Properties of Molten Magnesium Oxide

(ceramic materials/molecular clustering/high temperature/molecular model/partition function)

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ABSTRACT The Significant Structure Theory of Liquids has been used to calculate the thermodynamic properties, viscosity, self-diffusion coefficient, and specific conductance of molten magnesium oxide, taking account of the decomposition of MgO to Mg and O₂ species in the gas-like part of the partition function.

Introduction

Magnesium oxide and many other metal oxides are well known refractory materials which in general have very high melting points and have been widely used in applications where high heat resistance is required.

The available experimental data for MgO are limited to its solid state properties with very little being known about this material above its melting point. In this study, a theory is proposed which is expected to give reasonable predicted values of the thermodynamical and transport properties of magnesium oxide in its molten state.

The Theory of Molten Salts by Significant Structure Method was developed by Eyring *et al.* (1-5). In this theory, a liquid near its melting point is considered to have a quasi-lattice structure with mobile "fluidized vacancies" that are fairly sharply distributed about molecular size and randomly distributed throughout the structure. Such fluidized vacancies change three vibrational degrees into translations as they are cooperatively moved about by the neighboring molecules. These vacancies also give rise to a positional degeneracy for neighboring solid-like molecules. The Significant Structure Theory of Liquid is based on the assumption that a portion of the liquid molecules, V_s/V , have solid-like degrees of freedom and the remainder have gas-like degrees of freedom. Here, V_s is the molal volume of the solid-like portion while V is the molal volume of the liquid. Since a particular molecule is fenced in by neighbors the fraction of the time, V_s/V , it is natural to think of this fraction of molecules behaving like a solid, with the remaining fraction $1 - V_s/V$ behaving like a gas.

In the present work, the partition function used by Carlson *et al.* (4), is modified to take account of the existence of equilibration of MgO with gaseous magnesium atoms and oxygen molecules.

Partition function

In the solid-like structure, the magnesium ion and the oxygen ion oscillations are approximated by a single average Einstein frequency. Because 1 mole of MgO crystal contains $2N$ particles, the solid-like partition function is raised to the $2N(V_s/V)$ power. The potential energy (energy of sublimation) per ion is then given by $E_s/2N$. To correct for the long

range nature of the coulombic interionic potential resulting in clustering as compared with the Van der Waals potential, the sublimation energy, E_s , for the solid has been multiplied by the factor $(V/V_s)^{1/3}$.

Since a portion of MgO decomposes into Mg and O₂ in the gas phase (6, 7), the gas-like partition function should consist of partition functions for all these three species. The contribution due to each of these species depends on the dissociation energy D_0 . The value of D_0 cannot be too great if there are to be significant concentrations of Mg and O₂.

Based on these considerations the overall partition function for molten magnesium oxide is written as:

$$f = \left\{ \frac{e^{E_s/2RT} (V/V_s)^{1/3}}{(1 - e^{-\theta/T})^{1/3}} \left[1 + n \left(\frac{V}{V_s} - 1 \right) e^{\frac{-aE_s(V/V_s)^{1/3}}{2(V/V_s - 1)RT}} \right] \right\}^{2N(V/V_s)} \\ \cdot \left\{ \left(\frac{2\pi m_1 kT}{h^3} \right)^{3/2} \cdot \frac{8\pi^2 I_1 kT}{h^2} \cdot \frac{1}{1 - e^{-h\nu_1/RT}} \right. \\ \left. + e^{-D_0/RT} \left[\frac{(2\pi m_2 kT)^{3/2}}{h^3} \right] \cdot \left[\frac{3(2\pi m_3 kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I_3 kT}{2h^2} \right. \right. \\ \left. \left. \cdot \frac{1}{1 - e^{-h\nu_3/kT}} \right]^{1/2} \cdot \left(\frac{2eV}{N} \right)^{1/2} \right\} \frac{eV}{N} \left(\frac{V - V_s}{V} \right)^N \quad [1]$$

Where θ is the Einstein characteristic temperature; V_s is the molar volume of the solid at the melting point; V is the molar volume of the liquid; n and a are parameters; the subscripts 1, 2, and 3 appearing on the molecular masses m , are the moments of inertia, I ; and the frequencies ν , indicate MgO, Mg, and O₂, respectively. T , R , k , h , and N are the absolute temperature, the gas constant, Boltzmann's constant, and Avogadro's number, respectively.

In the calculations, the following physical constants are used:

$m_1 = 6.697 \times 10^{-23}$ g; $m_2 = 5.314 \times 10^{-23}$ g; $m_3 = 4.05 \times 10^{-23}$ g; $I_1 = 7.06648 \times 10^{-39}$ g cm² (8); $I_3 = 1.938 \times 10^{-39}$ g cm² (ref. 9, moment of inertia is calculated by $r_e = 1.2704$ Å); $\nu_{\text{MgO}} = 2.706 \times 10^{13}$ sec⁻¹ (8); $\nu_{\text{O}_2} = 4.73754 \times 10^{13}$ sec⁻¹ (9); $D_0 = 99,000$ cal mole⁻¹ (7).

The parametric values obtained are $V_s = 12.8$ cm³, $a = 0.0063$, $n = 4.926$, $\theta = 460$ deg, and $E_s = 144750$ cal mole⁻¹.

Because of the lack of experimental data on the properties for liquid MgO, we have also calculated the solid thermodynamic properties as a reference using the solid-part of the partition function in Eq. [1].

TABLE 1. Entropy and heat capacities of molten MgO (c.g.s. units)

T(°K)	S(e.u.)				
	JANAF			JANAF	
	Calc.	table (13)	C _v Calc.	C _p Calc.	table (13)
3098.16 (m.p.)	39.94		11.16	24.40	
3100.0		40.331			14.5
3200.0	40.77	40.792	11.04	23.95	14.5
3300.0	41.54	41.238	10.94	23.75	14.5
3400.0	42.26	41.671	10.85	23.66	14.5
3500.0	42.95	42.091	10.76	23.64	14.5
3600.0	43.62	42.500	10.68	23.65	14.5
3700.0	44.26	42.897	10.60	23.70	14.5
3800.0	44.87	43.284	10.52	23.74	14.5
3873.2 (b.p.)	45.31		10.47	23.79	14.5

Results

(a) *Thermodynamic Properties.* The Helmholtz free energy, A , is

$$A = -kT \ln f \quad [2]$$

Other thermodynamic properties can be derived from this equation.

(i) *The Melting and Boiling Point:* At the melting point, the solid and liquid phases are in equilibrium and the Gibbs Free Energies of the respective phases are the same, i.e., $G_s = G_l$. At the boiling point, the liquid and vapor phases are in equilibrium, and in this case $G_l = G_g$.

The melting point calculated from our partition function is 3098.16°K which agrees well with the observed value $3098 \pm 20^\circ\text{K}$ (10). Our calculated boiling point, 3873.2°K, agrees with the value reported by Mott (11) and others (12) but is 340° higher than the value reported in the JANAF Thermodynamical Data (13).

(ii) *Entropy:* The entropies of molten MgO, which were calculated from Eq. [1] by the expression:

$$S = -\left(\frac{\partial A}{\partial T}\right)_v = \left[\frac{\partial}{\partial T} (kT \ln f)\right]_v \quad [3]$$

are given in Table 1. Our theory agrees well with the JANAF thermodynamical tables (13).

The calculated entropy of fusion is 5.28 entropy units and the entropy of vaporization is 28.08 entropy units.

(iii) *Heat Capacities:* The heat capacity at constant volume is

$$C_v = \left[\frac{\partial}{\partial T} \left(kT^2 \frac{\partial \ln f}{\partial T}\right)\right]_v \quad [4]$$

TABLE 2. Molar volume, coefficient of thermal expansion, and compressibility of molten MgO (c.g.s. units)

T(°K)	V(cm ³)	$\alpha(\text{deg}^{-1}) \times 10^4$	$\beta(\text{atm}^{-1}) \times 10^6$
3098.16 (m.p.)	15.5	2.15	4.04
3200.0	15.8	2.10	4.19
3300.0	16.1	2.09	4.38
3400.0	16.5	2.09	4.60
3500.0	16.8	2.10	4.85
3600.0	17.1	2.11	5.13
3700.0	17.5	2.13	5.43
3800.0	17.8	2.16	5.76
3873.2 (b.p.)	18.1	2.17	6.02

and that at constant pressure is

$$C_p = C_v + TV \alpha^2 / \beta \quad [5]$$

The values for these quantities which are predicted by our theory are also listed in Table 1.

(iv) *The Compressibility and the Coefficient of Thermal Expansion:* For the compressibility we have

$$\beta_f = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V(\partial^2 A / \partial V^2)_T} \quad [6]$$

and the coefficient of thermal expansion

$$\alpha_f = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V} \left(\frac{\partial^2 A}{\partial V \partial T}\right) / \left(\frac{\partial^2 A}{\partial T^2}\right)_T \quad [7]$$

are calculated from our liquid partition function. Since the melting point and the boiling point of the molten MgO are about 800 degrees apart, the change in solid volume over this temperature range cannot be ignored. The contribution to the compressibility, β_s , and the coefficient of thermal expansion, α_s , by the solid lattice is added to the value contributed by fluidized vacancies in the following way:

$$\beta_l = \beta_f + \frac{V_s}{V} \beta_s \quad [8]$$

$$\alpha_l = \alpha_f + \frac{V_s}{V} \alpha_s \quad [9]$$

The solid-like coefficients β_s and α_s were calculated by using the solid-like partition function. The results are shown in Table 2.

(v) *Critical Properties:* The critical temperature T_c , critical pressure P_c and critical volume V_c were calculated by applying the following conditions:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T; \quad \left(\frac{\partial P}{\partial V}\right)_T = 0; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad [10]$$

The calculated critical values are listed in Table 3.

TABLE 3. Melting point, boiling point, and critical properties

T _{m.p.} (°K)		T _{b.p.} (°K)		T _c (°K)		T _{b.p.} /T _c	P(atm)	$\bar{V}_c$ (cm ³)	P _c $\bar{V}_c$ /RT _c
Calc.	Obs.	Calc.	Obs.	Calc.	Obs. ^a				
3098.16	3098 ± 20	3873.2	3873	5950.0	>6000	0.65	33.47	209.5	0.0144

^a Ref. 24.

Fig. 1. The heat capacity at constant pressure for solid MgO.

(b) *Transport Properties.* (i) Viscosity and Self-Diffusion Coefficients: According to Eyring *et al.* (14), the viscosity of a liquid is given by the expression

$$\eta = \frac{Nh}{Zk} \frac{6}{\sqrt{2}} \frac{1}{V - V_s} \frac{1}{1 - e^{-\theta/T}} \exp \left[\frac{aE_s V_s}{RT(V - V_s)} \right] + \frac{V - V_s}{V} \frac{2}{3d^2} \left(\frac{mkT}{\pi^2} \right)^{1/2} \quad [11]$$

where k is the transmission coefficient, d is the diameter of the molecule. The self-diffusion coefficient is given by the expression

$$D = \frac{kT}{6 \left(\frac{\sqrt{2} V_s}{N} \right)^{1/2} \eta} \quad [12]$$

In this calculation the transmission coefficient, κ , is taken as 0.4 in agreement with previous findings. The calculated values are listed in Table 4.

(ii) The Ionic Mobilities and the Specific Conductivity: The ionic mobilities and specific conductivity may be calculated from the viscosity by the following relations:

$$U_0^+ = Z_+ \epsilon / 4\pi\eta r_+ \quad [13]$$

$$U_0^- = Z_- \epsilon / 4\pi\eta r_- \quad [14]$$

$$\sigma = \frac{N(V_s/V)}{V} \epsilon (U_0^+ + U_0^-) \quad [15]$$

where U_0^+ and U_0^- are the ionic mobilities, Z_+ and Z_- are the valence charge of the ions, r_+ and r_- are the ionic radius, “+” and “-” signs refer to the cation and anion, respectively; ϵ is the charge of an electron (1.6×10^{-19} coulomb); σ is the specific conductivity in $\text{ohm}^{-1} \text{cm}^{-1}$. The calculated values are listed in Table 4.

Discussion

Because there is no observed information for the molten MgO except the melting point and estimated boiling point, we have used as a check a comparison of calculated and observed solid properties.

TABLE 4. Calculated viscosity, self-diffusion coefficient, ionic mobilities, and specific conductivity of molten MgO (c.g.s. units)

$d = 2.105 \text{ \AA}^a$	$r = 0.65 \text{ \AA}^b$	$r = 1.40 \text{ \AA}^b$			
$T(^{\circ}\text{K})$	$\eta \times 10^2$	$D \times 10^4$	$U_0^+ \times 10^2$	$U_0^- \times 10^2$	σ
3098.16 (m.p.)	1.41	1.61	27.78	12.77	20.9
3200.0	1.25	1.90	31.4	14.6	22.7
3300.0	1.12	2.18	35.0	16.3	24.3
3400.0	1.02	2.37	38.5	17.9	25.7
3500.0	0.94	2.75	41.0	19.3	26.5
3600.0	0.88	3.04	44.5	20.7	27.5
3700.0	0.82	3.33	47.7	22.1	28.2
3800.0	0.78	3.70	50.5	24.4	28.7
3873.2 (b.p.)	0.75	3.84	52.5	24.4	29.0

^a Ref. 22.

^b Ref. 23.

In accord with previous experience with molten salts and the nature of the problem, the volume dependence is introduced as follows:

$$E_s = E_{s0} \left[2 \left(\frac{V_{s0}}{V_s} \right)^q - \left(\frac{V_{s0}}{V_s} \right)^{2q} \right]; \theta = \theta_0 \left(\frac{V_{s0}}{V_s} \right)^\gamma \quad [16]$$

where V_{s0} , E_{s0} , and θ_0 are the volume, sublimation energy, and Einstein characteristic temperature at absolute zero, respectively; q and γ are parameters. Both q and γ were taken to be 1.0; this gives the best solid-state properties.

The calculated solid-state properties are listed in Tables 5 and Fig. 1, where they are compared with the observed value. The results show very good agreement for entropy (13, 15), specific heat (13, 15, 16) (constant pressure), and coefficient of thermal expansion (17, 18; in ref. 18, the linear expansion percentage is given and 0°F should be used as a reference point).

The calculated α value for the molten MgO is about three times the solid value and the β value for the liquid is also about three times the solid value. A comparison with other salts (19, 20) indicates this ratio is not unreasonable. Comparing our results with the JANAF Thermodynamical Table (13) for the entropy of the molten state, the entropy of fusion and the entropy of vaporization are in reasonable agreement. Thus, we expect our results are about right. The major differences between our results and the JANAF Table are the specific heat C_p and the boiling point. In obtaining the JANAF Tables the C_p value above the presumed glass transition temperature 2066°K were assumed to have the constant value $14.5 \text{ (cal deg}^{-1} \text{ mole}^{-1})$. Our results do not agree with this assumption.

Our boiling point, estimated as the temperature at which the Gibbs free energy of the liquid phase equals that of the vapor phase, is considerably higher than the boiling point given in the JANAF Thermodynamical Tables. Nevertheless, it agrees with Mott's boiling point, estimated by comparing the crater distance of the arc image deposits with reference compounds (11). A second reference also agrees with this value (12).

The ratio of $T_{b,p}/T_c$ for MgO is calculated as 0.65 which is almost the same as that of the other gases (21). The calculated compressibility factor of MgO under critical conditions is a very small number (0.0144). The very low calculated critical pressure as indicated by the results $P_c V_c / RT_c = 0.0144$ as

TABLE 5. Thermodynamic properties of solid MgO (c.g.s. units)

T(°K)	S(e.u.)				C _p					
	Calc.	JANAF (13)	Obs.		C _v		Calc.	JANAF (13)	Obs.	
			a	b	Calc.	Obs. ^c			d	f
100	0.373	0.608		0.521	1.648	1.864	1.676	1.866		1.513 (93°)
200	3.269	3.369		3.370	6.841	6.328	6.873	6.370		5.204 ^e (173°)
300	6.593	6.495		6.584	9.258		9.347	8.915	8.939	9.325 (323°)
400	9.46	9.251	9.27 (298.1°)		10.334		10.484	10.169	10.190	9.83 (373°)
600	13.93	13.616	13.62		11.192		11.461	11.285	11.324	11.179 (673°)
900	18.70	18.355	18.34		11.597		12.049	12.257	12.090	11.757 (873°)
1200	22.21	21.891	21.89		11.742		12.385	12.507	12.505	12.335 (1073°)
1700	26.60	26.312	26.32		11.834		12.832	12.900		14.358 (1773°)
2200	29.97	29.686			11.871		13.183	13.293		15.01 (2273°)
2700	32.74	32.448			11.890		13.797	13.686		16.86 (2773°)
3098.16	34.66				11.897		14.279			

T(°K)	$\alpha \times 10^6$				$\beta \times 10^6$		V(cm ³) Calc.
	Calc.	Obs.		Calc.	Obs. ^c		
		e	e				
100	5.7			8.0	0.911	0.649	11.083
200	23.4			22.0	0.929	0.651	11.100
300	32.0				0.931		11.132
400	36.1	35.1 (373°)			0.945		11.170
600	40.1	36.3 (573°)			0.977		11.256
900	43.2	40.2 (973°)			1.029		11.398
1200	45.6	42.0 (1173°)			1.087		11.551
1700	49.6	47.1 (1773°)			1.200		11.829
2200	54.1				1.338		12.139
2700	59.4				1.511		12.488
3098.16	64.6				1.683		12.801

^a Ref. 25.^b Ref. 15.^c Ref. 26.^d Ref. 27.^e Ref. 17.^f Ref. 28.

compared with the experimental mean value 0.292 for the rare gases, can only be understood in terms of twenty times as large an average degree of clustering at the critical temperature for MgO as for the rare gases. The long-range forces between ions as well as ionic attraction for many neighbors would tend to cause this kind of ionic clustering. However, such a large mean degree of clustering is surprising and may indicate a defect in our partition function in the high temperature range. The result indicates it would be very interesting, although difficult, to measure the critical pressure and so establish the mean degree of clustering. In any case, it is instructive to see the type of partition function that gives large mean clustering at the critical point.

Because of the lack of experimental data, this study can only be justified through indirect comparisons. Our results on viscosity and self-diffusion coefficients are well within the range reported for other fused salts (5). The ionic mobilities and specific conductivity compared to alkaline-metal salt (5) are several-fold larger because of the valence of two and also because MgO has a smaller molar volume. We expect that only minor adjustments in the parameters used will be needed for further improvement in our calculations as more experimental data become available.

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