

THE PRINCIPLE OF IONIC ADDITIVITY AND INTERACTION PARAMETERS FOR THE SYSTEMS WATER-SALT

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A theoretical approach to the evaluation of water-salt phase diagrams has been developed which leads to the concentration dependence of the activity coefficient of water. Literature data for water-alkali halide systems were used to evaluate these dependences in an empirical manner and by using an equation derived from the lattice model of electrolytes. As an alternative, a joint evaluation of all the data was made by invoking the applicability of the principle of ionic additivity to the interaction parameters. In this way, an economical prototype of a data bank of interaction parameters of electrolyte systems has been established. The approach adopted represents a significant step forward in the generalization and prediction of solid-liquid phase equilibria in the systems water-salt.

A number of problems arise in the evaluation of phase diagrams for the systems water-salt. In the empirical approach, we obtain a statistically significant linear term of the polynomial used for fitting the concentration dependence of the logarithm of the activity coefficient of water. This contradicts the theory, since the linear term has no counterpart in the expansion of ΔG^E . When we try to use the entire phase diagram, including the liquidus curve of salt, which is coupled with the liquidus curve of water through the Gibbs-Duhem relationship, we encounter the problems of the occurrence of hydrates and the discontinuity of the phase diagram up to the point of pure salt. The use of the liquidus curve of salt in this case would require precise thermochemical data for the crystal modification of salt to which the liquidus curve relates, including ΔC_p , whose knowledge is necessary when a wide temperature range, from the melting point up to the eutectic temperature, is considered.

To avoid these problems, we have confined our attention to the liquidus curves of water over as wide a concentration range as possible, *i.e.* up to the eutectic point. This approach represents a sort of generalization of cryoscopy. Its success depends critically upon the knowledge of precise thermochemical data for pure water, including the temperature dependence of ΔH_f . A study of this kind has been made for another purpose¹.

In describing the non-ideality of a system, it is helpful to compare the real system with the so-called ideal mixture². This requires an exact definition of the activity

of water in the ideal mixture rather than the use of the so-called mole fraction on an ionized basis.

Recently, we have presented a lattice model of electrolytes for the whole concentration range³ which leads to a two-parameter equation for ΔG^E and which is analogous to the regular model, but takes into account the nature of the species in the system. This model provides a method of correctly evaluating the liquidus curve of water from both the statistical and theoretical points of view.

To make up for the information loss due to ignoring the liquidus curve of salt, we took into consideration all available data for the systems water-alkali halide. This suggested to us the idea of applying the principle of ionic additivity to the interaction parameters, in much the same way as recently used successfully for molar volumes of salts in evaluating density data over the whole concentration range⁴.

THEORETICAL

Thermodynamics of Phase Transitions

Experimental data of a phase diagram consist of pairs of T and x coordinates. The aim of the evaluation is to obtain a continuous curve for T as a function of x , $T = f(x)$, which gives the best fit to the experimental points. This may be achieved by an approach in which the activity of a component is expressed first as a function of temperature, $a = f(T)$, and in the second stage as a function of composition, $a = f(x)$.

The fundamental equation relating activity to temperature is the so-called Le Chatelier-Schröder equation, also called van Laar's equation, whose differential form is

$$d \ln a = (\Delta H^{s/l}/RT^2) dT, \quad (1)$$

where $\Delta H^{s/l}$ is the difference between the enthalpies of pure solid and the component in solution. In general, the activity ratio, a_s/a_l , should appear on the left-hand side of the equation, but since we do not consider the formation of a solid solution and the activity of the pure solid component is unity, a has the meaning of the activity of the component in solution. When integrating this equation, we must allow for the temperature dependence of $\Delta H^{s/l}$, which is expressed by Kirchhof's equation

$$\Delta H^{s/l} = (\Delta H)_{T_r} + \Delta C_p(T_r - T). \quad (2)$$

This equation can only be used directly in integrating Eq. (1) if ΔC_p is independent of temperature. In our case, however, where the component considered is water and the eutectic temperatures reach down to minus several tens of degrees, we must consider ΔC_p as a function of temperature. In our previous work⁵, we called atten-

tion to the following convenient form of the temperature dependence of ΔC_p ,

$$\Delta C_p = (\Delta C_p)_{T_f} + \sum_{k=1}^m A_k (T_f - T)^{n_k}, \quad (3)$$

where A_k are parameters, and n_k are integer-valued exponents. Substituting Eqs (3) and (2) into (1) and integrating, we obtain the integral form of the Le Chatelier–Schröder (van Laar's) equation

$$\ln a = \frac{(\Delta H)_{T_f}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) + \frac{(\Delta C_p)_{T_f}}{R} \left(\frac{T_f}{T} - 1 - \ln \frac{T_f}{T} \right) + \sum_{k=1}^m A_k K_k. \quad (4)$$

The symbol K_k represents expressions obtained by integrating the terms $(T_f - T)^{n_k}$. The values for various exponents are tabulated in our previous paper⁵.

The following thermochemical parameters for water were taken from the literature⁶: $T_f = 273.15$ K; $(\Delta H_f)_{T_f}/R = 722.8$ K; $(\Delta C_p)_{T_f}/R = 4.484$. The parameters of the temperature dependence of BC_p were obtained by fitting experimental data measured by Angell⁷ to the equation¹

$$\Delta C_p/R = (\Delta C_p)_{T_f}/R + A_1(T_f - T) + A_2(T_f - T)^4, \quad (5)$$

where $A_1 = 0.01586$ and $A_2 = 2.37 \cdot 10^{-6}$. This equation is adequate over a temperature range from 0 to -40°C . The expressions for K_1 and K_2 corresponding to the powers 1 and 4 in Eq. (5) are as follows:

$$K_1 = \frac{T}{2} \left[\left(\frac{T_f}{T} \right)^2 - 1 \right] - T_f \ln \left(\frac{T_f}{T} \right) \quad (6a)$$

$$K_2 = \left(\frac{T_f}{T} - 1 \right) (24T_f^4 + 154T_f^3T - 86T_f^2T^2 + 34T_fT^3 - 6T^4) / \left[120 - T_f^4 \ln \left(\frac{T_f}{T} \right) \right]. \quad (6b)$$

On substitution into Eq. (4), values of the logarithm of water activity were calculated for the temperatures of experimental points on the liquidus curves of water.

Thermodynamics of Water–Salt Mixtures

We shall now be concerned with the relationship between activity and concentration. As we are dealing with real systems, the activities and mole fractions of the components are generally different in value. Their comparison provides information about

the deviation of a system from ideality. However, this would only be true for con-formal systems. In our case, one component is water, composed of polar molecules, and the other is a salt completely dissociated into ions. If we allow for the fact that by adding one mole of MX salt to the solution we introduce two moles of M and X species, this must necessarily be reflected in the entropy of the system.

The classical method of obtaining the activity coefficients, $\gamma = a/x$, and hence a measure of the deviation from ideality, by comparing activities and concentrations of components is thus impracticable here. A general approach using the relationship $\gamma = a/a^*$ is to compare the actual activity of a component with the activity in the ideal mixture, a^* . This method of expressing the non-ideality is based on Haase's concept and its description is given in our previous paper². Some authors avoid this problem by using the so-called mole fraction on an ionized basis. In our opinion, this approach is not rigorous from the thermodynamic point of view.

The expression for the water activity in the ideal mixture (for a $\text{H}_2\text{O}-\text{M}_p\text{X}_q$ system) is of the form

$$a^* = (1 - x)/(vx + 1 - x), \quad (7)$$

where x is the mole fraction of the salt, and $v = p + q$ is the sum of the stoichiometric coefficients of the salt. For 1 : 1 electrolytes, where $v = 2$, the final expression for the activity coefficient is

$$\ln \gamma = \ln a - \ln [(1 - x)/(1 + x)]. \quad (8)$$

This equation was used to convert $\ln a$ values obtained from Eq. (4) to values of $\ln \gamma$, and the latter were then treated by a regression method.

RESULTS AND DISCUSSION

Experimental Data

Experimental data for liquidus curves of water in the systems water-salt, covering all salts containing the cations Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , and the anions F^- , Cl^- , Br^- , and I^- (except the system water-RbBr for which no data are available), were taken from the literature^{8,9}.

The raw data were first sorted to eliminate those subject to errors. In the case of an outlier due to a misprint in some significant figure, we tried to reconstruct the correct value. If this was impossible, the point was rejected. Another kind of error was a wrong concentration unit, resulting in a significant departure of the entire T - x plot from the set of the remaining experimental points. In this case we also tried first to reconstruct the data by assigning the appropriate concentration unit.

The sorted data set comprised a total of 962 experimental points for 19 systems.

Evaluation of Liquidus Curves with Each System Considered Separately

To obtain an unbiased view of the character of the concentration dependence of $\ln \gamma$, we first performed an empirical evaluation using two equations for $\ln \gamma$ as a function of the mole fraction of salt, x . For a start, we used a one-parameter relationship of the form

$$\ln \gamma = bPx^m, \quad (9)$$

where P is the T_i/T ratio, and b is the corresponding empirical interaction parameter. The evaluation was made for seven values of the exponent, namely 1, $4/3$, $3/2$, $5/3$, 2, 2.5, and 3. The criterion used in the evaluation was the minimization of the sum of the squares of the deviations of $\ln \gamma$. Each system was evaluated separately, and the obtained sums of the squares of the deviations were added together. The overall sums, which characterize the suitability of the exponent values for all the systems under consideration, are given in the second column of Table I. The smallest value of this statistical criterion is found for the exponent $m = 2.5$.

A substantial improvement of the fit was achieved by using the two-parameter equation

$$\ln \gamma = bPx^n + cPx^m. \quad (10)$$

The values of the exponents n and m were varied in the same manner as previously, except the cases where $n = m$. The corresponding sums of the squares of the deviations are given in Table I. As seen, the smallest sum was obtained for $n = 4/3$ and

TABLE I

The sums of the squares of the deviations (10^3S) of the fits of data for the concentration dependence of $\ln \gamma$ to one-parameter equation (9) and two-parameter equation (10)

m	Eq. (9)	Eq. (10)					
		n					
		1	$4/3$	$3/2$	$5/3$	2	$5/2$
1	65.40						
$4/3$	38.81	9.98					
$3/2$	30.13	8.87	7.73				
$5/3$	23.74	8.11	7.42	7.28			
2	16.00	7.36	7.22	7.23	7.28		
$5/2$	12.36	7.52	7.55	7.60	7.65	7.78	
3	13.87	8.50	8.28	8.21	8.17	8.13	8.15

TABLE II

Parameters b and c of Eq. (10) with $n = 4/3$ and $m = 2$, and statistical characteristics of evaluated liquidus curves. $Y = 10^3 \ln \gamma$; S is the sum of the squares of the deviations; s_1 and s are the standard deviations^a

Salt	Mole % range	b $s(b)$	c $s(c)$	$S(Y)$ $s_1(Y)$	$S(T)$ $s_1(T)$	Number of exp. points
LiF	0-0.045	2.032 0.209	-51.466 37.850	0.000 0.001	0.000 0.000	9
LiCl	0-9.28	1.708 0.199	-28.672 1.135	1.211 4.189	13.021 0.434	69
LiBr	0-7.22	1.946 0.097	-37.205 0.663	0.075 1.262	0.787 0.129	47
LiI	0-6.14	1.495 0.826	-37.880 5.692	0.180 4.048	1.898 0.415	11
NaF	0-1.72	2.515 0.259	-36.809 4.444	0.004 0.425	0.042 0.044	22
NaCl	0-8.78	1.509 0.092	-12.575 0.516	3.425 3.964	35.734 0.405	218
NaBr	0-10.75	0.250 0.110	-6.292 0.537	0.750 2.988	7.909 0.307	84
NaI	0-9.28	1.311 0.223	-15.398 1.243	0.417 3.793	4.389 0.389	29
KF	0-8.11	1.727 0.270	-17.056 1.579	0.187 2.789	1.946 0.285	24
KCl	0-5.80	1.197 0.046	-5.815 0.337	0.245 1.092	2.561 0.112	205
KBr	0-6.69	1.237 0.089	-6.568 0.606	0.231 1.677	2.413 0.172	82
KI	0-10.60	0.440 0.119	-2.804 0.563	0.486 2.999	5.065 0.306	54
RbF	0-3.95	1.158 0.035	-12.439 0.328	0.000 0.118	0.000 0.012	16
RbCl	0-4.75	1.319 0.028	-5.673 0.259	0.001 0.190	0.011 0.019	29
RbI	0-7.81	1.593 0.131	-4.176 0.787	0.008 1.065	0.084 0.110	7
CsF	0-1.94	0.752 0.022	-14.407 0.342	0.000 0.030	0.000 0.003	9

TABLE II
(Continued)

Salt	Mole % range	<i>b</i> <i>s</i> (<i>b</i>)	<i>c</i> <i>s</i> (<i>c</i>)	<i>S</i> (<i>Y</i>) <i>s</i> ₁ (<i>Y</i>)	<i>S</i> (<i>T</i>) <i>s</i> ₁ (<i>T</i>)	Number of exp. points
CsCl	0–3.56	1.607 0.057	–6.385 0.586	0.002 0.236	0.019 0.024	33
CsBr	0–1.94	1.576 0.011	–3.442 0.162	0.000 0.013	0.000 0.001	10
CsI	0–2.56	0.694 0.148	10.777 1.758	0.000 0.192	0.002 0.020	4

^a All systems: $S(Y) = 7.221$; $s_1(Y) = 2.740$, $S(T) = 75.882$, $s_1(T) = 0.281$. Number of experimental points 962.

$m = 2$. The parameters b and c evaluated with this combination of exponents and the statistical characteristics for each system are listed in Table II.

This result is in excellent agreement with conclusions of our previous work³, in which the lattice model was used to propose a relationship for ΔG^E of the system water–salt over the whole concentration range in the form

$$\Delta G^E = L_1 x(1 - x)/(1 + x) + L_2 x \{ [2x/(1 + x)]^{1/3} - 1 \}, \quad (11)$$

where L_1 and L_2 are the true interaction parameters. Hence, it is easy to derive the following relationship for $\ln \gamma$:

$$\begin{aligned} \ln \gamma &= [\Delta G^E - x \partial(\Delta G^E) / \partial x_2] / RT = \\ &= L_1 2x^2 / (1 + x)^2 - L_2 [2x / (1 + x)]^{4/3} / 6. \end{aligned} \quad (12)$$

In the limit of small x , Eq. (12) leads to a relationship identical with Eq. (10) with exponent values of $4/3$ and 2 . For comparison, we also performed an evaluation on the basis of this theoretical relationship. The obtained sum of the squares of the deviations, $7.2198 \cdot 10^{-3}$, is only insignificantly smaller than the smallest value in Table I.

In addition, we tested the applicability of a three-parameter equation with exponent values of $4/3$, 2 , and 3 . The value of 3 for the additional exponent was not an arbitrary choice; in fact, it is another possible exponent implied by the regular model when interactions of larger particle clusters rather than pairs, are considered. The sum of the squares of the deviations exhibited a slight decrease to $6.53 \cdot 10^{-3}$.

Evaluation Based on the Principle of Ionic Additivity

If Eq. (10) were to be used to keep a file on smoothed liquidus curves of all the systems, the number of parameters required would be twice that of the systems, *i.e.* $2 \cdot 5 \cdot 4 = 40$ parameters (if data for the system water-RbBr were available).

To achieve a more economical representation of the liquidus curves, we have used the principle of ionic additivity or the assumption that the parameters b and c may be split into contributions from cations, B_i and C_i , and from anions, B_j and C_j :

$$(\ln \gamma)_{ij} = (B_i + B_j) Px^{4/3} + (C_i + C_j) Px^2. \quad (13)$$

As the number of ions is $5 + 4 = 9$, there are 18 contributions, a substantial drop from 40 in the previous case. This difference increases with increasing number of

TABLE III

Parameters of Eqs (13), (14), and (15), and their standard deviations

i	Eq. (13)		Eq. (14) ^a	Eq. (15) ^b	
	B_i	C_i	C_i	C_i	D_i
Li	0.980	0.000	0.000	0.00	25.16
	0.180	0.000	0.000	0.00	13.77
Na	0.859	16.256	15.541	16.28	15.56
	0.132	0.882	0.178	0.85	9.71
K	0.097	27.467	22.296	17.67	94.43
	0.103	0.981	0.206	0.86	7.00
Rb	-0.271	35.159	27.007	18.27	170.20
	0.241	1.702	0.427	1.50	21.43
Cs	1.328	21.112	27.952	26.33	-37.33
	0.608	6.694	1.464	5.66	183.73
F	0.919	-40.514	-33.655	-39.41	-40.10
	0.261	1.726	0.437	2.16	21.98
Cl	0.459	-27.829	-23.871	-33.47	20.27
	0.131	0.814	0.318	1.40	9.04
Br	-0.227	-24.640	-24.584	-38.52	69.16
	0.145	0.887	0.317	1.39	9.40
I	0.000	-28.895	-26.828	-36.48	0.00
	0.000	1.062	0.287	1.39	0.00

^a $B = 0.733$; $s(B) = 0.046$. ^b $B = 1.828$; $s(B) = 0.102$.

systems considered. The implications of this reduction in relation to future data banks have been pointed out in our previous paper⁴.

To implement the idea, we subjected all the experimental data to a joint regression treatment, with the number of parameters reduced by two. One of the *B* and one of the *C* parameters were arbitrarily chosen, as otherwise the set of linear equations would have been insoluble. Results of the joint regression treatment, *i.e.* individual ionic contributions to interaction parameters and standard deviations of both the optimized quantity $\ln \gamma$ and the temperature, are listed in Tables III and IV. The sums of the squares of the deviations given in Table IV may be compared with

TABLE IV

Standard deviations for joint evaluation of all liquidus curves by means of Eqs (13), (14), and (15). $Y = \ln \gamma$

Salt	Eq. (13)		Eq. (14)		Eq. (15)	
	$s_1(Y)$	$s_1(T)$	$s_1(Y)$	$s_1(T)$	$s_1(Y)$	$s_1(T)$
LiF	0.000	0.000	0.026	0.003	0.003	0.000
LiCl	1.462	0.504	5.192	0.558	4.679	0.507
LiBr	1.237	0.556	5.087	0.551	4.374	0.475
LiI	0.906	0.961	9.619	1.018	8.629	0.912
NaF	0.005	0.051	1.478	0.152	0.522	0.054
NaCl	3.502	0.413	4.575	0.471	4.051	0.418
NaBr	0.921	0.347	3.619	0.381	2.159	0.225
NaI	0.940	0.598	7.472	0.784	4.148	0.434
KF	0.242	0.349	3.490	0.361	2.984	0.309
KCl	0.825	0.205	1.937	0.197	1.517	0.155
KBr	0.909	0.341	2.505	0.255	2.534	0.259
KI	0.670	0.361	3.779	0.388	3.139	0.321
RbF	0.029	0.139	1.077	0.110	1.266	0.130
RbCl	0.192	0.262	2.787	0.284	1.951	0.199
RbI	0.277	0.643	3.945	0.403	6.192	0.632
CsF	0.083	0.311	1.401	0.144	2.769	0.284
CsCl	0.015	0.070	0.927	0.095	0.499	0.051
CsBr	0.017	0.134	1.111	0.114	0.774	0.079
CsI	0.119	0.560	4.522	0.464	4.239	0.435
All systems	3.583	0.375	3.851	0.403	3.225	0.337
	$S(Y)$	$S(T)$	$S(Y)$	$S(T)$	$S(Y)$	$S(T)$
All systems	12.352	135.406	14.264	155.879	10.007	109.445

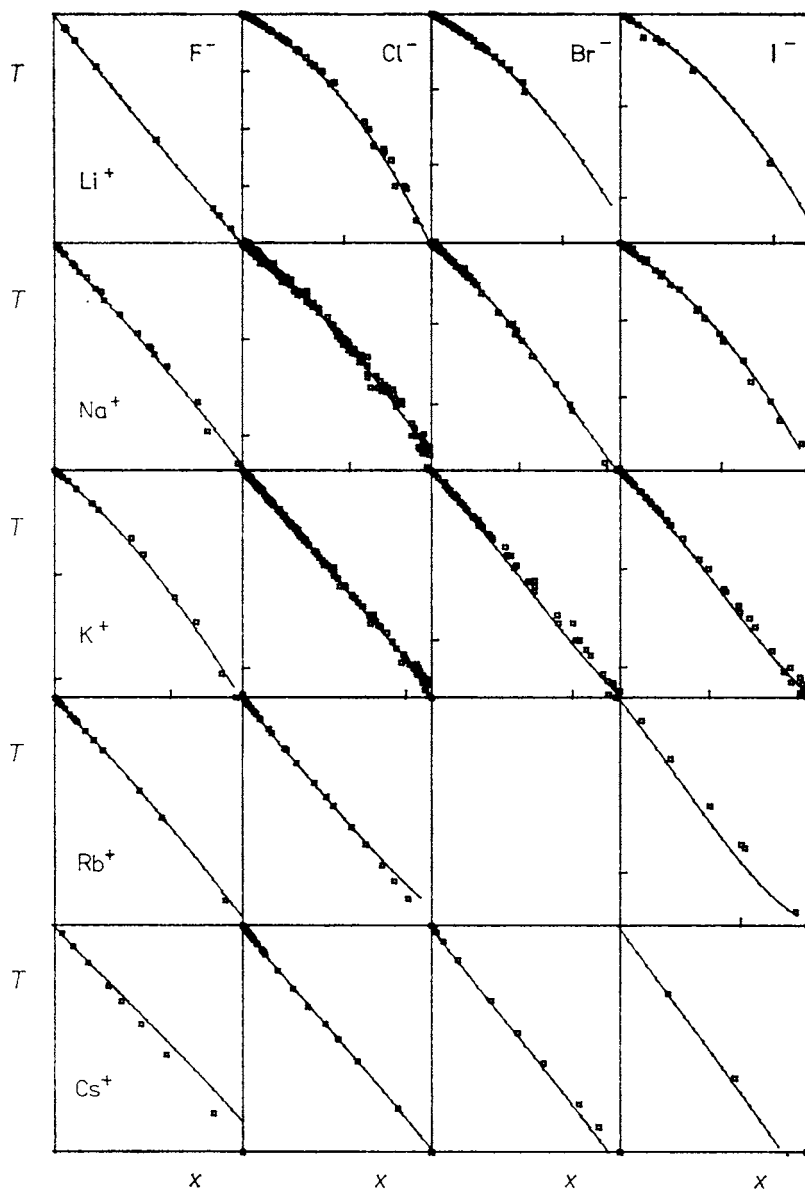


FIG. 1

Comparison of experimental liquidus curves of water in the systems water-salt with those calculated from the concentration dependence of $\ln \gamma$ (Eq. (15)) on the basis of the principle of ionic additivity. The tick marks along the axes are in steps of 0.05 for x and 5 K for T

values listed in Table II. The comparison shows that the reduction of the number of parameters from 40 to 18 increased the sum of the squares of the deviations by a factor of 1.7 only, corresponding to about a 30% increase in the overall standard deviation.

It should be noted that the contributions from the Rb^+ and Br^- ions may be used to calculate the parameters of the concentration dependence of $\ln \gamma$ and hence the liquidus curve of water for the system water–RbBr, whose phase diagram has not as yet been measured. So far unknown phase diagrams may be predicted in this way.

Another attempt at a still more economical representation starts from the assumption that the interaction parameter L_2 in Eq. (11), and hence also parameter b in Eq. (10), is composed of coulombic contributions from cations and anions that are all equal for our type of electrolyte (1 : 1). This reduces Eq. (13) to

$$(\ln \gamma)_{ij} = BPx^{4/3} + (C_i + C_j) Px^2. \quad (14)$$

As a result, the number of parameters shrinks from 18 to just 10. Results of the evaluation based on Eq. (14) are given in the second columns of Tables III and IV. Neither the resulting sum of the squares of the deviations nor the standard deviation is much greater than that for the previous evaluation.

The final attempt to improve the fit extends Eq. (14) to include a third parameter

$$(\ln \gamma)_{ij} = BPx^{4/3} + (C_i + C_j) Px^2 + (D_i + D_j) Px^3. \quad (15)$$

In this equation, the principle of ionic additivity is only applied to the parameters of the terms in x^2 and x^3 . Although the number of parameters is greater just by one compared to the first case, the fit is better, as can be seen in Tables III and IV. Fig. 1 shows a comparison of experimental and theoretical liquidus curves of water. The latter were obtained by an iterative technique for the calculation of liquidus temperatures with the aid of Eqs (4), (8), and (15). Considering the existing scatter of experimental data from various sources, the fit may be judged as good.

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