
Multicomponent Reciprocal Salt Systems of Metals: Determination of the Maximum Work of Chemical Exchange Reactions by the Differential Thermal Analysis Conversion Method

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Differential thermal analysis of complete conversion points of reciprocal salt systems in melts shows the energy nonequivalence of stable and metastable salt pairs which can be interpreted as the work of a chemical exchange reaction; it is necessary to quantitatively determine this work when choosing salt compositions with optimal heat-storage properties.

The conversion method for investigating reciprocal salt systems in melts¹ is based on the differential thermal analysis (DTA) of salt mixtures corresponding to conversion elements. The points, lines, surfaces and volumes of conversion are represented by geometric models of the intersection of stable and metastable complexes in systems.² A stable complex in ternary reciprocal systems consisting of four salts A,B//X,Y (where A and B are cations, X and Y are anions) is represented by one stable diagonal AX+BY dividing a composition diagram (square) into two simple ternary systems. The stable

diagonal intersects the metastable diagonal AY+BX at the point of complete conversion (PCC) which is at the centre of the composition square. The maximum reaction work determines the diagonal stability.^{3,4}

$$U_{AY} + U_{BX} = U_{AX} + U_{BY} (+A)$$

where U_{ij} is the total energy of the salt molecules and A is the maximum work of the exchange reaction.

We take two salts of equivalent mass to record PCC

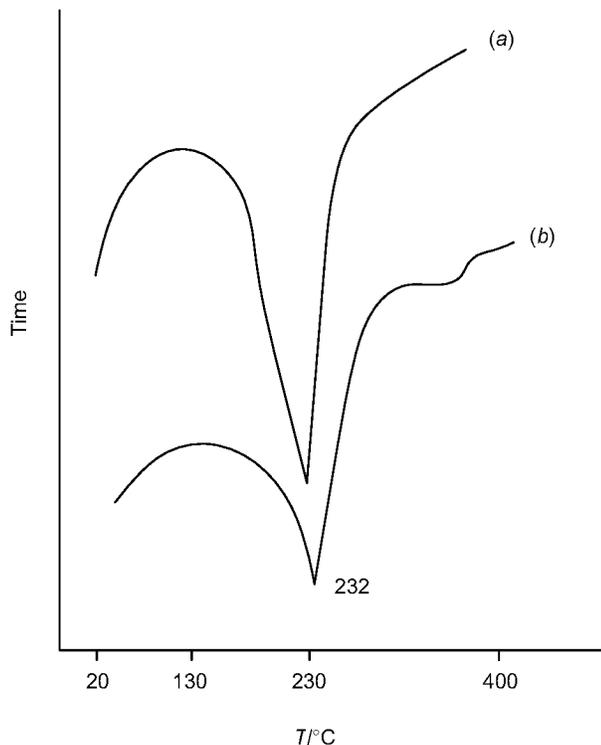
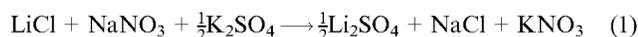


Fig. 1 Thermograms of the complete conversion point in the ternary reciprocal system of Li,Na//Cl,NO₃ (mol%): (a) 50% LiCl + 50% NaNO₃; (b) 50% LiNO₃ + 50% NaCl.

thermograms which may be both stable and metastable salt pairs. The same thermal effects are determined in the PCC thermograms of both salt pairs but their peak areas are different. Quantitative thermography shows that the metastable salt pairs have larger peak areas than the stable ones. The difference between the peak areas of the two pairs is proportional to the so-called thermal effect of an exchange reaction q_i (the change in the total system energy) and characterizes the work of the chemical reaction. Fig. 1, as an example, shows the PCC thermograms of melts for the Li,Na//Cl,NO₃ system (the stable pair is LiNO₃+NaCl, the thermal effect of the reaction is 20.167 kJ mol⁻¹).

The energy nonequivalence in stable and metastable salt compositions in more complex (multicomponent) reciprocal systems is determined by a set of exchange chemical reactions. Thus, the total chemical process in a five-component reciprocal system consisting of nine salts is to convert three metastable salts with ions of both signs into three stable salts. For example, in the system Li,Na,K//Cl,NO₃,SO₄ (thermochemical type “A \rightleftharpoons B”) the reaction is:



An axial nonequilibrium triangle corresponds to three metastable salts in the composition diagram and an axial (base) equilibrium triangle to three stable salts. These triangles in the four-dimensional space of the composition diagram are in different hyperplanes and intersect at one common point which is the point of complete conversion in the axial triangles. This is one of the conversion types which is peculiar to five-component reciprocal systems of thermochemical type “A \rightleftharpoons B”.

The thermograms of salt mixtures corresponding to the complete conversion point for the two triangles have a common thermal effect, *viz.* the temperature of melting mixtures which is the same for both salt compositions. The other effects corresponding to the cocrystallization of three salts (eutectic and peritectic points) can be identical only when the exchange reaction products appear at the liquidus

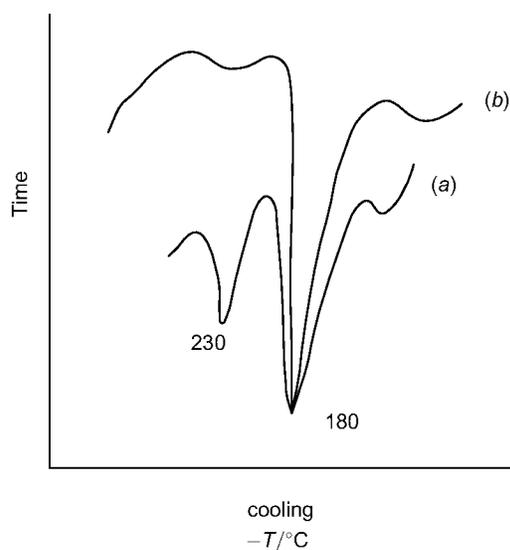
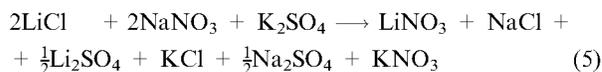
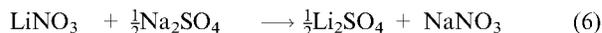


Fig. 2 Thermograms of the complete conversion point in axial triangles in a five-component reciprocal system consisting of nine salts of Li,Na,K//Cl,Br,NO₃ (type “B \rightleftharpoons A”, mol%): (a) 33.33% LiBr + 33.33% NaNO₃ + 33.33% KCl; (b) 33.33% LiNO₃ + 33.33% KBr + 33.33% NaCl.

surface of a nonequilibrium triangle. The total peak areas in the thermogram for the equivalent mixture of metastable salts is larger than the total area of the thermogram peaks at the central point of an equilibrium triangle (Fig. 2) because the two triangles are thermochemically nonequivalent, *i.e.* their fine energy structure is different.⁵ This structure for the thermochemical type “A \rightleftharpoons B” is as follows: an axial triangle of type A is formed by two diagonals of stage III and one diagonal of stage I; and a triangle of type B is formed by a diagonal of stage IV and two diagonals of stage II. Therefore, the total heat content of the salt mixtures (*i.e.* the total heat effects of three exchange reactions for three salt pairs) is different. For example, for the system consisting of chlorides, nitrates and sulfates of lithium, sodium and potassium in the nonequilibrium axial triangle of type B the LiCl+NaNO₃ (q_6) pair is a diagonal of stage II, the NaNO₃+ $\frac{1}{2}$ K₂SO₄ (q_5) pair is a diagonal of stage II, and the $\frac{1}{2}$ K₂SO₄+LiCl (q_9) is a diagonal of stage IV. The $\frac{1}{2}$ Li₂SO₄+NaCl (q_8) pair in an equilibrium axial triangle (type A) is a diagonal of stage III, the $\frac{1}{2}$ Li₂SO₄+KNO₃ (q_7) is stage III, and the KNO₃+NaCl (q_2) is stage I. Since $Q_{ne} = q_6 + q_5 + q_9$ and $Q_e = q_7 + q_8 + q_2$, the difference $Q_{ne} - Q_e$ is equal to the total maximum work of the reactions, which is shown in the PCC thermograms of axial triangles (Fig. 3):



The products of reaction (5) react with each other:



The sum of reactions (5)–(7) leads to reaction (1).

Thus, the thermochemical nonequivalence of axial triangles in five-component reciprocal salt systems consisting of nine salts manifests itself as a difference in the fine energy structure, thermochemical relations, chemical interactions and, as a consequence, in the thermograms of complete

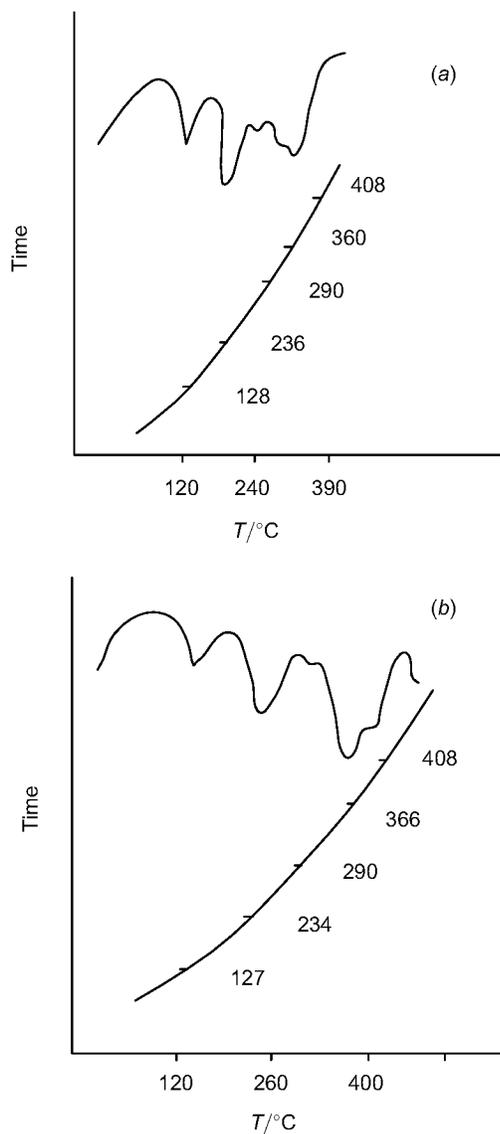


Fig. 3 Thermograms of the complete conversion point in axial triangles in a five-component reciprocal system consisting of nine salts of Li,Na,K//Cl,NO₃,SO₄ (type "A \rightleftharpoons B", mol%): (a) 33.33% LiCl + 33.33% NaNO₃ + 33.33% $\frac{1}{2}$ K₂SO₄; (b) 33.33%

conversion points. All this is in good agreement with Kurnakov's correspondence principle.⁶ In practice this implies that when choosing salt compositions for heat storage we prefer metastable ones whose melting temperature is similar to that of stable salts but whose energy capacity is larger. At the same time we should take stable salt compositions to decrease the energy capacity of salt mixtures, e.g. in compositions for chemical power sources and other technical objects.^{7,8}

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Received: Moscow, 1st February 1994
 Cambridge, 15th April 1994; Com. 4/00753K