

lifetime is assumed to vary inversely with the vibrational quantum number. Radiation trapping is insignificant at the density levels of interest, and has been ignored in the present calculations. From the theory of Treanor⁶ we infer that under the conditions of the experiment the N₂ vibrational temperature is about 1700°K in the lowest vibrational levels. Thus, only the zeroth and first vibrational levels of N₂ have a significant population. Because of the difference in the vibrational energy level spacing of N₂ and CO, only the lowest levels of the CO couple strongly with the N₂ first vibrational level. In the present calculations, the effects of CO-N₂ collisions are ignored except in the levels $v=0, 1$. In these levels, the $V-V$ exchange processes between N₂ and CO are assumed to dominate due to the preponderance of N₂ in the mixture. To simulate this, the ratio $N_1/N_0 = \exp[-E_1/kT_V]$ of the population of the levels $v=1, 0$ is held fixed. The initial distribution is assumed to be a Boltzmann corresponding to the temperature T_V of the lowest two levels. The integration is carried out at constant translational temperature until the distribution reaches a steady state.

Some steady-state results for the levels $0 < v < 20$ in CO are shown in Fig. 1. To insure conservation of molecules, collision processes involving excitation of either molecule to levels above $v=20$ are assumed to have zero probability (this corresponds to a reflecting boundary condition at $v=20$). The calculations were performed for conditions corresponding approximately to Legay's experimental conditions.^{1,2} We see that in the low vibrational levels the $V-V$ processes dominate, and the vibrational distribution is close to that predicted by Treanor *et al.*⁶ (solid curve), who considered nonresonant $V-V$ processes among anharmonic oscillators, but neglected $T-V$ and radiative processes. In the high vibrational levels the calculated distribution functions fall below the Treanor prediction due to radiative decay processes. As we see, these processes become increasingly important as the pressure is reduced.⁷ Although $T-V$ processes are included in the calculation, they are unimportant compared with radiative decay at the CO pressures and temperatures considered here. The dashed curves demonstrate the increasing effectiveness of radiative decay in comparison with $V-V$ collision processes as the pressure is reduced.

The numerical results, including energy drain, are in qualitative agreement with the measurements of Legay,^{1,2} which follow the Treanor distribution in the lower levels and indicate a vibrational temperature of approximately 15 000°K in the upper levels, $10 < v < 15$.⁸ A total inversion has not been observed experimentally. This might occur at higher pressures for which the $V-V$ processes become more important and the distribution extends to higher levels. At sufficiently high densities the deactivation should be dominated by $T-V$ collisions.

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Exact Solution of an Integral Equation for the Structure of a Primitive Model of Electrolytes*

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We consider the "primitive model" of an electrolyte,¹ i.e., a mixture of charged hard spheres with a "direct" pair potential between an ion of species i and an ion of species j at a separation r , $v_{ij}(r) = \infty$, $r < R_{ij}$, and $v_{ij}(r) = (e_i e_j / \epsilon r)$ for $r > R_{ij}$. Here R_{ij} is the distance of closest approach between the ions i and j and ϵ is the dielectric constant of the solvent. The system is assumed to be over-all neutral; $\sum e_i \rho_i = 0$. The existence of the thermodynamic limit for this kind of system has been proven recently by Lebowitz and Lieb.²

The M.S.M. approximate integral equation was constructed by Lebowitz and Percus³ as a generalization to continuum systems of the well-known spherical model for Ising spin systems which are isomorphic to lattice gases. Calling $g_{ij}(r)$ the radial distributions functions of a mixture and $C_{ij}(r)$ the direct correlation functions the M.S.M. supplements, the defining equations⁴ for the C_{ij} are

$$g_{ij}(r) = 0, \quad r < R_{ij}; \quad (1a)$$

$$C_{ij}(r) = -\beta v_{ij}(r), \quad r > R_{ij}, \quad (1b)$$

where β is the reciprocal temperature $(kT)^{-1}$. Note that (1a) is true for the exact radial distribution functions and the M.S.M. approximation consists of (1b).

TABLE I. Comparison of results of M.S.M. with HNC¹ aqueous solution for 1-1 electrolyte; $T = 25^\circ\text{C}$; $R = 4.6 \text{ \AA}$; $Z = 1$; $\epsilon = 78.358$ and assumed temperature independent.

C (moles) ^a	ρR^3	$x = KR$	$-E^{\text{ex}}$ (cal/mole·liter)		$(\beta P/\rho)$	
			M.S.M.	HNC	M.S.M.	HNC
0.002	0.0002	0.0677	58.514	58.983	0.9848	0.98444
0.020	0.0024	0.2141	163.743	165.778	0.9630	0.96272
0.200	0.0234	0.6770	388.449	390.052	0.9644	0.96406
0.900	0.1056	1.4362	600.862	605.028	1.1412	1.1356
1.000	0.1172	1.5138	617.003	621.663	1.1728	1.1666

^a C: moles of electrolyte per liter.

Accepting (1), we can solve for $C_{ij}(r)$ when $r < R_{ij}$ and for $g_{ij}(r)$ for $r > R_{ij}$.

We have solved exactly the M.S.M. equation for the primitive model of a 1-1 electrolyte when the diameter of the ions are equal, i.e., $R_{ij} = R$, $e_1 = |e_2| = Ze$, $\rho_1 = \rho_2 = \frac{1}{2}\rho$, and are working on the more general case. Our method of solution is similar to that used by Lebowitz⁴ for solving the PY equation for a mixture of hard spheres [which is identical to the M.S.M. equation when $v_{ij}(r) = 0$ for $r > R_{ij}$ in (1)]. We find that

$$C_{ij}(r) = C_{ij}^0(r) + (-1)^{i+j} (2\pi\rho R^3)^{-1} (Bx^2 - 2\lambda r/R), \quad r < R, \quad (2)$$

where $C_{ij}^0(r)$ is the direct correlation function for a system of uncharged hard spheres⁴; $x = KR$ with K the inverse Debye length, $K^2 = 4\pi(Ze)^2\rho\beta/\epsilon = x^2/R^2$, $\lambda = -(Bx)^2/4$, and

$$B = \pi\rho R \int_R^\infty [g_{ii}(r) - g_{ik}(r)] r dr = -[1 + x - (1 + 2x)^{1/2}]/x, \quad i \neq k. \quad (3)$$

It should be noted that since we are considering the case where the hard cores of the two components are of equal size, we have $C_{ij}^0(r) = C^0(r)$, where $C^0(r)$ is the direct correlation function found by Wertheim⁵ and Thiele from the solution of the PY equation for a one-component system of hard spheres at density ρ . By combining (1b) and (2), we know $C_{ij}(r)$ for all r from which the Laplace and Fourier transforms of $g_{ij}(r)$ can be obtained explicitly. However, even without the explicit computation of $g_{ij}(r)$ we know from the work of Groeneveld⁶ that the assumptions of the M.S.M., Eq. (1), force the resulting $g_{ij}(r)$ to satisfy the Stillinger-Lovett⁷ relations

$$2\pi\rho \int_R^\infty [g_{ii}(r) - g_{ik}(r)] r^{2(1+n)} dr = -(6/K^2)^n, \quad n = 0, 1; \quad i \neq k. \quad (4)$$

As shown in Ref. 7, Eq. (4) implies, for $x^2 > 6$, the

existence of oscillations in the charge cloud density

$$Q_j(r) = \sum_{i=1}^2 \rho_i e_i g_{ij}(r)$$

about a fixed ion of type j . When $\rho R^3 \rightarrow 0$, our results will approach the Debye-Hückel results which show no oscillations in the screening charge. We plan to examine the nature of these oscillations in detail.

Turning now to the thermodynamic properties of our model system it is well known¹ that these may be computed from the $g_{ij}(r)$ in many different ways, i.e., virial or compressibility pressure, energy, etc., and these will generally give different results. These matters are discussed extensively by Rasaiah and Friedman¹ for the $g_{ij}(r)$ coming from the numerical solutions of various integral equations (not the M.S.M.). They come to the conclusion that the hyper-netted-chain equation is probably the best among the ones they considered (for this system). Their conclusion seems strengthened by the agreement between the results of this equation and Monte Carlo computations.¹ In Table I we compare the excess energy per unit volume given by

$$E^{\text{ex}} = \frac{1}{2} \sum_i \sum_j \rho_i \rho_j \int_R^\infty \left(\frac{e_i e_j}{\epsilon r} \right) g_{ij}(r) 4\pi r^2 dr = (\beta 4\pi R^3)^{-1} B x^2, \quad (5)$$

obtained from our solution of the M.S.M. and those obtained by Rasaiah and Friedman from the HNC equation (considering ϵ temperature independent).

The Helmholtz free energy density a is related to E^{ex} by the relation

$$\beta a - \beta a^0 = \int_0^\beta E^{\text{ex}}(\rho, \beta') d\beta' = -(12\pi R^3)^{-1} [6x + 3x^2 + 2 - 2(1 + 2x)^{3/2}], \quad (6)$$

where a^0 is the free energy density of the uncharged hard-sphere system. Note that $(\beta a - \beta a^0) \rightarrow -K^3/12\pi$, the Debye-Hückel limiting law when $KR \rightarrow 0$. Using (6) we may compute the osmotic pressure from the

relation

$$P/\rho = \rho[\partial(\rho a)/\partial\rho] = (4\pi\rho R^3)^{-1}[x + x(1+2x)^{1/2} - \frac{2}{3}(1+2x)^{3/2} + \frac{2}{3}] + P^0/\rho, \quad (7)$$

where P^0 is the uncharged hard-sphere pressure. Our results are compared with those of Rasaiah and Friedman in Table I.

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Notes

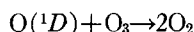
O(¹D) Quenching Efficiency of O₂ Relative to Other Gases*

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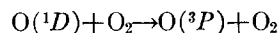
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Some disagreement persists regarding the O(¹D) quenching efficiency of O₂. For example, measurements based on competition between the reactions



and



seem to give low O₂ quenching efficiencies.¹⁻³ By contrast, other methods⁴ indicate that O₂ quenches O(¹D) at a high rate.

This note reports measurements of the relative quenching efficiencies of O₂, CO, N₂, CO₂, and Ar at 22°C. The technique involved photolysis of O₃-N₂O-He mixtures in a 40-m White cell, with various pressures of the added quencher. The method was based on the fact that O(¹D), produced by O₃ photolysis at 2537 Å, reacts rapidly with N₂O to produce some NO, whereas O(³P) does not.⁵ In the presence of O₃, the NO was rapidly converted to N₂O₅, and the N₂O₅ concentration was monitored at 1718 cm⁻¹. For the present purposes,

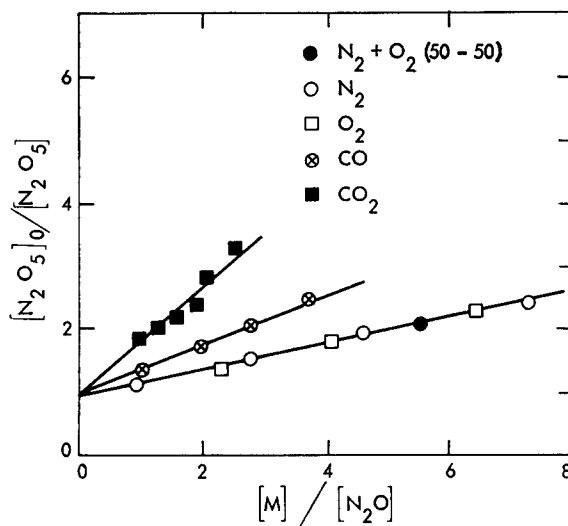


Fig. 1. Suppression of N₂O₅ formation by different quenchers of O(¹D). Slope is proportional to quenching efficiency.

it is only necessary that the amount of N₂O₅ formed be proportional to the NO formed, and the linearity of data obtained for different concentrations of a given quencher (Fig. 1) tends to verify this point. The basic mixture consisted of 10 torr N₂O, about 0.05 torr O₃, the added quencher, and sufficient He to bring the total pressure to 700 torr. The rate of N₂O₅ formation was found to be independent of the N₂O/He ratio in the range of N₂O pressures employed, indicating negligible O(¹D) quenching by He.

The N₂O₅ disappeared at a slow and approximately first-order rate, apparently on the walls. Given a constant rate of light absorption by O₃ for a specified radiation interval (1 min), a kinetic treatment (which takes into account the N₂O₅ loss) yields the following expression:

$$[\text{N}_2\text{O}_5]_0/[\text{N}_2\text{O}_5] = 1 + k_d[M]/k_{N_2O}[\text{N}_2\text{O}]. \quad (1)$$

The term on the left-hand side represents the ratio by which N₂O₅ formation was suppressed by the added quencher and was obtained by measuring the peak N₂O₅ concentrations for experiments with and without added quencher. The constant k_{N_2O} is the total rate constant for O(¹D) removal by N₂O, and k_d is the quenching rate constant.

During each experiment the O₃ absorption at 2537 Å was monitored photometrically. Except for the CO experiments, the initial O₃ concentrations were nearly identical, and the same fraction (about 10%) of O₃ was decomposed. For CO, some initial O₃ decomposition occurred upon mixing the gases, and therefore a correction for the reduced rate of light absorption was made. The magnitude of the correction ranged from 0% to 27%. A mixture of O₂ and N₂ in equal amounts was shown to give the same quenching as that predicted