

## Monte Carlo Studies on Fused Salts

### II. Calculations on a Model of Fused Lithium Chloride at 1073°K

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The possibility of using the Monte Carlo method for estimating the configurational thermodynamic properties of ionic liquids has previously been tested on hypothetical two-dimensional systems. The calculations are now extended to a three-dimensional model for fused lithium chloride at 1073°K, containing 64 ions in the Monte Carlo cell. The calculated potential energy difference between the model at 1073°K and the ideal crystal at 298°K is for the two cases tested 3.5 and 5.8 kcal/mole as compared with 10.8 kcal/mole estimated from experiments. The calculated radial distributions compare reasonably well with experimental curves, though remnants of a crystalline structure is evident even after 125 499 configurations were calculated. The observed shifts in average interatomic distances on melting as well as the observed coordination numbers in the melt are reproduced.

In an earlier paper the Monte Carlo method for estimating thermodynamic data was applied to a two-dimensional ionic liquid.<sup>1</sup> The results were deemed sufficiently promising to warrant similar calculations on a three-dimensional system. It was decided to work with a model for fused lithium chloride. For this liquid in particular, adequate experimental data on the radial distribution functions exist,<sup>2</sup> which allow comparisons with the M.C. results. Moreover, sufficiently reliable experimental enthalpy functions for this system are also available for an evaluation of the M.C. calculations. The present report gives the result from a single system at only one temperature. The high cost in computer time unfortunately has so far seriously limited the amount of work which can be done.

## PROCEDURE

The interaction potential between two atoms  $i$  and  $j$  separated by a distance  $r_{ij}$  is taken as before<sup>1</sup> to be:

$$u_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + \frac{b_{ij} e^2}{r_{ij}^n} \quad (1)$$

where  $Z_i e$  and  $Z_j e$  are the charges on atoms  $i$  and  $j$  respectively,  $b_{ij}$  is the Born-Landé repulsion coefficient and  $n$  an integral number ranging from 5 to 12 depending on the nature of the ions present.

In the present computations all coefficients  $b_{ij}$  were set equal for simplicity, though obviously the repulsion term for a cation pair, an anion pair and a cation-anion pair will be different. The single overall repulsion coefficient used here is essentially typical of the interaction of the oppositely charged ions, since these ions approach each other most closely in the structure.

We shall now proceed to derive the equation used to obtain a numerical value for the repulsion term. This equation is presented in many textbooks (see for instance Ref. 3), but for clarity some details will be repeated.

If the interaction potential of eqn. 1 is summed up for an infinite ideal crystal, the potential energy,  $U$ , for a gram formula weight of the system becomes:

$$U = - \frac{Z_c |Z_a| A N e^2}{R} + \frac{b B N e^2}{R^n} \quad (2)$$

Here  $A$  is the Madelung number,  $B$  is a corresponding Madelung number for the summation of the repulsive terms,  $N$  the Avogadro number,  $Z_c e$  and  $Z_a e$  the charge of cations and anions, respectively, and  $R$  the smallest cation-anion separation in the ideal lattice.  $b$  and  $n$  have the same meaning as in eqn. 1.

Differentiating  $U$  with respect to  $R$ , we have:

$$\frac{dU}{dR} = \frac{Z_c |Z_a| A N e^2}{R^2} - \frac{n b B N e^2}{R^{n+1}} \quad (3)$$

For minimum potential energy, occurring with the equilibrium distance  $R=R_0$ ,  $dU/dR$  is equated to zero, giving with some rearrangement an expression for the repulsion coefficient  $b$ :

$$b = \frac{Z_c |Z_a| A R_0^{n-1}}{n B} \quad (4)$$

This equation is used to derive from crystal data the numerical value of  $b$ , for later use with eqn. 1. The pertinent crystal data are summarized in Table 1. The two different values of  $b$ , given in Table 1, were used in the M.C. calculations.

(The  $R_0$  value at 298°K was utilized, though the  $R_0$  value at 0°K might have been preferable if it had been known accurately. An estimate of 2.54 Å can be found in the literature<sup>4</sup> (for  $R_0$  at 0°K.)

Table 1. Numerical values introduced in eqn. 4 to obtain the  $b$ -value for crystalline lithium chloride (sodium chloride structure) and the  $b$ -value for two cases.

Case No.	Charge $Z_c= Z_d $	Madelung constant $A$	Madelung constant $B$	$n$	$R_0, \text{Å}$	$b, \text{Å}^6$
1	1	1.748	6.937	7	2.57	10.37
2	1	1.748	7.420	7	2.57	9.698

With the above numerical value of  $b$  (from Table 1) and appropriate values for the other constants, eqn. 2 for crystalline lithium chloride becomes:

$$U = -332.1 \left( \frac{1.748}{R} - \frac{71.94}{R^7} \right) \text{ kcal/mole} \quad (5)$$

when  $R$  is given in Ångström units.

The M.C. calculations were carried out for a temperature of 800°C (or 1073°K). At this temperature molten lithium chloride is found experimentally to have a density of 1.428 g/cm<sup>3</sup>.<sup>5</sup> A hypothetical crystal (of sodium chloride structure type) with mole weight  $M$  and density  $d$  will have an anion-cation shortest distance:

$$R = \left( \frac{M}{2dN} \times 10^{24} \right)^{1/2} \text{ Å} \quad (6)$$

( $N$  being as before the Avogadro number).

For the lithium chloride melt at 800°C eqn. 6 gives an  $R$  value of 2.90 Å. The energy of the ideal expanded infinite crystal associated with this  $R$  value is from eqn. 5 found to be 186.3 kcal/mole, as compared with the value 193.6 kcal/mole for the 298°K equilibrium crystal with  $R=R_0=2.57$  Å.

The starting configuration of the M.C. calculations was the expanded crystal with  $R=2.90$  Å. The fundamental cell contains  $4 \times 4 \times 4=64$  ions, in a cube with edge length  $4 \times 2.90 \text{ Å}=11.60 \text{ Å}$ . The cell was surrounded by a set identical repetition cells to minimize effects of the limited size of the system. This starting configuration of 64 ions in the fundamental cell was calculated to have an energy of 185.2 kcal/mole when  $b=10.37 \text{ Å}^6$  and 186.1 kcal/mole when  $b=9.698 \text{ Å}^6$  as compared with the value of 186.3 kcal/mole obtained from eqn. 5 for the ideal infinite lattice. The discrepancy between the first value and the value for the ideal infinite lattice (eqn. 5) is due to a too high  $b$ -value ( $10.37 \text{ Å}^6$ ).

The procedure for the M.C. calculations followed that described previously for the two-dimensional case,<sup>1</sup> and the earlier paper should be consulted for a further account. As before the atoms were not allowed to approach each other closer than a fixed minimum value in order to prevent large numbers of rejected states. The minimum allowed value was taken as 2.1 Å in the present calculations.

## THE M.C. CONFIGURATIONAL ENERGY

A total of 126 499 accepted configurations were calculated with the expenditure of 54 hours of computing time on the UNIVAC 1107 computer. The average energy calculated for 1000 consecutive configurations is plotted in Fig. 1 as a function of the configuration number of the last of these 1000 configurations (*i.e.* the chain length). It is seen that this average for the first 50 000 configurations exhibit a trend towards more negative values. Above 50 000 configurations the energy fluctuates around a value of 2.6 kcal/mole relative to the expanded ideal crystal when  $b=10.37 \text{ \AA}^6$  and 4.0 kcal/mole when  $b=9.698 \text{ \AA}^6$ . It is of course an assumption that the configuration space has been adequately sampled, and hence that these energies are characteristic of the models. The plot in Fig. 1, however, has an appearance consistent with an adequate sampling, and the average energy is apparently entering a region with no long range trend.

Only about 10 000 configurations were calculated with the  $b$ -value of  $9.698 \text{ \AA}^6$ . Since the starting configuration in this case was a late configuration (typical of the molten state) of the earlier run, it was assumed that typical values for the energy would be rapidly attained.

The energy of the 298°K equilibrium crystal is found from eqn. 5 to be 193.6 kcal/mole when  $R$  is taken to be  $2.57 \text{ \AA}$ . The M.C. calculations predict a change in potential energy of lithium chloride from the crystal in the standard state (at 298°K) to the melt (at 1073°K) equal to 5.8 and 3.5 kcal/mole, respectively, for the two different  $b$ -values (see Table 2).

Table 2. Increase in potential energy (calculated lattice energy) of lithium chloride from the crystal in the standard state at 298°K (193.6 kcal/mole) to the melt at 1073°K.

Case	$b, \text{ \AA}^6$	$\Delta E, \text{ kcal/mole}$
1	10.37	$-(187.8 - 193.6) = 5.8$
2	9.698	$-(190.1 - 193.6) = 3.5$

These energies may be compared with experiments. According to JANAF tables<sup>6</sup> the enthalpy difference between the crystal at 298°K and the melt at 1073°K is 15.4 kcal/mole. From this value the kinetic energy  $3RAT = 3 \times 1.986 \times (1073 - 298) = 4.6 \text{ kcal/mole}$  should be subtracted. If PV terms are neglected, the experimental potential energy increase will then amount to 10.8 kcal/mole. In view of the simplified interaction potential and the small size of the cell employed in the M.C. calculations, the computed values may be considered reasonable. To ensure rapid stabilization of the energy in future M.C. calculations, it may be an advantage to use another starting configuration than the expanded crystal. For possible use as starting configuration, the cartesian coordinates of the 64 atoms in the fundamental cell from a late configuration of the present study are reported in Table 3.

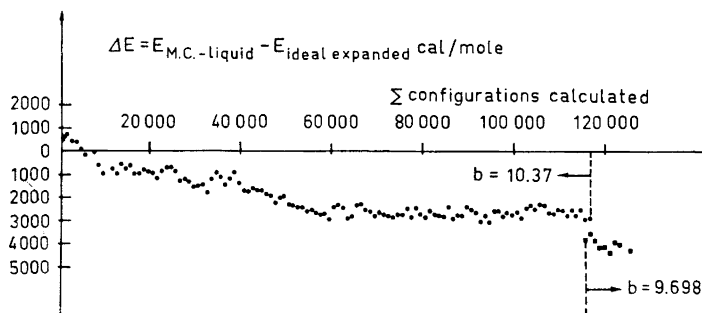


Fig. 1. Configurational energy in kcal/mole relative to the ideal expanded crystal of the three-dimensional model of fused lithium chloride *versus* chain length in number of configurations.

The different points represent the average over only those configurations generated since the preceding point (1000 configurations). ●:  $b=10.37 \text{ \AA}^3$ ; ■:  $b=9.698 \text{ \AA}^3$ .

Table 3. Cartesian coordinates in fractions of cell edge at configuration number 125 499.

No.	$x$	Anions $y$	$z$	No.	$x$	Cations $y$	$z$
1	0.16074	0.07627	0.03596	1	0.43019	0.11068	0.12884
2	0.66926	0.12508	0.14405	2	0.95413	0.09081	0.06721
3	0.44961	0.53135	0.16477	3	0.13456	0.50962	0.01744
4	0.92370	0.53711	0.02097	4	0.65177	0.53666	0.16603
5	0.22973	0.69287	0.01253	5	0.34387	0.70823	0.16609
6	0.70334	0.73446	0.17316	6	0.83124	0.73139	0.00681
7	0.43789	0.95025	0.21631	7	0.14104	0.88888	0.01322
8	0.94189	0.89638	0.03133	8	0.65148	0.92905	0.22065
9	0.14533	0.22573	0.71156	9	0.45890	0.23650	0.45229
10	0.66700	0.22293	0.46138	10	0.93603	0.24640	0.69920
11	0.38140	0.42617	0.47260	11	0.21939	0.41178	0.66121
12	0.88198	0.42406	0.68250	12	0.75605	0.43467	0.48758
13	0.15502	0.62219	0.65884	13	0.45004	0.60544	0.50617
14	0.66889	0.61590	0.51824	14	0.95327	0.62836	0.63958
15	0.44682	0.06603	0.55425	15	0.17304	0.03172	0.63812
16	0.95870	0.03379	0.62759	16	0.63508	0.05120	0.56102
17	0.33198	0.20380	0.27906	17	0.15666	0.15540	0.24392
18	0.96043	0.10910	0.26283	18	0.73140	0.22424	0.28380
19	0.13797	0.41899	0.22694	19	0.32356	0.42581	0.28154
20	0.77677	0.44431	0.27938	20	0.96698	0.48194	0.24225
21	0.33772	0.71776	0.39706	21	0.14637	0.75358	0.45622
22	0.96284	0.65203	0.41505	22	0.77789	0.72766	0.38578
23	0.14164	0.93905	0.46506	23	0.37694	0.93948	0.41384
24	0.75817	0.92491	0.38770	24	0.93482	0.99241	0.41828
25	0.46040	0.20593	0.96138	25	0.27250	0.16652	0.89336
26	0.84894	0.20210	0.89715	26	0.65004	0.14478	0.94577
27	0.25941	0.42985	0.88224	27	0.44112	0.42663	0.95836
28	0.63072	0.48989	0.91241	28	0.82302	0.43068	0.88163
29	0.45056	0.73853	0.71461	29	0.27899	0.72553	0.79239
30	0.83386	0.70419	0.77233	30	0.63444	0.63875	0.75683
31	0.30247	0.97129	0.80119	31	0.47585	0.93982	0.73238
32	0.67056	0.98017	0.73189	32	0.86050	0.93017	0.76810

## THE EXPERIMENTAL RADIAL DISTRIBUTIONS

Levy *et al.*<sup>2</sup> have determined radial distribution curves for molten LiCl by X-ray diffraction as well as neutron diffraction. These distributions have been processed in our earlier paper<sup>1</sup> to extract the chlorine-chlorine distribution,  $\rho_{\text{Cl-Cl}}(r)$  and the lithium-chlorine distribution,  $\rho_{\text{Li-Cl}}(r)$ , from the composite experimental curves. The method used was not described, however. Hence the details will be given in the following.

The general procedure for resolving composite radial pair distribution functions have been discussed by Krogh-Moe.<sup>7</sup> The method indicated, reduces to the so-called difference method if all the different atomic form factor curves for a given type of radiation are taken to be proportional with a proportionality constant independent of the scattering angle. The proportionality requirement is not quite fulfilled for X-ray scattering, but may serve to give useful estimates. The proportionality constant is for X-rays roughly equal to the total number of electrons belonging to the atom or ion. If this approximation is accepted, the radial distribution curve,  $\rho_x(r)$ , obtained by X-ray scattering of molten LiCl may be written:

$$\rho_x(r) = 2 \times 2 \times 18 \rho_{\text{Li-Cl}}(r) + 2^2 \rho_{\text{Li-Li}}(r) + 18^2 \rho_{\text{Cl-Cl}}(r) \quad (7)$$

where  $\rho_{\text{Li-Cl}}(r)$ ,  $\rho_{\text{Li-Li}}(r)$ , and  $\rho_{\text{Cl-Cl}}(r)$  are the individual atomic center distributions we wish to resolve. The number of electrons belonging to the lithium ion and chlorine ion are taken as 2, respectively 18.

Similarly, we may write the radial distribution curve,  $\rho_N(r)$ , obtained by neutrons in terms of the individual distributions:

$$\rho_N(r) = 2(-0.25 \times 0.98) \rho_{\text{Li-Cl}}(r) + (-0.25)^2 \rho_{\text{Li-Li}}(r) + (0.98)^2 \rho_{\text{Cl-Cl}}(r) \quad (8)$$

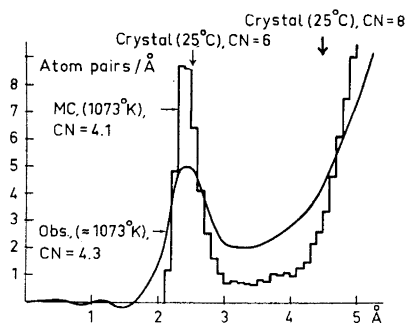
Here the coherent neutron scattering amplitudes of <sup>7</sup>Li and Cl are taken as  $-0.25 \times 10^{-12}$  cm and  $0.98 \times 10^{-12}$ , respectively.<sup>2</sup>

Finally it is assumed that

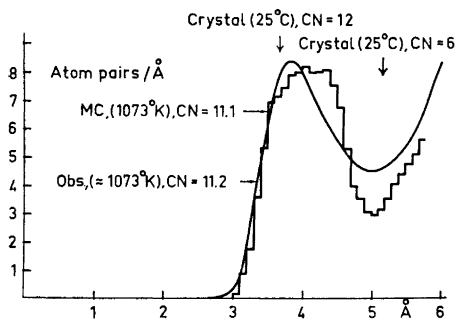
$$\rho_{\text{Li-Li}}(r) = \rho_{\text{Cl-Cl}}(r) \quad (9)$$

This assumption is not likely to create large errors since the terms in eqns. 7 and 8 containing  $\rho_{\text{Li-Li}}(r)$  are comparatively small. Moreover these two distributions are probably not very different because of the charge symmetry.

The necessary equations for obtaining estimates for  $\rho_{\text{Li-Cl}}(r)$  and  $\rho_{\text{Cl-Cl}}(r)$  from the experimental radial distribution curves  $\rho_x(r)$  and  $\rho_N(r)$  are now available. The individual distributions obtained from eqns. 7, 8, and 9 are shown in Figs. 2 and 3 and for a larger range of  $r$  values in our earlier paper.<sup>1</sup> It should be recognized that these curves are not very accurate since the more rigorous method of resolving the curves<sup>7</sup> was not used. The rigorous method was not attempted, however, because tabulated values of the observed intensities were not available. Still the peak positions are presumably quite reliable for the first peaks, the values remaining the same as those reported from the unresolved curves.<sup>2</sup>



*Fig. 2.* Radial distribution functions (RDF) versus the distance  $r$  of the three dimensional model of lithium chloride. The RDF is defined at the distance  $r$  as the number of ions of one kind in the shell between  $r-0.05$  Å and  $r+0.05$  Å surrounding a given atom. The ordinate unit is scaled as to correspond to a shell of 1 Å thickness. The histogram gives the anion-cation distribution for the MC model. The fully drawn curve gives the anion-cation distribution calculated from experimental RDF's of Levy, Agron, Bredig and Danford.<sup>2</sup>



*Fig. 3.* Radial distribution functions (RDF) versus the distance  $r$  of the three dimensional model of lithium chloride. The RDF is defined at the distance  $r$  as the number of ions of one kind in the shell between  $r-0.05$  Å and  $r+0.05$  Å surrounding a given atom. The ordinate unit is scaled as to correspond to a shell of 1 Å thickness. The histogram gives the anion-anion distribution for the MC model. The fully drawn curve gives the anion-anion distribution calculated from experimental RDF's of Levy, Agron, Bredig and Danford.<sup>2</sup>

#### THE M.C. RADIAL DISTRIBUTIONS

The radial distribution histograms obtained as an average over the 10 000 steps in the M.C. chain from configuration No. 108 510 to No. 118 510, are given in Figs. 2 and 3. (Continuous curves replaces histograms only when the number of configurations become infinite, though for convenience the histograms have been shown as curves in our earlier paper.<sup>1</sup> The histograms represent the number of atoms of one kind in a shell 0.1 Å thick surrounding a given atom. (The ordinate unit is scaled so as to correspond to shell of 1 Å thickness.) The distribution is collected from a section of the chain where the energy exhibit no long range trend. Essentially the same distribution is found anywhere in the configuration range above configuration No. 30 000 for chain sections of 10 000 configurations or more. The change in  $b$ -value did not influence significantly the radial distribution.

Important features of the experimental curve are very well reproduced by the M.C. results. For the lithium-chlorine distribution in the melt, the first peak comes at 2.45 Å for the experimental and slightly below for the M.C. results. In the crystal this peak is at 2.57 Å at room temperature and at 2.66 Å at the melting point. The area under the peak corresponds to a coordination number 6 for the crystal as compared with 4.3 and 4.1 for experimental and M.C. results, respectively, taking 3.2 Å as the upper limit of the first shell. The positions and the coordination numbers of the first Li-Cl and Cl-Cl distances are tabulated in Table 4. The M.C. peak is sharper than the experi-

Table 4. Positions ( $R_0$ ) and coordination numbers (C.N.) of the first Li-Cl and Cl-Cl distances observed in the crystal and the melt compared with the results obtained from the M.C. model.

	Li-Cl peak		Cl-Cl peak	
	$R_0$ (Å)	C.N.	$R_0$ (Å)	C.N.
Crystal at 25°C	2.57	6	3.63	12
Crystal at melting point	2.66	6	3.76	12
Melt (observed)	2.45	4.3	3.85	11.2
M.C. model	2.40	4.1	4.10	11.1

mental peak. One of the causes for this discrepancy is probably an incomplete transformation of the M.C. model from the crystalline to the liquid state (perhaps due to the small M.C. cell size). The remnants of crystallinity can be seen from Fig. 4 which shows projections of the cell content along the  $X$ ,  $Y$ , and  $Z$  axes for configuration number 125 499.

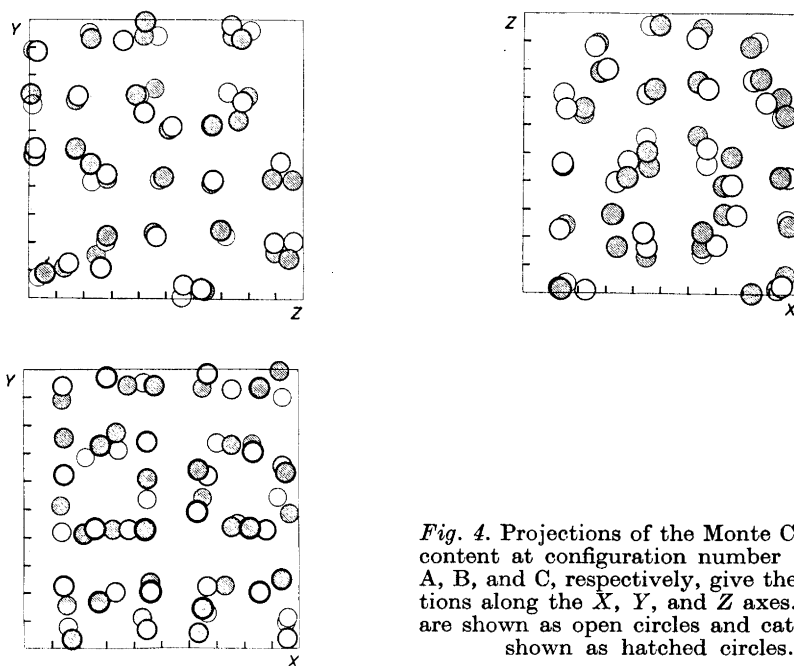


Fig. 4. Projections of the Monte Carlo cell content at configuration number 125 499. A, B, and C, respectively, give the projections along the  $X$ ,  $Y$ , and  $Z$  axes. Anions are shown as open circles and cations are shown as hatched circles.



The second lithium-chlorine peak in the crystal at 4.45 Å has vanished in the observed and M.C. molten state. Actually the experimental and M.C. curves show the same general shape over the whole region where M.C. data are available. The larger density of the experimental curve between 3 and 4.5 Å may arise from deficiencies both in the experimental curves and in the M.C. model.

The M.C. chlorine-chlorine distribution shown in Fig. 3, agrees well with the experimental curve in shape and peak position. The first M.C. peak occurs at 4.10 Å *vs.* 3.85 Å for the experimental curve. In both cases the peaks are shifted to higher values from the value 3.76 Å for the corresponding peak in the crystal at the melting point. (The first lithium-chlorine peak, it will be recalled, was shifted in the opposite direction from the value for the crystal at the melting point.) The area under the peak corresponds to a coordination number 11.2 for the experimental curve *vs.* 11.1 for the M.C. curve, counting 5 Å as the upper limit of the first shell. In our earlier paper<sup>1</sup> it was observed that the radial distribution curves were influenced by the Monte Carlo cell size. This effect, however, was rather small for the first coordination shell, but became more important for the second coordination shell when the two-dimensional cell contained 16 atoms only. This cell size in the twodimensional case corresponds to 64 atoms in the threedimensional case. The discrepancy between the M.C. chlorine-chlorine distribution and the experimental chlorine-chlorine distribution may therefore be due, partly at least, to the M.C. cell size.

To summarize, the M.C. distributions reproduce the following experimental observations (see Table 4): The first coordination shell is contracted and the second is expanded relative to the room temperature crystal or the melting point crystal. The coordination numbers are decreased on melting. This agreement with experiment is encouraging and the M.C. approach is believed to merit further investigations.

Since the present investigation has indicated that we may have encountered ergodic problems due to the cell size, we are now attempting calculations of a cell eight times larger than the present one in order to ensure a better sampling of phase space.

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