enthalpy and entropy at 298°K; ΔH_{melt} and ΔS_{melt} are the changes in the heat of melting (crystallization), ΔC_p is the dif-

ness of the sums of the molar heat capacities of the products and starting substances of the reaction.

In the calculation, the heats and entropies of polymorphic transformations of the components were also taken into account.

The procedure for carrying out the thermodynamic calculations is as follows:
1) It is assumed that at the initial moment all four salts—AX, BY, BX—are present in an equivalent ratio. ΔH_{298} and ΔS_{298} were calculated

Table 1

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
1	$2NaCl + K_2SO_4 \rightleftarrows 2KCl + Na_2SO_4$	837	−90	−3928	−4.026	3369	−559	(14)
2	$2NaNO_3 + K_2SO_4 \rightleftarrows 2KNO_3 + Na_2SO_4$	838	−160	−6357	−6.9058	5787	−570	(15)
3	$2NaBr + K_2SO_4 \rightleftarrows 2KBr + Na_2SO_4$	851	−1120	−4751	−4.0175	3418	−733	(15)
4	$NaNO_3 + KCl \rightleftarrows KNO_3 + NaCl$	773	−70	−2253	−2.4805	1917	−346	(15)
5	$NaBr + KNO_3 \rightleftarrows KBr + NaNO_3$	723	−1060	149	1.5822	−1105	−956	(15)
6	$KCl + NaBr \rightleftarrows NaCl + KBr$	883	−1030	−1841	−0.79	697	−1148	(15)
7	$NaJ + KBr \rightleftarrows NaBr + KJ$	821	−2470	−1799	−0.2602	213	−1528	(15)
8	$AgCl + NaBr \rightleftarrows AgBr + NaCl$	923	−4918	−5915	−2.0107	1859	−4056	(15)

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
9	$PbBr_2 + 2TlCl \rightleftarrows PbCl_2 + 2TlBr$	649	−2260	−2003	−0.9105	590	−1413	(15)
10	$PbCl_2 + 2KBr \rightleftarrows 2KCl + PbBr_2$	788	−720	−527	−0.2122	167	−360	(17)
11	$2NaBr + PbCl_2 \rightleftarrows 2NaCl + PbBr_2$	923	−1750	−2033	1.0661	701	−2734	(18)
12	$KBr + TlCl \rightleftarrows TlBr + KCl$	883	−2980	−1380	1.4086	−1243	−2623	(19)
13	$AgCl + KBr \rightleftarrows AgBr + KCl$	799	−3888	−3981	−1.296	1033	−2948	(15)
14	$TlCl + NaBr \rightleftarrows NaCl + TlBr$	900	−4010	−3411	0.24	−216	−3627	(20)
15	$NaNO_3 + KF \rightleftarrows NaF + KNO_3$	1135	−7940	−13042	−8.2487	9362	−3680	(15)
16	$KCl + NaJ \rightleftarrows NaCl + KJ$	810	−4070	−4217	−1.19	936	−3283	(15)

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
17	$KF + NaCl \rightleftarrows NaF + KCl$	1036	−7870	−7906	−2.8646	2960	−4946	(15)
18	$KF + NaJ \rightleftarrows NaF + KJ$	1113	−11930	−12094	−4.1521	4621	−7473	(15)
19	$KF + NaBr \rightleftarrows KBr + NaF$	1059	−8900	−8606	−1.763	1867	−6739	(15)
20	$NaJ + KNO_3 \rightleftarrows KJ + NaNO_3$	725	−3990	−2496	0.4635	−336	−2832	(15)
21	$2AgCl + PbBr_2 \rightleftarrows 2AgBr + PbCl_2$	601	−3078	−3868	−2.3575	1416	−2502	(15)
22	$2LiCl + BrF_2 \rightleftarrows 2LiF + BaCl_2$	1020	−8580	−6566	−1.7462	1763	−4803	(15)
23	$2NaF + BCl_2 \rightleftarrows BrF_2 + 2NaCl$	1020	−2050	−3671	−1.2995	−1325	−4996	(15)
24	$2NaF + Li_2SO_4 \rightleftarrows 2LiF + Na_2SO_4$	926	−4248	−5084	−4.309	3990	−1094	(15)

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
25	$2LiF + CaCl_2 \rightleftarrows 2LiCl + CaF_2$	1000	−1450	−3963	−0.232	232	−3731	(15)
26	$2KJ + PbCl_2 \rightleftarrows PJJ_2 + 2KCl$	828	−3405	−1390	3.2816	2682	−4107	(15)
27	$2LiCl + Na_2SO_4 \rightleftarrows 2NaCl + Li_2SO_4$	900	−6445	−3404	1.16	−1044	−4448	(15)
28	$CaCl_2 + K_2SO_4 \rightleftarrows 2KCl + CaSO_4$	1120	−9080	−7716	−1.9577	2204	−5512	(15)
29	$LiCl + NaNO_3 \rightleftarrows NaCl + LiNO_3$	773	−4710	−3501	−0.458	−265	−3766	(15)
30	$2LiCl + CaSO_4 \rightleftarrows Li_2SO_4 + CaCl_2$	1073	2650	−1039	4.048	−4382	−5382	(15)
31	$2NaCl + PbSO_4 \rightleftarrows PbCl_2 + Na_2SO_3$	873	−345	−6100	−1.7114	1494	−4606	(15)
32	$CdSO_4 + 2NaCl \rightleftarrows CaCl_2 + Na_2SO_4$	801	−3040	−5550	−1.2087	968	−4587	(15)

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
33	$2KCl + PbSO_4 \rightleftarrows K_2SO_4 + PbCl_2$	904	−255	−3095	2.4095	−2178	−5273	(15)
34	$2LiNO_3 + K_2SO_4 \rightleftarrows 2KNO_3 + Li_2SO_4$	770	−1805	−4666	−0.1671	129	−4557	(15)
35	$2LiNO_3 + Na_2SO_4 \rightleftarrows 2NaNO_3 + Li_2SO_4$	720	−1465	−2546	5.7433	−4135	−4221	(15)
36	$2NaF + PbSO_4 \rightleftarrows PbF_2 + Na_2SO_4$	873	1450	−6245	−1.034	902	−5343	(15)
37	$CaCl_2 + BaF_2 \rightleftarrows CaF_2 + BaCl_2$	1232	−9930	−9959	−1.321	1627	−8024	(15)
38	$2KF + Na_2SO_4 \rightleftarrows 2NaF + K_2SO_4$	1031	−7780	−3997	3.4075	−3513	−7510	(15)
39	$CaCl_2 + 2NaF \rightleftarrows CaF_2 + 2NaCl$	1340	−11982	−11987	−1.446	1937	−10050	(15)
40	$2LiCl + K_2SO_4 \rightleftarrows 2KCl + Li_2SO_4$	845	−6440	−6363	3.7998	−3211	−9574	(15)

No.	Reaction	T, °K*	Change in enthalpy of the reaction at 298°K, ΔH_{298}, cal/g-equiv	Change in enthalpy of the reaction at T, ΔH_T, cal/g-equiv	Change in entropy of the reaction at T, ΔS_T, cal/g-equiv	$T\Delta S_T$	Change in isobaric potential of the reaction at T, ΔZ_T, cal/g-equiv	Source
41	$2KF + CaCl_2 \rightleftarrows CaF_2 + 2KCl$	1260	−19850	−20670	−4.4438	5599	−15071	(15)
42	$2KF + BaCl_2 \rightleftarrows 2KCl + BaF_2$	1128	−9920	−11516	−1.383	1560	−9956	(15)

* T—temperature of the onset of crystallization of the composition at the point of intersection of the diagonals of the square of the reciprocal system.

from the heats of formation and absolute entropy values of the components under standard conditions, according to Hess' s law, on the basis of equation (1).

2) As the upper temperature limit, the temperature of the onset of crystallization of the composition at the point of intersection of the diagonals of the square of the reciprocal system was taken.

(Fig. 1). We shall denote this temperature by T. The lower temperature limit is taken as 298° K.

3) The initial substances AX and BY are heated from 298° K to their melting, pass into the liquid state, and at temperature T the exchange reaction takes place with formation of the reaction products AY and BX, which crystallize from the melts.

We selected reciprocal systems for which the necessary calculation data are available in the literature. The heat capacities of salts were calculated from approximate equations for BaF_2, $PbCl_2$, TlCl, AgI, PbI_2, the nitrates of Li, Na, K, taken from (^{6}); $BaCl_2$, CaF_2, KI, Na_2SO_4, $CaSO_4$ (^{7}); $CaCl_2$, $CdCl_2$, K_2SO_4, $PbSO_4$ (^{8}); LiF, NaF, KF, LiCl, NaF, KCl (^{9}); Li_2SO_4 (^{10}); AgCl, NaBr, KBr, AgBr (^{11}).

The literature data on heats of formation (H_{298}), entropy (S_{298}), and heats of fusion for some compounds differ so much from one another that here we proceed from values taken mainly from ($^{7-9}$).

In calculating C_p for substances melting below the temperature of the exchange reaction, the heat capacities of the liquid state were also taken into account. In the absence of heat-capacity data, in some cases the temperature ranges of the C_p equation were somewhat extended.

The results of calculations for 42 reciprocal systems are given in Table 1. Analyzing the data of Table 1, the following conclusions may be drawn.

The best characteristic of reciprocal systems is the change in isobaric potential calculated at the temperature corresponding to the occurrence of the exchange reaction. The reaction is directed toward a decrease in the isobaric potential, which is in full agreement with the numerous studied diagrams of ternary reciprocal systems.

If the signs of the quantities ΔH_{298} and ΔH_T are the same, and the sign of $T\Delta S$ coincides with the sign of ΔH_T, or the value of $T\Delta S$ is smaller than the value of ΔH_T, then in reciprocal systems of the type considered the direction of the exchange reaction can be determined from the thermal effects, both ΔH_{298} (“conditional”) and ΔH_T (“actual”). In these cases Berthelot’ s principle gives correct qualitative conclusions.

ΔH_T characterizes reciprocal systems better than ΔH_{298}, contrary to the calculations of N. K. Voskresenskaya (^{4}). It should be assumed that the temperature ΔT chosen by us and adopted in carrying out the calculations is apparently closer to the actual temperature.

In conclusion, we point out that in systems in which, along with the exchange reaction, reactions of formation of complex compounds also occur, it is necessary to take into account the thermal effects and entropy changes of the latter. For this, one must know the thermal effects and entropies of formation of complex compounds, data for which are absent for many reactions. In such systems, determination of the direction of the exchange reaction without taking into account the thermal effect and entropy of the complex compounds has a somewhat conditional character.

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