

Thermodynamic Properties of Silicates and of Alumino-Silicates From Montecarlo Calculations

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Some thermodynamic properties of silicates, aluminates and aluminosilicates have been calculated with the Montecarlo method. This method, developed by Salzburg *et al*, has been applied in the present paper to the calculation of the canonical ensemble partition function. The calculated results are satisfactorily in agreement with the experimental data collected from the literature.

THE structure and thermodynamic properties of slags are of fundamental importance for understanding ironmaking and steelmaking processes and for improving the related technology.

Direct experimental measurement of slag thermodynamic data is a difficult, expensive (and sometimes impossible) task, mainly because of the high temperature involved in the operation; as a result, theoretical methods are being increasingly used.

These methods are based on statistical physics and require for their application to set up an appropriate physical model of the slag being investigated.

Presently the lattice model representation¹⁻⁴ and the quasichemical calculation procedure⁵ are the traditional and more widely used tools for investigating the behavior and influence of slag constituents. The quasichemical procedure, however, presents two main disadvantages. Formerly, it tends to underestimate probability correlations between different lattice particles occupying different sites,⁶ underestimation being larger as the energy of possible interaction increases.

Therefore, the mathematical formulation of the procedure becomes increasingly difficult as the physical model of the system being investigated becomes more complex.

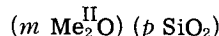
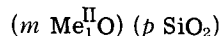
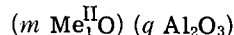
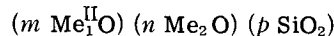
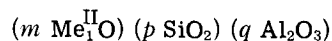
With bigger and faster computers, the Montecarlo method has become increasingly common as a tool for studying lattice statistics, instead of the more traditional techniques such as the quasichemical method. Actually, the Montecarlo method permits a fairly simple mathematical formulation and involves only approximations inherent to the physical model selected to represent the system. While the method has the drawback of a large computing time even using a modern computer, nevertheless it has the advantage of giving (as an additional output) information on the ionic species present in the system. A result of this kind would only be possible with the more traditional statistical physics methods by introducing additional hypotheses.³

On the basis of the above considerations, an attempt was made to use the Montecarlo method for determining the thermodynamical and structural properties

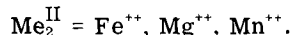
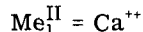
of slags. The present work describes the first results obtained by applying the Montecarlo method.

1. SYSTEMS INVESTIGATED AND THEIR PHYSICAL MODEL

The slag systems investigated can be represented by the following formulas:

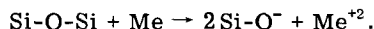


in which:



The procedure adopted for representing these slag systems with a lattice model is described in Ref. 2. The model was applied regardless of whether the slag was in the solid or in the liquid phase at operating temperature; in addition, tetrahedral coordination was assumed for all lattice sites.

The formation of silicates takes place according to a reaction of the following type:³



It is well known⁹⁻¹³ that in slag systems containing aluminosilicate constituents, the aluminum atom can replace the silicon atom and consequently can coordinate four oxygen atoms tetrahedrally, provided that atoms such as Ca, Mg are present in the slag system; these atoms are capable of transferring one valence electron to the aluminum thus making the aluminum tetravalent. Accordingly and in the particular case of $(m \text{ CaO}) (q \text{ Al}_2\text{O}_3)$ and of $(m \text{ CaO}) (p \text{ SiO}_2) (q \text{ Al}_2\text{O}_3)$ systems, tetrahedral coordination was assumed for the aluminum whenever the CaO molar fraction exceeded the Al_2O_3 molar fraction.

Furthermore, metal cations were represented in the model by appropriate silicon and/or aluminum lattice vacancies.

The following correspondences were established between model configurations and the chemical species present in the real systems:

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Model	Chemical Species	
Si-Si	Si-O-Si	(a)
Si-Vac	Si-O ⁻	(b)
Vac-Vac	O ⁻	(c)
Al-Al	⁻ Al-O-Al ⁻	(d)
Al-Vac	Al ⁻ -O ⁻	(e)
Al-Si	Al ⁻ -O-Si	(f)

where:

- (a), (d), (f) = oxygen with covalent bonds,
 (b), (e) = terminal parts of anions,
 (c) = free oxygen ion, and
 Vac = vacancy.

2) APPLICATION OF MONTECARLO METHOD TO LATTICE SYSTEMS

The basic problem to be solved when calculating the thermodynamic properties of a system is the determination of the correct partition function. For systems having a constant number of particles and for constant volume and temperature the appropriate partition function is the canonical function Q . The canonical partition function Q is related to Helmholtz's free energy F by the equation

$$F = -KT \ln Q$$

where:

- K = Boltzmann's constant, and
 T = absolute temperature.

For the systems such as those investigated here, Helmholtz's free energy F can be considered approximately equal to Gibbs's free energy G ; hence,

$$G = -KT \ln Q.$$

If the normal approximations described by Guggenheim⁸ are now introduced, the value of Q can be determined simply by calculating the configurational partition function (Q_{conf}).

For calculating the configurational energy E , the following assumptions have been made: a) only interactions between next neighbors could take place; b) the energy bond between two given lattice species was not influenced by other species eventually present and was equal to the bond between the same two lattice species when the model was applied to the pure compound formed by them; for instance, it was assumed that the energy of the Si-O-Si bond was the same both in silica and in silicates.

To comply with the second assumption, $\text{CaO} \cdot \text{Al}_2\text{O}_3$ was chosen instead of Al_2O_3 as reference state for aluminates, since the aluminum in $\text{CaO} \cdot \text{Al}_2\text{O}_3$ is entirely tetrahedral with an aluminum to oxygen ratio equal to the silicon to oxygen ratio of silica.

The configurational energy E was calculated with the formula:

$$E = \sum_{j=1}^n \sum_{k=j}^n n_{jk} \epsilon_{jk}$$

where:

- n = number of lattice species present,
 n_{jk} = number of (jk) pairs present in the lattice, and
 ϵ_{jk} = interaction energy of (jk) pairs.

The ϵ_{jk} energies were obtained from the heat content required for forming the (jk) binary compounds at zero absolute temperature. It was accepted that the ϵ_{jk} energies obtained in this way were the same for all compounds in which the species j and k were present.

A brief description of the procedure⁷ used for applying the Montecarlo method to slag systems is required at this point. At the beginning the particles are randomly distributed in the lattice sites. A Markovian chain of configurations is then generated according to the following criteria. Let j be the present configuration and l the configuration obtained when two particles located at any two lattice sites exchange positions; moreover, let E_j and E_l be their respective configurational energies. If $E_l > E_j$, the new configuration l is accepted unconditionally for the next step in the chain; if instead $E_l < E_j$, the new configuration is accepted only when $\exp[(E_l - E_j)/KT]$ is greater than a random number selected between 0 and 1. Otherwise the configuration j is the next step in the chain.

When this iterative process is developed to a sufficient extent using a counter for each E value obtained, the number $m(E)$ of times a specific E value has occurred along the chain will be established. Let $P(E)$ now be the statistical weight of the E energy level; one has from statistical mechanics.

$$P(E) = \Phi(E) \cdot e^{\frac{E}{KT}} \cdot Q_{\text{conf}} \quad [1]$$

where:

$\Phi(E)$ = probability of observing the E energy level, and

Q_{conf} = configurational partition function.

As the lattice (B sites) contains N_i particles of i type, the conditions for normalizing with respect to $P(E)$ is given by:

$$\sum_E P(E) = \frac{B!}{N_1! \cdot N_2! \cdot \dots \cdot N_i!}$$

equal, in other words, to the number of distinct configurations of the system; Expression [1] becomes:

$$\sum_E P(E) = Q_{\text{conf}} \sum_E \Phi(E) \cdot e^{\frac{E}{KT}} = \frac{B!}{N_1! \cdot N_2! \cdot \dots \cdot N_i!}$$

and therefore:

$$Q_{\text{conf}} = \frac{B!}{\sum_E \Phi(E) \cdot e^{\frac{E}{RT}}}$$

in which $\Phi(E)$ is estimated by:

$$\Phi(E) = m(E) / \sum_E m(E).$$

The accuracy with which Q_{conf} is determined will be greater the closer $\Phi(E)$ is estimated, *i.e.*: the longer the iterative process for expanding the Markovian chain is continued. Usually, a compromise has to be made between a fairly accurate estimate and an excessive number of steps, involving a large computer time. In this connection, it was found that the magnitude of the error introduced by arresting the iterative

process after $2 \times 10^6 + 3 \times 10^6$ steps was small compared with the error of ϵ_{ijk} estimates.

For binary compounds with free energies of the order of $-20,000$ cal/mole, an error of 1, 2 pct in the estimate of ϵ_{ijk} generally produces an error of $\pm 1,000$ cal in the estimate of their free energy, *i.e.*: a closer approximation than when experimentally determining free energies.

An other error source was estimated by starting the Markovian chain from two different configurations. It was found that after approximately 10^6 steps the results, for a given compound, differed at maximum by 10, 20 cal/mole.

The free energies obtained in the course of this study were referred to *B* sites lattices. The corresponding thermodynamic quantities were extrapolated for $B \rightarrow \infty$; practically, this was done by plotting the free energy values of the *B* sites lattices against the parameter $1/B$ and extrapolating for $1/B \rightarrow 0$. Larger lattices were obtained by regular three-dimensional repetition of an 8 sites unit cell. The surface effects

resulting from the use of small lattices were minimized by laying down the usual periodic boundary conditions.

3) RESULTS

a) Free Energies of Binary and Ternary Systems

The values obtained for the free energy of formation at 1800 K of seven binary systems are given in Table I. When investigating ternary systems of the type $(m \text{ Me}_1^{\text{II}}\text{O}) (n \text{ M}_2^{\text{II}}\text{O}) (p \text{ SiO}_2)$, the energy of interaction between the two vacancies (the one associated with Cation 1 and the other with Cation 2) was determined as suggested by Niwa,² Richardson,²³ and Toop and Samis,¹ *i.e.*: the mixture of vacancies associated with the two cations was assumed to behave as an ideal mixture and the interaction energy was therefore set equal to zero. For the $(m \text{ Me}_1^{\text{II}}\text{O}) (p \text{ SiO}_2) (q \text{ Al}_2\text{O}_3)$ ternary system, the interaction energy of the Al-Si pair was instead estimated on the basis of the enthalpy of formation (at 0 K) for obtaining anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) from calcium aluminate and silica. Given the stoichiometric proportions with which calcium oxide, alumina and silica combine together to form anorthite, this compound can be represented in the model as a mixture of tetrahedrally coordinated aluminum and silicon atoms. The following value was determined for the Al-Si pair:

$$\epsilon_{\text{Al-Si}} = -0.37 \times 10^{-20} \text{ cal/bond.}$$

Table II gives the results obtained for the three ternary systems mentioned above.

b) Determination of Ternary System Activities

Free energy values were also used for estimating activities of individual components. The following determinations were carried out for comparison purposes:

- 1) CaO-Al₂O₃-SiO₂ system: CaO activity for pct SiO₂/pct Al₂O₃ = 1.16 and for $T = 1873$ K (1600°C):
- 2) FeO-CaO-SiO₂ system: FeO activity for: a) $T = 1623$ K (1350°C); pct CaO/pct SiO₂ = 0.80; and b) $T = 1873$ K (1600°C); pct CaO/pct SiO₂ = 0.46.

The free energies of mixing determined for the three cases mentioned above are shown in Figs. 1 and 2. The activity values are listed in Tables III, IV and V, where they are also compared with the corresponding values obtained: i) experimentally; and ii) with the

Table I. Free Energies of Formation of Binary Compounds

Compound	$\epsilon \text{ X-Vac}^*$, cal/bond	ΔG cal- culated, cal/mole	ΔG exp., cal/mole	Refer- ence
2CaO SiO ₂	-1.33×10^{-20}	-35600^\dagger	-33860	14
			-35519	15
			-34840	16
CaO SiO ₂	-1.33×10^{-20}	-20000^\dagger	-19600	14
			-22360	17
			-20645	16
2MgO SiO ₂	-0.53×10^{-20}	-15000^\dagger	-14940	14
			-15040	15
			-14504	16
2MnO SiO ₂	-0.25×10^{-20}	-8700^\dagger	-7700	2
2FeO SiO ₂	0.00	-5100^\dagger	-3110	14
			-5200	18
			-5800	19
			-4900	20
			-5300	21
3CaO Al ₂ O ₃	0.10×10^{-20}	-5300^\ddagger	-3380	14
			-5640	15
			-6500	16
12CaO 7Al ₂ O ₃	0.10×10^{-20}	-28000^\ddagger	-23700	14
			-30500	15

*X = Si, Al.

† Starting from oxides.

‡ Starting from CaO·Al₂O₃ and CaO.

Table II. Free Energy of Formation of Ternary Compounds

Compound	$\epsilon \text{ Si-Vac (Ca}^{++}\text{)}$, cal/bond	$\epsilon \text{ Si-Vac (Mg}^{++}\text{)}$, cal/bond	$\epsilon \text{ Si-Vac (Fe}^{++}\text{)}$, cal/bond	$\epsilon \text{ Al-Si}^*$ cal/bond	$\epsilon \text{ Al-Vac (Ca}^{++}\text{)}$, cal/bond	<i>T</i> K	ΔG cal- culated, cal/mole	ΔG exp., cal/mole	Ref
CaO·MgO·SiO ₂	-1.33×10^{-20}	-0.53×10^{-20}	—	—	—	1,773	-29900	-26800	24
							-28000	25	
							-21500	26	
2FeO·2SiO ₂ ·CaO	-1.33×10^{-20}	—	0.00	—	—	1,873	-28000	-30000†	27
2CaO·Al ₂ O ₃ ·SiO ₂	-1.33×10^{-20}	—	—	-0.37×10^{-20}	$0.10 \cdot 10^{-20*}$	1,800	-28400	-32400†	14
							-30800‡	28	

*In calcium silicoaluminate.

† Evaluated on the basis of the activities reported in the reference quoted.

‡ Starting from CaO·Al₂O₃, CaO and SiO₂.

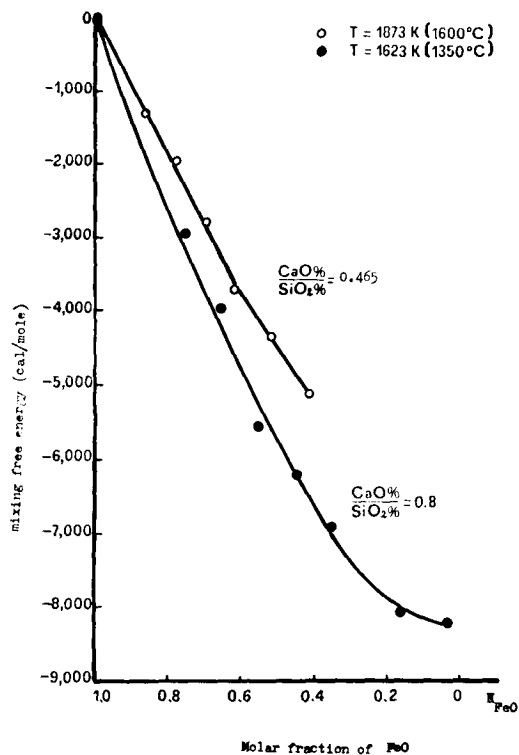


Fig. 1—FeO-CaO-SiO₂ system: calculated free energy of mixing.

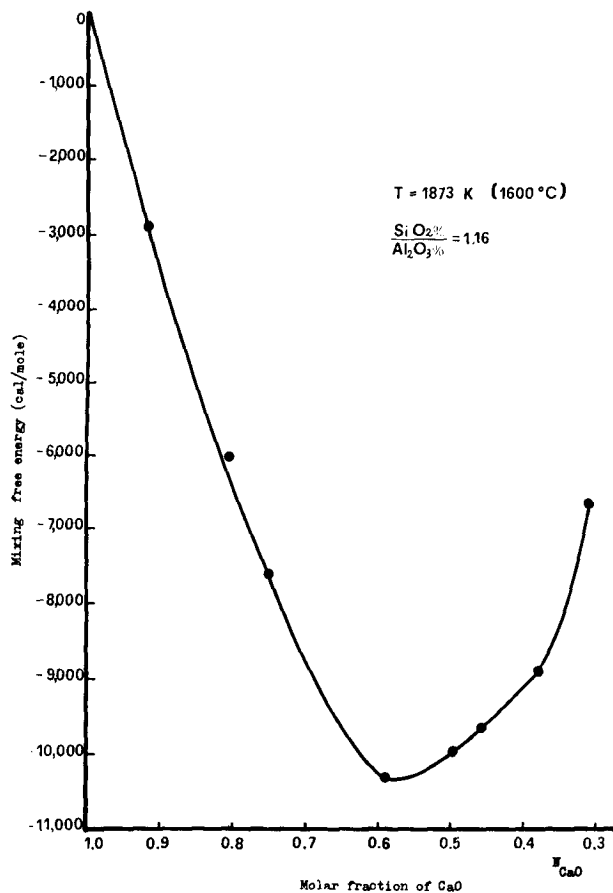


Fig. 2—CaO-SiO₂-Al₂O₃ system: calculated free energy of mixing.

Hagemark²⁹ quasi-chemical method adopting the same interaction energy values used for calculations with the Montecarlo method. A comparison of the data in the three tables leads to the following conclusions.

1) The values calculated for the activities are fairly close to those obtained experimentally; this agreement confirms the validity of the hypotheses made for the present investigation.

Table III. CaO Activities in the System CaO-SiO₂-Al₂O₃

System CaO Al ₂ O ₃ SiO ₂			Pct SiO ₂ / Pct Al ₂ O ₃ = 1.16 T = 1873 K		
Pct CaO	Pct SiO ₂	Pct Al ₂ O ₃	Monte Carlo Activity	Quasi-chemical Method Activity ²⁹	Activity, exp. ¹⁵
89.31	5.74	4.95	0.91	0.77	
76.63	12.55	10.82	0.73	0.47	
69.44	16.41	14.15	0.61	0.32	0.5*
52.74	25.38	21.88	0.12	0.07	Between 0.1 and 0.2*
43.07	30.57	26.36	0.029	0.021	0.025
38.86	32.83	28.31	0.016	0.012	0.014
32.28	36.37	31.35	0.005	0.005	0.005
25.19	40.18	34.63	0.001	0.002	0.003

*Estimated on the basis of the values of the CaO-SiO₂ binary system, and of the isoactivity line referred to under Ref. 15.

Table IV. FeO Activities in the System FeO-CaO-SiO₂
T = (1573 to 1673) K

System CaO-FeO-SiO ₂			Pct CaO / Pct SiO ₂ = 0.80 T = (1573 to 1673) K		
Pct FeO	Pct CaO	Pct SiO ₂	Monte Carlo Activity	Quasi-chemical Method Activity ²⁹	Activity, exp. ³⁰
80.00	8.89	11.11	0.88	0.91	0.89
70.00	13.33	16.67	0.84	0.88	0.81
60.00	17.78	22.22	0.71	0.82	0.70
50.00	22.22	27.78	0.60	0.77	0.60
40.00	26.67	33.33	0.45	0.69	0.42
30.00	31.11	38.89	0.28	0.48	0.30
20.00	35.56	44.44	0.17	—	—
10.00	40.00	50.00	0.10	—	—

Table V. FeO Activities in the System FeO-CaO-SiO₂
T = 1873 K

System CaO-FeO-SiO ₂			Pct CaO / Pct SiO ₂ = 0.465 T = 1873 K		
Pct FeO	Pct CaO	Pct SiO ₂	Monte Carlo Activity	Quasi-chemical Method Activity ²⁹	Activity, exp. ²⁷
89.11	3.47	7.42	0.99	0.87	0.98
82.67	5.51	11.82	0.96	0.82	0.97
75.42	7.82	16.76	0.92	0.76	0.90
67.16	10.45	22.39	0.87	0.69	0.86
57.67	13.47	28.86	0.86	0.61	0.83
46.68	16.97	36.35	0.69	0.50	0.73

2) The more the behavior of the oxide system deviates from ideality, the less accurate are the results obtained by the quasichemical method. The trend is clearly evident in the FeO-SiO₂ systems in which Si-Si and Vac (Fe)-Vac (Fe) interactions are zero (in compliance with the chosen reference state) and the Si-Vac (Fe) interaction is practically zero; for these systems therefore, the real system matches the behavior of the ideal system as closely as possible. As FeO is increasingly replaced with CaO, the real system deviates always more from the ideality and the values obtained with the quasichemical method become more inaccurate (see Tables IV and V). A similar trend can be identified also in Table III where the quasichemical method produces always more acceptable results as the CaO percentage of the system decreases (*i.e.*: the interaction energies involved decrease).

4) CONCLUSIONS

On the basis of the results obtained, it appears that the physical model set up and the Montecarlo technique applied do provide a suitable tool for calculating thermodynamic properties of oxide systems. In addition, the processing form seems adequate also for nonideal systems.

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