Table I. Activities of Silver and Silver Sulfide at 1200 °C

Mole Fraction of Sulfur	Log $p(S_2)^{0.5}$	$a(Ag)$ from $p(S_2)$	$a(Ag_2S)$ from $a(Ag)$	$a(Ag_2S)$ from $p(S_2)$
0.333	−0.980	0.678	1.000	1.000
0.32	−1.065	0.746	0.994	0.994
0.30	−1.152	0.816	0.974	0.974
0.25	−1.220	0.867	0.936	0.939
0.20	−1.256	0.888	0.902	0.907
0.15	−1.306	0.910	0.842	0.849
0.10	−1.378	0.932	0.741	0.754
0.07	−1.447	0.946	0.647	0.663
0.05	−1.529	0.957	0.546	0.562
0.04	−1.587	0.963	0.483	0.498
0.03	−1.691	0.972	0.385	0.399
0.02	−1.872	0.982	0.254	0.269
0.01	−2.181	0.993	0.116	0.135
0.00	0.000	1.000	0.000	0.000

products and reactants—given by GEF $= (G_T^\circ - H_{298}^\circ)/T$—to estimate the standard heat of formation of Ag_2S ($\Delta H_{f,298}^\circ$), using Eq. [7].[13]

$$\Delta H_{f,298}^\circ / T = -R \ln K_T - \Delta(G_T^\circ - H_{298}^\circ)/T \qquad [7]$$

Gibbs energy functions were taken from Reference 11, those for Ag_2S being extrapolated from 1000 K. The standard heat of formation of silver sulfide was calculated to be −100.9 kJ/mol, with a standard deviation of 1.0 kJ/mol. Published values include −96.3 and −96.9 kJ/mol.[11,12]

It is appropriate in this note to acknowledge the many and valuable contributions made by Professor Terkel Rosenqvist to the field of extractive metallurgy; his work stands the test of time. He has long been associated with the Norwegian Institute of Science and Technology (Trondheim). At the time the study of the silver-sulfur system was made (1949), he was with the Institute for the Study of Metals, University of Chicago.

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Analysis of Interfacial Area Changes during Spontaneous Emulsification of Metal Droplets in Slag

M.A. RHAMDHANI, G.A. BROOKS, and K.S. COLEY

In some metal/slag reactions involving spontaneous emulsification, there is a significant increase of interfacial area, which in turn affects the global rate. In previous work by the authors, the reaction between Fe-Al alloy droplets and $CaO-SiO_2-Al_2O_3$ slag was investigated. Re-evaluation of the data has shown that at an initial reaction rate above 9×10^{-7} mol min^{-1} mm^{-2}, the maximum change in interfacial area increases linearly with the initial rate and with the change of free energy due to chemical reaction. There were found to be two sources of interfacial area increase: (a) flattening of the original droplet, which was independent of initial rate; and (b) separation of smaller droplets, which was dependent on the initial rate.

DYNAMIC interfacial phenomena during reactions between liquid metal droplets and slag have been observed by many investigators.[1–7] These include droplet flattening, interfacial turbulence, and spontaneous emulsification, accompanied by spontaneous increase of interfacial area. The increase of interfacial area is significant, *i.e.,* can be up to 300 to 500 pct of the initial droplet area.[8,9] Therefore, in analyzing the kinetics, one needs to take into account these interfacial area changes. Recent work by the authors[9] proposed an approach for analyzing kinetics of reaction during spontaneous emulsification by incorporating the time-averaged interfacial area.

Change in reaction rates may induce dynamic interfacial phenomena and alter the reacting interfacial area. The spontaneous increase of interfacial area will again affect the reaction rates. This inter-relationship is not fully understood. Both kinetic information and interfacial area data during the reaction are vital for better understanding of the inter-relation. Unfortunately, such information is rather scarce. In our previous work,[9] the increase in interfacial area and the reaction rate between Fe-Al alloy droplets with $CaO-SiO_2-Al_2O_3$ slag was measured. In the course of this work, interesting relationships were found between the

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change in interfacial area and the initial rate of reaction as well as the free energy change during reaction. The authors are not able to offer an explanation for these observations, however believe them to be of sufficient importance, thus justifying this article. The purpose of this article is to stimulate debate in the hope that an explanation will emerge.

The experiments involved reactions between Fe-Al alloy droplets of different weights (1.7, 2.35, 2.5, and 3.45 g), containing 3.5, 4, 4.45, and 5 wt pct Al, with CaO-SiO_2-Al_2O_3 slag (40:40:20 in wt pct) at 1550 °C, 1600 °C, and 1650 °C. The amounts of slag used were 50 and 140 g. Chemical composition, interfacial areas, droplet shapes, sizes, and distributions were measured for each reaction time by quenching reacting samples. Details of the experiments, including experimental procedure, interfacial area measurement, and chemical analysis, have been described elsewhere.[8,9]

The recovered droplets from each reaction time show a similar sequence of shape change to that observed by previous investigators using X-ray radiography.[3,5] In the early stage of reaction, the recovered droplet has a nearly flat shape, indicating a decrease in interfacial tension. Numerous droplets, millimeter and micrometer in size, were recovered in the intermediate stage where the reaction was at its most intense. In general, during this emulsification period, the droplet disintegrated mainly into a single droplet of a weight less than the original accompanied by numerous much smaller droplets. The large droplet was flattened such that it had a much larger surface area than the original. The droplets recovered near the end of the reaction were nearly spherical and similar in shape to the equilibrium shapes observed by other investigators using X-ray radiograph.

Table I shows the summary of the effect of experimental conditions and parameters on the percentage increase of interfacial area, initial rate, and maximum number of droplets at maximum emulsification. The percentage increase of interfacial area was defined as 100 pct $\times$ $(A_{max} - A_0)/A_0$, where A_{max} and A_0 are the maximum and the initial interfacial areas, respectively. The initial rate was computed

from the slope of the curve concentration change of the metal droplet at initial, i.e., $(dn_{Al}/dt)_{t = 0}$, where n_{Al} is the aluminum content (in mol) and t is the reaction time (in minutes).

There is no obvious effect of the reaction temperature, the initial Al content, or the droplet size on the maximum number of droplets recovered. Rather, these parameters affect the percentage increase of interfacial area. In considering the number of droplets recovered from the reaction, it should be noted that, although the maximum number of droplets for some of the experiments is higher, this does not necessarily mean that they have a higher increase in interfacial area. This depends mainly on the interfacial area distribution of the recovered droplets. For example, in the case of Fe-4 wt pct Al alloy, 132 droplets were recovered; however, the increase of interfacial area is less than in the case of Fe-5 wt pct Al alloy, although only 103 droplets were recovered. Table II and Figure 1 show some of the results of the interfacial area change and the droplet distributions obtained from the current work. The solid and broken lines in Figure 1 represent the total and main (parent) droplet interfacial area changes.

The percentage increase in interfacial area tends to increase with increasing initial aluminum content in the metal droplet. The percentage interfacial area increase in the case of Fe-3.5 wt pct Al alloy droplet was about 218 pct, where for higher Al content, i.e., Fe-5 wt pct Al alloy, was up to 300 pct. This can be understood by looking at the initial rate of reaction ($A_0^{-1} \times dn_{Al}/dt$). As the initial Al content is increased, the initial rate increases. This will also increase the driving force for mass transfer. Assuming droplet flattening and emulsification are related to the rate of mass transfer, this will increase the driving force for flattening and emulsification, leading to higher interfacial areas.

It was also found that the percentage increase of interfacial area increased with decreasing initial droplet size. The increase of interfacial area was 254 pct for a droplet weight of 3.45 g (~10-mm o.d.) and up to 380 pct for a 1.7 g droplet (~7-mm o.d.). The mass transfer of Al in the droplet will be proportional to $1/r$, where r is the radius of the

Table I. Effect of Experimental Conditions and Parameters

	Maximum Number of Droplets	Total Increase of A $A (A_{max} - A_0)/A_0 \times 100$ pct	Initial Rate $\times 10^7$ (mol min^{-1} min^{-2})	$(A_{main\ drop} - A_0)/A_0$ $\times 100$ pct
Effect of initial Al content		2.3 g Fe-Al alloys at 1650 °C		
3.5 wt pct Al	29	218 ± 35	12 ± 1.2	155
4.0 wt pct Al	132	240 ± 32	15 ± 1.5	150
5.0 wt pct Al	103	300 ± 36	24 ± 2.4	178
		Fe-Al alloys at 1600 °C		
4.45 wt pct Al*	28	316	12 ± 1.2**	—
5.0 wt pct Al	36	294 ± 32	15 ± 1.5	293
Effect of temperature		2.35 g Fe-5 wt pct Al alloys		
$T = 1550$ °C	27	278 ± 20	11 ± 1.1	190
$T = 1600$ °C	36	294 ± 32	15 ± 1.5	193
$T = 1650$ °C	103	300 ± 36	24 ± 2.4	178
Effect of droplet size		Fe-5 wt pct Al aloys at 1650 °C		
wt = 1.71 g	35	380 ± 23	32 ± 3.2	194
wt = 2.35 g	103	300 ± 36	24 ± 2.4	178
wt = 3.45 g	18	254 ± 32	9.2 ± 1	154

*2.5 g droplet in 140 g slag.
**Maximum rate not at initial.

droplet. Again, assuming droplet flattening and emulsification are related to the rate of mass transfer, a larger droplet will have less driving force for flattening and emulsifica-

Table II. Interfacial Area Distribution during Reactions for the 2.35 g Fe-4.0 Wt Pct Al and 2.35 g Fe-5.0 Wt Pct Al Systems at 1650 °C

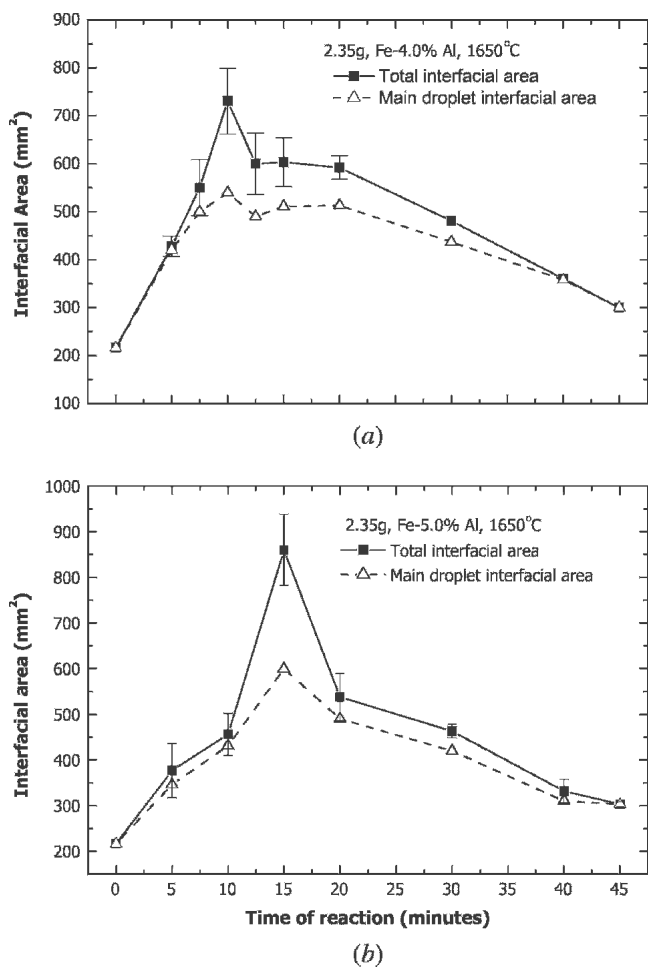| Area (mm²)	0	5	7.5	10	12.5	15	20	30	40	45
				Time (Min)						
2.35 g Fe-4.0 wt pct Al at 1650 °C										
<10	0	0	10	123	20	26	12	8	1	0
10 to 50	0	0	3	5	2	7	10	2	0	0
50 to 100	0	0	2	3	2	2	1	2	0	0
>100	1	1	1	1	1	1	1	1	1	1
Sum	1	1	16	132	25	36	24	13	2	1
2.35 g Fe-5.0 wt pct Al at 1650 °C										
<10	0	1	—	2	—	79	15	6	6	0
10 to 50	0	3	—	2	—	22	9	2	0	0
50 to 100	0	0	—	1	—	1	2	4	0	0
>100	1	1	—	1	—	2	1	1	1	1
Sum	1	5	—	6	—	104	27	13	7	1

Fig. 1—The total and main droplet interfacial area changes during the reaction between (a) 2.35 g Fe-4 wt pct Al and (b) 2.35 g Fe-5 wt pct Al droplets with CaO-SiO₂-Al₂O₃ slag at 1650 °C.

tion, leading to a lower interfacial area increase. It should be noted that, although the increase of interfacial area for the 1.7 g droplet is higher than that of 3.45 g, the actual interfacial area, A_{max}, is smaller.

In the temperature range studied, the effect of temperature on the maximum increase of interfacial area was not pronounced, although it was observed that the initial rate increases with increasing temperature. The interfacial area increase for $T = 1550$ °C was 278 pct, whereas for $T = 1650$ °C, it was 300 pct.

General observation of the experimental data suggests that the percentage increase of interfacial area is affected by the initial rate. Figure 2 shows the effect of initial rate on the percentage increase of interfacial area. Each data point in Figure 2 was extracted from a composite of many experiments. In the case of a chaotic process such as spontaneous emulsification, some scatter in the experimental results, e.g., interfacial area value, can be expected. The scatter, however, is still in the acceptable limit. The errors in the value of $\Delta A_{max}/A_0$, for example, were determined to be in the range between ±6 and ±6 pct with an average of ±11 pct.

In this case, the initial droplet areas were used in calculating the initial rates. The total increase consisted of an increase of interfacial area of the parent droplet due to droplet flattening and interfacial roughening and an increase due to formation of smaller droplets due to spontaneous emulsification. The solid and open symbols represent data for the total and the parent droplet interfacial area, respectively. It was found that the component of the total increases in interfacial area arising from the generation of new droplets increases linearly with the increasing initial
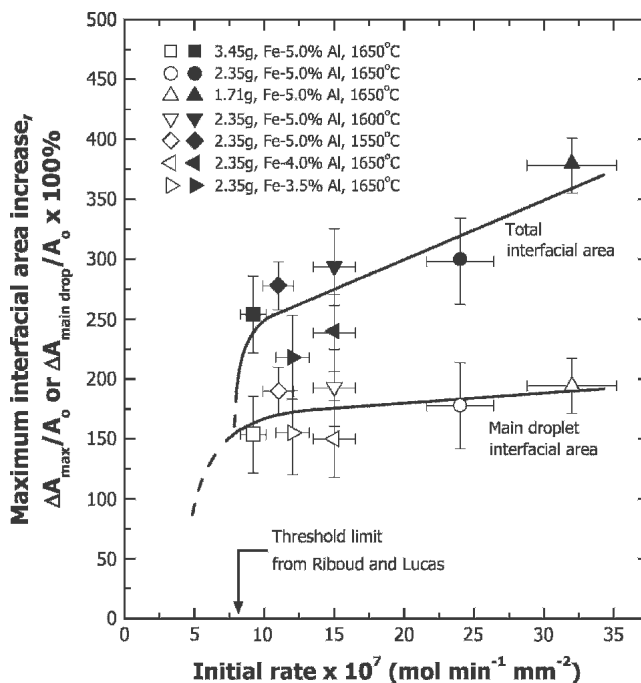

Fig. 2—The relationship between the initial rate with the total (solid symbols) and with the main droplet (open symbols) interfacial area increases at maximum emulsification. Also shown is a threshold limit from Riboud and Lucas.

rate. The increase in the parent droplet interfacial area, however, is rather independent of the initial rate. These results are interesting because they may suggest the following: the intensity of the reaction, and possibly its nonuniformity, induced some form of tangential forces acting on the droplet. In response to these forces, the droplet flattened and its interfacial area increased. At some threshold reaction rate, the forces required to cause further flattening may exceed those required to generate small droplets. At this rate, small droplets will break off the parent droplet, which will flatten no further. This threshold rate appears to be somewhere below the rate of 9×10^{-7} mol min^{-1} mm^{-2}. To the authors' knowledge, there is no available published work consisting of both interfacial area and rate data for rates below 9×10^{-7} mol min^{-1} mm^{-2}.

Riboud and Lucas[3] investigated the influence of mass transfer on interfacial phenomena by evaluating an equivalent oxygen flux, $\dot{n}_{(O)}$, from various slag metal reactions. The equivalent oxygen flux was calculated from the flux of the oxidizable elements (in the case of Fe-Al alloy reacting with CaO-SiO$_2$-Al$_2$O$_3$, is the flux of Al), and Riboud and Lucas considered an interfacial area of twice the initial droplet area to account for surface roughness. The apparent interfacial tension changes during reaction were measured from X-ray photographs. Riboud and Lucas reported, for the various reactions, that the apparent interfacial tension seemed to disappear when the value of equivalent-oxygen-flux was larger than 0.1 mol m^{-2} s^{-1}. For values of this flux lower than 0.01, interfacial tension recovers rapidly to a value very close to the equilibrium value. This value was calculated using an interfacial area of twice the initial droplet area. Correcting this value, *i.e.,* considering flux over the initial droplet area, one will obtain the value $\dot{n}_{(O)} = 0.02$ mol m^{-2} s^{-1} (=12 $\times 10^{-7}$ mol mm^{-2} min^{-1}). Reconverting this value in terms of the rate of Al decrease by reaction in Eq. [1],[3]

$$2\underline{Al} + 3(O)_{slag} = Al_2O_3 \qquad [1]$$
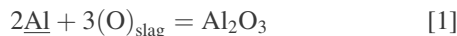
and by considering that $\dot{n}_{(O)} = 1.5 \ \dot{n}_{\underline{Al}}$, the value of $\dot{n}_{\underline{Al}} = 8 \times 10^{-7}$ mol mm^{-2} min^{-1} is obtained. Riboud and Lucas[3] did not report the actual value of the interfacial area increase for this particular rate. This, considered as the threshold value, is also shown in Figure 2. Below this value, dynamic interfacial phenomena last for only a short time.

Further increase in interfacial area beyond the threshold value is solely due to the formation of small droplets. The higher the initial rates, the higher the interfacial area due to droplet emulsification. Dynamic secondary ion mass spectrometry (SIMS) work suggested the presence of pockets of fluid of the scale 1 to 2 μm with different oxygen contents moving about within the bulk near the interface during the early stages of reaction.[10] These length scales are similar in size to protrusions from the droplet observed using scanning electron microscopy.[11] The pockets of fluid may have caused oxygen concentration gradients along the interface at the same length scale and may be in part responsible for the turbulence that led to the formation of the protrusions and emulsification on a microscale (1 to 2 μm). This may suggest that a high initial rate is associated with an increase in the number of local instabilities at the beginning of reaction, *i.e.,* inducing more pockets of O-rich metal.

The maximum increase of interfacial area was also evaluated in terms of the change in the free energy due to chemical reaction. In the case of reaction between Fe-Al alloy droplets and CaO-SiO$_2$-Al$_2$O$_3$ slag, the following overall chemical reaction occurs:

$$\underline{Al} + \tfrac{3}{4}(SiO_2)_{slag} = \tfrac{3}{4}\underline{Si} + \tfrac{1}{2}(Al_2O_3)_{slag} \qquad [2]$$
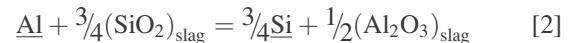
Let us define λ as the total decrease of free energy up to maximum emulsification due to chemical reaction as represented by the following equation:

$$\lambda = \int_0^{t_{A-max}} \left(\frac{d\Delta G^{Reaction}}{d\zeta}\right)\left(\frac{d\zeta}{dt}\right)dt \qquad [3]$$

where $\Delta G^{Reaction}$ is the change in the free energy due to the chemical reaction in Eq. [2], $t_{A\text{-}max}$ is the reaction time, where the interfacial area is at maximum, and ζ is the extent of reaction (defined as $n_{Al} - n_{Al,0}$ and computed from the curve of Al concentration change). Thus, a plot of λ *vs* the maximum interfacial area increase, ΔA_{max}, for all the systems studied can be constructed, as shown in Figure 3. It can be seen from the plot that ΔA_{max} increases linearly with an increasing value of λ. The inverse of the slope of the line in Figure 3 has a unit of interfacial energy or interfacial tension and was determined to be 0.88 J/mm^2. The magnitude, however, is six orders higher than that of equilibrium interfacial tension of the systems studied. This strongly suggests that there are other forces at play not yet considered. It should also be noted that a considerable amount of this energy was dissipated as heat to the slag.[8]

In summary, the results presented are unique. However, a lot of work is required to fully explain the results as well as for comprehensive understanding of the inter-relationship between dynamic interfacial phenomena, reaction kinetics, and interfacial area generation. At an initial rate above 9×10^{-7} mol min^{-1} mm^{-2}, the maximum change in interfacial area was found to increase linearly with the initial rate and with the change of free energy due to chemical reaction. The increase in interfacial area due to the separation of smaller droplets and due to the flattening of the parent
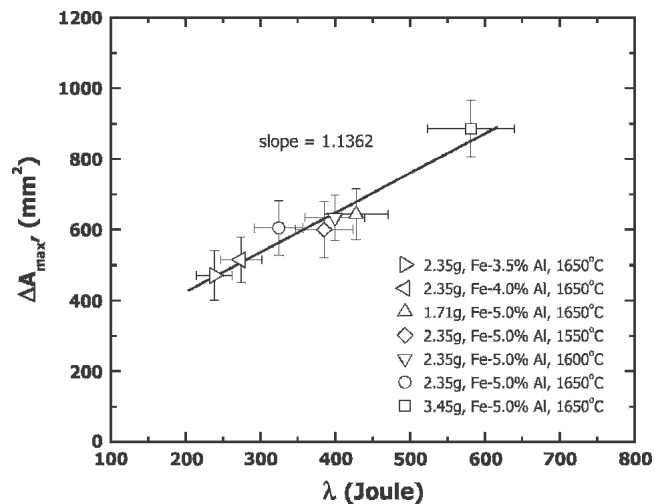

Fig. 3—A plot showing the relationship between lambda and the total decrease in interfacial area in the systems studied.

droplet was found to be dependent and independent of the initial rate, respectively. More experimental data, especially on the interfacial area changes during reaction with lower initial rates, are required for the determination of the onset of emulsification. To date, a consistent quantitative explanation of these results has eluded the authors. It is expected that this work will stimulate a level of discussion from which a clear explanation will emerge.

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Prediction of Activities of Three Components in the Ternary Molten Slag CaO-FeO-SiO$_2$ by the Molecular Interaction Volume Model

DONG PING TAO

In this article, a novel thermodynamic model—the molecular interaction volume model (MIVM)—was employed to predict the activities of three components in the ternary molten slag CaO-FeO-SiO$_2$ at different temperatures. The results show that the predicted values of activity of CaO and SiO$_2$ are in reasonable agreement with the experimental data in a range of lower concentrations, which are about $x_{CaO} < 0.2$ for CaO and about $x_{SiO_2} = 0.15$ to 0.50 for SiO$_2$

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at 1823 K, respectively, and that the predicted values of activity of FeO are in good agreement with the experimental data in a range of entire concentrations at 1623, 1823, and 1873 K. This shows that MIVM is an alternative for the estimation of activity coefficients of all components in a ternary molten slag, where its activity data are absent or their accuracies are questionable only when its sub-binary activities are known and reasonably reliable.

THE molten slag CaO-FeO-SiO$_2$ is a basic system for process metallurgy such as steelmaking, tin or lead smelting, and matte making. It is indispensable to obtain activities of three components in the slag, especially ferrous oxide, for understanding and describing chemical reactions between the liquid metal or matte and molten slag. During the past 6 decades, various thermodynamic models have been proposed to predict activities of components in ternary molten slags, which have been reviewed and commented on in the literature.[1,2,3] In general, an oversimplification model leads to multicomponent interaction parameters, which are fitted by the multicomponent experimental data into modeling, whereas an overcomplication model brings about more restricted conditions in application. So, it is necessary to balance prediction accuracy and physical perspective due to lack of detailed melt structures and species interactions.

The purpose of this work is to show that the molecular interaction volume model (MIVM)[4,5] has certain physical meaning from the viewpoint of statistical thermodynamics and so is an alternative for the estimation of activity coefficients of all components in a ternary molten slag, where its activity data are absent or their accuracies are questionable only when its sub-binary activities are known and reasonably reliable.

The MIVM was obtained from the physical perspective of molecular or atomic movements of liquid in that liquid molecules or atoms differ from gas molecules, which are in continuous irregular motion and differ from solid ones, which vibrate constantly at lattice sites but migrate nonrandomly from one cell to another. It implied that the cell molecules are not stable and they have a chance to move into an adjacent hole as a central molecule; namely, it was assumed that liquid molecules can freely move through a cell space and the molecular interaction separation approaches the cell diameter at a certain temperature. Thus, the so-called central molecules and their closest molecules are relative and exchangeable, and cells are movable and indistinguishable. For a ternary solution, there are three types of molecular cells and the molecular pair interaction is taken into account. Its molar excess Gibbs energy can be expressed as

$$G_m^E = RT \left[\sum_{i=1}^{3} x_i \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{\Delta \varepsilon_p}{2kT} \right] \quad [1]$$

where x_i is the molar fraction of component i; $\varphi_i = x_i V_{mi}/V_m$ is the molar volume fraction of component i in the system; and V_{mi} and V_m are the molar volumes of component i and the system, respectively. The excess potential energy function of the system is