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Interaction Second Virial Coefficients for Sodium–Inert Gas Mixtures

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Interaction second virial coefficients for binary mixtures of sodium vapor and the inert gases are evaluated for the 200–2000 K temperature range. The calculations are based on the best experimental interatomic potential functions available for NaHe, NaNe, NaAr, NaKr, and NaXe.

Introduction

Interest in the alkali-inert gas excimers has increased in recent years because of their potential utility in the development of new high-power visible lasers. Consequently, the Na-inert gas systems have been the object of numerous experimental investigations, which include collisional line broadening (*1*), scattering (*2–6*), and laser excitation spectroscopy (*7–10*). Several theoretical calculations have also been reported (*11–15*). In addition, thermodynamic properties and second virial coefficients for pure alkali vapors (*16*, *17*) and pure inert gases (*16*, *18*) are available in the literature, but, to our knowledge, no alkali-inert gas interaction virial coefficients have been reported. The purpose of this paper is to present calculated values of interaction second virial coefficients for Na-inert gas mixtures that can then be used to calculate the thermodynamic properties of such mixtures from knowledge of the properties of the pure component gases.

Basic Equations

In the present work the vapor mixture is treated as a nonideal monoatomic assembly whose equation of state is given by

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + D(T)/V^3 + \ldots \quad (1)$$

where $B(T)$, $C(T)$, and $D(T)$ are second, third, and fourth virial coefficients, respectively. We truncate this series at the $B(T)$ term, which for a vapor mixture of n components takes the form (*19*)

$$B(T) = \sum_{i=1}^{n} \sum_{j=1}^{n} X_i X_j B_{ij}(T) \quad (2)$$

where X_i is the mole fraction of the ith component and $B_{ij}(T)$ is given by

$$B_{ij}(T) = -2\pi N_0 \int_0^\infty \{\exp[-V_{ij}(R)/kT] - 1\}R^2\,dR \quad (3)$$

Here $V_{ij}(R)$ denotes the potential between the ith and jth components, R is the interatomic distance, k is Boltzmann's constant, and N_0 is Avogadro's number. For the special case of the binary mixture considered here, we write

$$B(T) = X_1^2 B_{11}(T) + 2X_1X_2B_{12}(T) + X_2^2B_{22}(T) \quad (4)$$

where the subscripts 1 and 2 are used to represent sodium and inert gas atoms, respectively.

Potential Functions

As can be seen from eq 3, potential energy data are needed for these calculations. Several investigators have reported experimental (*1–10*) and theoretical (*11–15*) ground-state potential energy functions for the Na-inert gas systems. For NaHe we adopt the potential function recently determined by Havey et al. (*10*) using the temperature dependence of the red wing of the 3P Na resonance line perturbed by He. They concluded that the NaHe ground state can be described by a repulsive potential of the form

$$V(R) = A \exp(-BR) \quad (5)$$

where $A = 61049.0$ cm^{-1} and $B = 1.5104$ Å^{-1}.

The Morse function

$$V(R) = D_e\{\exp[2a(R - R_e)] - 2\exp[a(R - R_e)]\} \quad (6)$$

constructed from the spectroscopic data of Ahmad-Bitar et al. (*8*) has been selected for the NaNe molecule. Here $D_e = 8.1$ cm^{-1}, $R_e = 5.29$ Å, and $a = 0.9311$ Å^{-1}.

The best ground-state potential function for NaAr reported to date is the one deduced by Tellinghuisen et al. (*9*) from the dispersed fluorescence spectrum of this molecule. The form of this potential is that of a modified Morse curve

$$V(R) = D_e\{\exp[2b_0(R - R_e)] - 2\exp[b_0(R - R_e)]\} \times \{1 - b_1\exp[(R - b_2)/b_3]\} \quad (7)$$

where $D_e = 40.4$ cm^{-1}, $R_e = 4.994$ Å, $b_0 = 0.98693$ Å^{-1}, $b_1 = 0.4988$, $b_2 = 2.5981$ Å, and $b_3 = 1.2129$ Å.

Finally, for NaKr and NaXe we choose a Lennard-Jones (12–6) potential

$$V(R) = D_e\{(R_e/R)^{12} - 2(R_e/R)^6\} \quad (8)$$

with parameters reported by Düren et al. (*3*) from atomic beam scattering experiments. Here we have $D_e = 68.97$ cm^{-1} and $R_e = 4.73$ Å for NaKr, and $D_e = 100.2$ cm^{-1} and $R_e = 4.91$ Å for NaXe.

Results

Using the integral above, we have numerically evaluated interaction $B_{12}(T)$ coefficients for the 200–2000 K temperature range using Newton–Cotes integration formulas. Contributions due to excited molecular states (*20*) were found to be negligible and thus were not included in our results, which are summarized in Table I. The uncertainties are estimated to be less than 3%.

Experimental values for the primary second virial coefficients $B_{11}(T)$ have been published by Ewing et al. (*17*) and calculated values have been given by Sannigrahi and Mohammad (*21*). For a list of $B_{22}(T)$ values for the various inert gases we refer the reader to the recent compilation by Dymond and Smith (*18*). With these pure component data and the $B_{12}(T)$ coefficients

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Table I. Interaction Second Virial Coefficients (cm^3/mol) for Sodium-Inert Gas Atom Pairs

T, K	NaHe	NaNe	NaAr	NaKr	NaXe
200	121.14	45.61	−12.31	−57.15	−146.18
300	101.83	44.94	11.83	−9.58	−58.51
400	89.50	43.18	21.74	11.82	−19.67
500	80.69	41.33	26.58	23.68	1.89
600	73.96	39.60	29.15	31.05	15.43
700	68.58	38.02	30.54	35.97	24.60
800	64.16	36.59	31.26	39.42	31.15
900	60.42	35.29	31.59	41.93	36.01
1000	57.22	34.12	31.68	43.80	39.73
1100	54.42	33.04	31.61	45.22	42.63
1200	51.96	32.06	31.44	46.32	44.94
1300	49.76	31.15	31.21	47.17	46.80
1400	47.79	30.31	30.93	47.84	48.33
1500	46.01	29.53	30.63	48.36	49.58
1600	44.38	28.80	30.31	48.77	50.62
1700	42.89	28.12	29.98	49.10	51.49
1800	41.52	27.48	29.65	49.35	52.23
1900	40.25	26.88	29.31	49.54	52.84
2000	39.08	26.31	28.98	49.69	53.37

listed in Table I it is now a straightforward task to evaluate $B(T)$ coefficients for any particular mixture of Na vapor and inert gases using eq 4. Subsequently, *PVT* properties for such mixtures can be easily derived by using a real gas as the model.

Registry No. Na, 7440-23-5; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; Xe, 7440-63-3.

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Sechenov Salt-Effect Parameter[†]

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The units used to express the electrolyte and nonelectrolyte concentrations affect the numerical value of the salt-effect parameter. Conversion factors among the different modes of expression of the salt-effect parameter are derived and some typical numerical values are presented. The effects of random errors in the nonelectrolyte concentrations in water and the aqueous electrolyte solution are discussed. A set of evaluated salt-effect parameters are presented for up to 12 gases dissolved in aqueous sodium chloride and potassium hydroxide solutions at 298.15 K.

Introduction

The effect of an electrolyte on the solubility of a nonelectrolyte has been systematically studied since the pioneering work of I. M. Sechenov (J. Setschenow) (*1*) on the solubility of carbon dioxide in blood and in various aqueous electrolyte solutions between 1874 and 1892. A nonelectrolyte will have a different solubility in water and in an aqueous electrolyte solution mainly because of the effect of the electrolyte on the nonelectrolyte activity coefficient. The electrolyte may increase the nonelectrolyte activity coefficient (decrease the nonelectrolyte solubility, salt-out) or it may decrease the nonelectrolyte activity coefficient (increase the nonelectrolyte activity coefficient, salt-in). There are many reviews of the salt-effect experimental data and theories (*2*-*10*). The usual experimental measure of the salt effect is the Sechenov salt-effect parameter.

Sechenov (*11*, *12*) proposed the empirical equation $\alpha = \alpha^0 \exp(-k/x)$ where α^0 and α are the Bunsen coefficients of the nonelectrolyte gas solubility in water and aqueous salt solution, x is the dilution, and k is the salt-effect parameter. Sechenov tested the equation by measuring the solubility of carbon dioxide in a concentrated (sometimes saturated) electrolyte solution, a number of dilutions of the solution, and pure water. He used the solubility in the most concentrated solution and water to establish the constant. He then calculated the solubility in the various solutions to compare with the experimental value. The agreement between equation and experiment was usually satisfactory. Many of Sechenov's original Bunsen coefficients for carbon dioxide in water and aqueous electrolyte solution agree within a few percent of modern values.

Rothmund (*13*) was apparently the first to put Sechenov's equation in the form commonly used today. In the notation of this paper that is

$$k_{scc}/(\mathrm{dm^3\ mol^{-1}}) = \{1/(c_s/(\mathrm{mol\ dm^{-3}}))\} \log \{(c_g{}^0/(\mathrm{mol\ dm^{-3}}))/(c_g/(\mathrm{mol\ dm^{-3}}))\} \tag{1}$$

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