ENDOTHERMIC CRYSTALLIZATION OF INORGANIC SUBSTANCES FROM AQUEOUS SOLUTIONS

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An account is given of common inorganic substances that crystallize from aqueous solutions by an endothermic process. The relation between the thermodynamic characteristics of the substances and the heat effect of crystallization is briefly discussed.

According to the simple notion of the nature of changes in the aggregation state of substances, the crystallization or solidification of a one-component system is accompanied, like the vapour condensation, by the liberation of heat. In crystallization of substances from supersaturated or undercooled solutions involving more components, the heat effects may be more diversified. The aim of this paper is to summarize the knowledge on simple electrolytes whose crystallization from aqueous solutions produces heat effects opposite to those observed for the majority of inorganic substances.

THEORETICAL

For most substances, the dissolution is an endothermic and the crystallization an exothermic process. In quantitative terms, the net heat of crystallization is given by the algebraic sum of the crystal-lattice enthalpy and the enthalpy of ion hydration at the saturation concentration. The liberated crystal-lattice enhalpy is usually higher than the sum of all the contributions to the enthalpy of ion hydration or dehydration. With strongly hydrophilic ions (Li^+, Mg^{2+}, Ca^{2+}, Co^{2+}), however, the enthalpy needed for the strongly endothermic dehydration is higher than the liberated crystal-lattice enthalpy, so that the crystallization is endothermic; this means that under adiabatic conditions the solution cools down as the salt crystallizes. Substances possessing this distinctive crystallization feature have not been reviewed in the literature.

The heat of crystallization, ΔH_c, is related to the temperature dependence of solubility by the equation[1]

$$\Delta H_c = RT^2(\varphi + d\varphi/d \ln m)_{m=m_s} \nu[1 - n m_s M_w/1000] \, d \ln m_s/dT , \qquad (1)$$

where R is the universal gas constant, φ is the osmotic coeffficient, m is the molality, m_s is the molality of saturated solution, ν is the stoichiometric number of ions in a molecule, n is the number of hydration water molecules in crystalline hydrate, M_w is the relative molecular mass of water, and T is the absolute temperature. Considering the inequalities $R > 0$, $\nu > 0$, $(\varphi + d\varphi/d \ln m) > 0$, $nm_sM_w < 1\,000$, it is apparent that the sign of the heat of crystallization is given by the sign of the slope of the temperature dependence of solubility, $m_s = m_s(T)$. Of the 526 inorganic substances listed in the solubility tables of Broul and coworkers[2], 67 salts exhibit negative slopes dm_s/dT within certain intervals, indicating endothermic crystallization. For about half of these 67 salts, there is a temperature at which the heat of crystallization is zero: the enthalpies of the exothermic and endothermic processes involved in crystallization or dissolution are just equal in magnitude. Obviously, $dm_s/dT = 0$ at this temperature. When consulting the table[2] (where w and x are used to denote the mass and mole fractions, respectively) to find out whether a substance crystallizes by an endothermic process, it is necessary to check whether the printed value of the slope dw/dT lies in the region of the existence of a hydrate of the salt concerned. In some cases, the negative value of the slope is only a result of unjustified extrapolation. This is revealed by finding a discrepancy between the trend in the solubility values, $x = x(T)$, and the sign of the dw/dT values, as is the case with $Cd(NO_3)_2.2$ aq [89], $Na_2HPO_4.12$ aq [204], $Na_2HPO_4.2$ aq [206], $Na_2CrO_4.6$ aq [323], LiI.1 aq [352], $FeBr_2.4$ aq [50], K_2SO_3[508], and $K_2SO_3.1/3$ aq [507], where the numbers in brackets represent the serial numbers of tables in the collection[2]. The results of re-examining the signs of slopes dm_s/dT are summarized in Table I, which gives the temperature intervals in which the salts crystallize from aqueous solutions by an endothermic process. The symbol t_c indicates the temperature at which the heat of crystallization is just zero. In most cases, t_c coincides with the boundary between the regions of endothermic and exothermic crystallization.

DISCUSSION

Considering the current state of knowledge on the thermodynamics of electrolytes, it is rather surprising that the available knowledge about heat effects of dissolution and crystallization is of purely empirical character. In the equation for the heat of crystallization

$$\Delta H_c = \Delta H_L + \Delta H_H \,, \qquad (2)$$

where ΔH_L is the crystal-lattice enthalpy, and ΔH_H is the enthalpy of hydration, the quantities ΔH_L and ΔH_H are usually up to an order of magnitude higher than ΔH_c and nearly equal in numerical value, $\Delta H_L \simeq -\Delta H_H$. While the value of the crystal-lattice enthalpy can be estimated theoretically, the quantity ΔH_H depends in a complex way on the nature of the salt molecules or ions and their bonding to the solvent molecules. The uncertainty in the estimates of the various contributions to the ent-

TABLE I

A survey of substances exhibiting negative values of the slope dm_s/dT within temperature intervals I (°C), *i.e.* of substances with endothermic heats of crystallization

Substance	I	t_c	Substance	I	t_c
$LiI . 1\ aq$	77—78	78	$Nd_2(SO_4)_3 . 8\ aq\alpha$	10—68	
$CdBr_2 . 4\ aq$	36—41	41	$Nd_2(SO_4)_3 . 8\ aq\beta$	69—93	93
$NiCl_2 . 4\ aq$	29—30	30	$Pr_2(SO_4)_3 . 8\ aq$	0—80	
$NiBr_2 . 6\ aq$	91—100	91	$Yb_2(SO_4)_3 . 8\ aq$	0—100	
$YCl_3 . 6\ aq$	65—75		$Y_2(SO_4)_3 . 8\ aq$	7—100	7
$FeCl_3$	66—77	77	$Th(SO_4)_2 . 4\ aq$	40—70	
MnF_2	25—75	75	Li_2CO_3	0—100	
AgF	40—100		$Na_2CO_3 . 1\ aq$	36—100	
$MgI_2 . 6\ aq$	44—64	64			
$CsOH$	15—30		$Co(IO_3)_2$	65—100	100
$Sr(OH)_2$	85—100		$Ca(IO_3)_2$	—	90
$Ca(OH)_2$	5—95		$Zn(ClO_3)_2 . 4\ aq$	16—22	22
			$Na_2Sn(OH)_6$	3—15	3
$Li_2SO_4 . 1\ aq$	0—100		Na_2SeO_4	32—100	
Na_2SO_4	33—100		Na_2HPO_4	96—100	
$CaSO_4 . 2\ aq$	40—75	40	$Na_3HP_2O_7 . 1\ aq$	30—50	
$CaSO_4 . 1/2\ aq$	20—100		$Na_2HAsO_4 . 1\ aq$	68—73	73
$BeSO_4 . 2\ aq$	93—100	93	$Na_2HPO_4 . 2\ aq$	49—50	50
$MgSO_4 . 1\ aq$	69—100		$Na_2Cr_2O_7$	83—86	86
$CdSO_4 . 8/3\ aq$	0—5	5	$CaCrO_4$	0—100	
$CdSO_4 . 1\ aq\alpha$	44—74		$Na_4P_2O_7$	80—100	
$CdSO_4 . 1\ aq\beta$	75—100		benzoate Li^+	52—79	79
$CoSO_4 . 1\ aq$	65—100		benzoate Na^+	0—26	26
$MnSO_4 . 1\ aq$	24—100		benzoate Zn^{2+}	15—60	
$ZnSO_4 . 1\ aq$	49—100		phthalate K	51—60	51
$FeSO_4 . 1\ aq$	64—100		acetate Ca . 2 aq	0—58	58
			acetate Ca . 1 aq	84—100	
Na_2SO_3	33—100		acetate Sr . 1/2 aq	9—85	85
$K_2S_2O_3 . 1\ aq$	35—37	37	acetate Ba . 1 aq	25—32	32
$MgSO_3 . 3\ aq$	40—100		acetate Ba	41—80	80
$Ce_2(SO_4)_3 . 9\ aq$	31—42				
$Ce_2(SO_4)_3 . 8\ aq$	0—30		$K_4Fe(CN)_6$	88—89	88
$Ce_2(SO_4)_3 . 4\ aq$	43—100		$K_2Pt(CN)_4 . 1\ aq$	75—78	78
$Al_2(SO_4)_3 . 6\ aq$	0—20	20	$Pr(NO_3)_3 . 6\ aq$	15—19	19
$La_2(SO_4)_3 . 9\ aq$	0—100		NH_4AlF_4	55—100	55
			$FeBr_2 . 4\ aq$	—	49

thalpy of hydration is the principal reason why both the magnitude and the sign of the heat of crystallization must be ascertained in an empirical way[5−8].

In estimating the heat of crystallization from the values of the integral heat of dissolution, $\Delta H(m)$,

$$\Delta H_c = - \lim_{m \to m_s} \left[\Delta H(m) + \mathrm{d}\, \Delta H(m)/\mathrm{d} \ln m \right], \tag{3}$$

the situation may be encountered, where the slope of the concentration dependence, $\mathrm{d}\, \Delta H(m)/\mathrm{d} \ln m$, is opposite in sign, and has a higher absolute value than the integral heat of dissolution, $\Delta H(m_s)$. The last differential heat of dissolution, equal – except in the sign – to the heat of crystallization, and the integral heat of dissolution are then opposite in sign (*cf.*, *e.g.*, potassium fluoride).

Let us recall the well-known, exceedingly pronounced exothermic nature of the dissolution of some acids (HNO_3, H_2SO_4), where the bonding between water molecules and the anions is extremely strong. By analogy, a very strongly exothermic hydration may be expected in dissolution of anhydrous substances that form stable crystalline hydrates. Accordingly, while the crystallization of the respective crystalline hydrates is exothermic, the crystallization of the same substances with a lower hydration degree or in the anhydrous state is always considerably less exothermic; in special cases, it may be even endothermic, as with NaOH, NaI, Na_2SO_4,

TABLE II

Heats of crystallization, ΔH_c (kJ/mol), from aqueous solutions at 25°C for some salts with different numbers of hydration water molecules

Salts	ΔH_c	Ref.	Salts	ΔH_c	Ref.
LiCl	−2·1	5	KF	1·7	5
	−2·5	4		−1·05	4
	+2·5	3		−0·6	4d
LiCl . 1 aq	13 ± 3	3	KF . 1 aq	24·5	4
				18·1	4d
$LiNO_3$	6·5	5	$ZnCl_2$	13·4	5
$LiNO_3$. 3 aq	33·5	5	$ZnCl_2$. 3/2 aq	20·2	9
NaOH	−2·9	5	$Ca(NO_3)_2$	−17·1	4
NaOH . 1 aq	13·3	3	$Ca(NO_3)_2$. 4 aq	33	7
Na_2SO_4	−6·4	8	$MnSO_4$. 1 aq	−11	7
Na_2SO_4 . 10 aq	69·5	7	$MnSO_4$. 5 aq	19	4
NaBr	−2·8	4	NaI	−6·7	5
NaBr . 2 aq	16·6	3	NaI . 2 aq	16·7	3

LiCl, $LiSO_4$.1 aq, KF, and $Ca(NO_3)_2$ at 25°C (see Table II for a list of heats of crystallization from aqueous solutions at 25°C for selected salts).

The values listed in Table II have been calculated as recommended by Williamson[1], *i.e.* from the temperature dependence of solubility, using solubility data of Broul and coworkers[2] and osmotic coefficient data of Voznesenska[9], or by analytical approximation and extrapolation of integral heats of dissolution taken from books of Parker[3] and Beggerow[4]. The notation 4d marks the cases where the calculation started from data for the concentration dependence of the differential heat of dissolution, which were fitted to an analytical function, and extrapolated to the saturation concentration. The differing heat-of-crystallization values evaluated from the two kinds of dissolution data point to a certain inconsistency of the data for the same compounds from the same source. Other heat-of-crystallization data have been taken from the literature[5,7,8].

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