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The Excess Properties of Nitric Oxid Mixtures**

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The excess properties of the three mixtures of nitric oxid with methane, krypton, and nitrogen are calculated and compared with experimental values. As nitric oxid is strongly dimerized in the liquid state, the calculation involves the assignment of potential parameters to the nitric oxid monomer and dimer, the statistical mechanical calculation of the excess properties of the fictitious mixtures with monomer and with dimer, and the calculation of the equilibrium properties in the pseudoternary system formed by monomer, dimer, and second component. The comparison with experimental values shows that the calculation gives the correct order of excess values, but fails in some numerical details.

(Keywords: Thermodynamics of mixtures; Nitric oxid; Statistical mechanics; Associating mixtures)

Die Exzeßeigenschaften von Stickstoffoxid-Mischungen

Die Exzeß-Eigenschaften der drei Stickstoffoxid-Mischungen mit Methan, Krypton und Stickstoff werden berechnet und mit experimentellen Werten verglichen. Da Stickstoffoxid im flüssigen Zustand überwiegend dimerisiert vorliegt, beinhaltet die Berechnung die Festlegung der Potentialparameter des Stickstoffoxid-Monomeren und -Dimeren, die statistisch-mechanische Berechnung der Exzeßeigenschaften der fiktiven Mischungen mit Monomer und mit Dimer, und die Berechnung der Gleichgewichtseigenschaften in dem pseudoternären System, das durch Monomer, Dimer und zweite Komponente gebildet wird. Der Vergleich mit den experimentellen Werten zeigt, daß die Berechnung die richtige Reihenfolge und Größenordnung der Exzeß-Werte wiedergibt, aber in manchen numerischen Details versagt.

** Dedicated to Prof. Dr. *A. Neckel* on the occasion of his 60th birthday.

Introduction

Three liquid mixtures with nitric oxid as one component have been measured: With methane [1], krypton [2] and nitrogen [3]. In all three cases, strongly positive deviations from *Raoult's* Law were observed, and interpreted as caused mainly by the strong association of nitric oxid to the nitric oxid dimer in the liquid state.

While this interpretation is undoubtedly correct, some details remained open: Is it true, that the properties of nitric oxid monomer should be in between oxygen and nitrogen? What is the reason that the dimerisation is very strong in the liquid state but almost absent in the gas phase? What is the reason that the positive deviations from ideality are increasing in the order krypton, methane, nitrogen?

In the case of the NO + Kr and NO + N_2 system, a first approximation was given for the activity coefficients between monomeric and dimeric nitric oxid and the second component. As the formulation of this approximation would violate the *Gibbs-Duhem-Margules* equation, the numerical values for the interaction constants are doubtful. It is the purpose of this paper to give theoretically founded estimates for these interaction constants. Use can be made of a recently developed statistical mechanical method [4] to calculate the properties of mixtures between molecules with one and two interaction sites, where the sites interact with the *Lennard-Jones* 12/6-pair potential [in short, one-center *Lennard-Jones* (1CLJ) and two-center *Lennard-Jones* (2CLJ) molecules]. This method was complemented [4] by a combining rule for the unlike interaction based on the simplified *London* formula for dispersion energies.

After a brief review of this theory, we will try to estimate the parameters for the interaction potential of nitric oxid monomer and dimer, treating the monomer (as well as nitrogen, krypton and methane) as 1CLJ and the dimer as 2CLJ. Together with the estimation of the parameters of the interaction potential, we will answer the first two questions of the second paragraph. Finally, we will estimate the excess properties of the three liquid mixtures, treating them as pseudoternary mixtures between nitric oxid monomer, dimer and second component.

Perturbation Theory for 1CLJ and 2CLJ Liquids and Mixtures

1CLJ Liquids

As was shown convincingly by *Weeks, Chandler,* and *Andersen* [5] for 1CLJ liquids, it is possible by suitable division of the pair potential to incorporate all structural contributions into the repulsively interacting assembly (superscript zero), and to treat all attractive contributions (superscript unity) as homogeneous background potential. The suitable division of the potential occurs at the minimum of the pair potential u.

$$\begin{aligned}
u^\circ &= 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right] && r < R \\
u^\circ &= 0 && r \geqslant R \\
u^1 &= -\varepsilon && r < R \\
u^1 &= 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] && r \geqslant R
\end{aligned} \tag{1}$$

Here the minimum value of the pair potential is denoted by $-\varepsilon$, the distance between two particles by r, the distance at the minimum by R, and the distance at the zero of the potential by σ, $\sigma = R/2^{1/6}$. The part u° may be called the repulsive force branch, and u^1 the attractive force branch (for illustration, cf. Ref. [6]). As for a sufficiently high density ρ the structure is solely determined by the pair distribution function g° of the repulsively interacting assembly, the residual reduced *Helmholtz* energy can be written

$$\frac{F^*}{NkT} = \left(\frac{F^*}{NkT}\right)^\circ + \frac{\rho}{2}\int g^\circ \frac{u^1}{kT}\,\mathrm{d}\boldsymbol{r} \tag{2}$$

Instead of calculating the residual *Helmholtz* energy of the repulsively interacting assembly $(F^*/NkT)^\circ$, it is easier to trace it back to the residual *Helmholtz* energy of a hard sphere assembly which can be given analytically provided that the diameter of the hard spheres is known. For the calculation of the hard sphere diameter d *Weeks, Chandler,* and *Andersen* have introduced the so-called blip formalism

$$\int_0^R \left(\mathrm{e}^{-u^H/kT} - \mathrm{e}^{-u^\circ/kT}\right) y^\circ\, 4\pi r^2\,\mathrm{d}r = 0 \tag{3}$$

with u^H the hard sphere potential of a sphere of diameter d, and y° the background correlation function

$$y^\circ = g^\circ\,\mathrm{e}^{u^\circ/kT}. \tag{4}$$

This formalism, though giving a weakly density dependent hard sphere diameter d, is slightly superior to the so-called *Barker-Henderson* 1 (BH 1) prescription [7]

$$\int_0^R \left(\mathrm{e}^{-u^H/kT} - \mathrm{e}^{-u^\circ/kT}\right)\mathrm{d}r = 0, \tag{5}$$

which gives a hard sphere diameter independent of density. The only problem remaining is the calculation of the pair distribution g° of the repulsive assembly. For reasons of consistency with the calculation of 2CLJ-liquids we calculate g° by the *Baxter* formalism [8] to solve the *Percus-Yevick* equation.

2CLJ Liquids

The 2CLJ potential is the sum of the four site-site interactions between the two sites of molecule 1 and the two sites of molecule 2. It is characterized by the parameters ε, σ of the site-site interactions and by the distance l between the two sites, frequently expressed in reduced way $L = l/\sigma$. The four site-site distances can be traced back to the center-center distance r by means of the three angles θ_1, θ_2, φ, where θ_i is between the center-center connecting line and the axis of molecule i and φ denotes the angle by which molecule 2 is turned out of the plane given by the center-center connecting line and the axis of molecule 1. The extension of the *Weeks, Chandler, Andersen*-type of division of the pair potential to 2CLJ is performed [9, 10] by dividing the pair potential at the minimum for each mutual orientation, i.e. for each set of θ_1, θ_2, φ. Now Eq. (2) becomes

$$\frac{F^*}{NkT} = \left(\frac{F^*}{NkT}\right)^\circ + \frac{\rho}{2} \int < g^\circ \frac{u^1}{kT} > \mathrm{d}\boldsymbol{r}, \tag{6}$$

where the angular brackets denote averaging over all orientations of the angle dependent quantities $g^\circ(r, \theta_1, \theta_2, \varphi)$ and $u^1(r, \theta_1, \theta_2, \varphi)$. The task can be much facilitated by breaking up g° into the background correlation function y° [Eq. (4)] and the *Boltzmann*-factor and assuming that y° is not orientation-dependent:

$$\left\langle g^\circ \frac{u^1}{kT} \right\rangle = y^\circ \left\langle \frac{u^1}{kT} \mathrm{e}^{-u^\circ/kT} \right\rangle. \tag{7}$$

This assumption is justified for the calculation of the center-center pair distribution function and the thermodynamic properties [11].

Again, the residual *Helmholtz* energy of the repulsive assembly is traced back to the residual *Helmholtz* energy of hard dumbells (hard fused spheres), where the sphere centers are just as much apart as the sites in the 2CLJ potential, and where the sphere diameters are again determined by the blip condition

$$B = \int \{\langle \mathrm{e}^{-u^H/kT} \rangle - \langle \mathrm{e}^{-u^\circ/kT} \rangle\} \, y^\circ \, 4\pi r^2 \, \mathrm{d}r = 0, \tag{8}$$

with u^H being the angle-dependent hard dumbell potential which contains the unknown sphere diameter. The background correlation function y° is calculated via the *Baxter* solution of the *Percus-Yevick* equation for the potential corresponding to the angle-averaged *Boltzmann*-factor $\langle e^{-u^\circ/kT} \rangle$, i.e. $\bar{u} = -kT \ln \langle e^{-u^\circ/kT} \rangle$.

This method has been proved to give reliable thermodynamic results within reasonable computer time, so that vapour pressures and orthobaric densities (in reduced units) could be calculated for a variety of elongations L. This way it became possible to determine the site-site interaction parameters ε and σ for non-polar molecules from orthobaric properties [12, 13]. The parameter L could be inferred from molecular models and from the steepness of the vapour pressure curve. Remarkably, the parameters ε, σ, L fixed on the liquid side of the orthobaric curve gave also satisfactory agreement to second virial coefficients. It should be mentioned that this method was successfully extended to 3CLJ, 4CLJ, and 6CLJ recently [14, 15].

Mixtures

The extension to mixtures was given by *Fischer* and *Lago* [16]. Now it is necessary to distinguish between like and unlike interactions. Eq. (6) transforms to

$$\left(\frac{F^*}{NkT}\right)_{Mi} = \left(\frac{F^*}{NkT}\right)^\circ_{Mi} + \frac{\rho}{2} \sum_{i,j=1,2} x_i x_j \times$$
$$\times \int y^\circ_{ij} \left\langle \frac{u^1_{ij}}{kT} e^{-u^\circ_{ij}/kT} \right\rangle \mathrm{d}\boldsymbol{r} \tag{9}$$

Again, the residual *Helmholtz* energy of the repulsive mixture is traced back to the residual *Helmholtz* energy of the hard body mixture, which can be expressed analytically. The crucial point is the determination of the hard sphere radii d_{ij} of the fused hard sphere bodies. For this, the following prescription of the blip conditions [cf. Eq. (8)] is used [4] (in accord with a suggestion by *Perram* [17])

$$x_i B_{ii} + x_j B_{ij} = 0 \tag{10a}$$
$$x_i B_{ij} + x_j B_{jj} = 0 \tag{10b}$$
$$d_{ij} = (d_{ii} + d_{jj})/2. \tag{10c}$$

These three equations determine the three contact distances between the hard spheres.

Combining Rules

A crucial problem in the treatment of mixtures is the assignment of the unlike interaction parameters ε_{12} and σ_{12}. For 1CLJ molecules, a possible answer was given by *Kohler* [18] and an improved version by *Kohler,* *Fischer, Wilhelm* [19]. Starting point was the simplified *London* formula [20] for dispersion energies, i.e. for like pairs

$$u_{\mathrm{disp}} = -\frac{3\alpha^2}{4r^6} h\nu, \tag{11}$$

and for unlike pairs

$$(u_{12})_{\mathrm{disp}} = -\frac{3}{4}\frac{\alpha_1 \alpha_2}{r^6}\frac{2h\nu_1 h\nu_2}{h\nu_1 + h\nu_2}. \tag{12}$$

Comparison with the long range part of the *Lennard-Jones* potential [Eq. (1)] gives

$$4\varepsilon_{11}\sigma_{11}^6 = \frac{3}{4}\alpha_1^2 h\nu_1 \tag{13 a}$$

or

$$4\varepsilon_{12}\sigma_{12}^6 = \frac{3}{4}\alpha_1\alpha_2\frac{2h\nu_1 h\nu_2}{h\nu_1 + h\nu_2}. \tag{13 b}$$

Eq. (13 a) may be used to calculate the characteristic energy $h\nu$ from the ε and σ values of the pure components, inserting literature values of the polarisability α. The energy $h\nu$ should be about equal to the ionization potential I, but due to the inadequacies of the 12/6 *Lennard-Jones* potential (which compensates too shallow a minimum by a too negative long range tail), it turns out that $h\nu/I$ comes out at a value near two. Inserting now the characteristic energies and polarisabilities of the pure components into Eq. (13 b), the unlike interaction potential minimum ε_{12} can be calculated, if σ_{12} can be estimated. The old method of *Kohler* [18] uses the approximation

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2, \tag{14 a}$$

the improved version [19] uses the additivity rule for the corresponding hard diameters

$$d_{12} = (d_{11} + d_{22})/2, \tag{14 b}$$

whereby the relation between σ and d was taken from the BH1 prescription [Eq. (5)]. As this relation is non-analytical, an iterative solution is necessary, which is easily obtained. It turned out that (14 b) gives mostly σ_{12} values slightly larger than (14 a), but the difference is only significant for large ratios of $\varepsilon_{11}/\varepsilon_{22}$.

The extension to 2 CLJ molecules is straight forward [4], considering that the *London* formula is for the long range tail of the potential, where the differences between site-site distances and center-center distances become negligible. Denoting the number of sites in molecule i by n_i (which might be one or two in the present work), Eq. (13a) and (13b) are transformed to

$$4\varepsilon_{11}\sigma_{11}^6 n_1^2 = (3/4)\alpha_1^2 h\nu_1 \tag{15a}$$

and

$$4\varepsilon_{12}\sigma_{12}^6 n_1 n_2 = (3/4)\alpha_1\alpha_2 2h\nu_1 h\nu_2/(h\nu_1 + h\nu_2). \tag{15b}$$

Usually the unlike interaction parameters are given relative to their *Lorentz-Berthelot* (*LB*) values, i.e. by the quantities ξ and η defined by

$$\varepsilon_{12} = \xi\sqrt{\varepsilon_{11}\varepsilon_{22}} \tag{16a}$$

and

$$\sigma_{12} = \eta(\sigma_{11} + \sigma_{22})/2. \tag{16b}$$

As said before, Eq. (14b) gives usually an η very near unity. If $\eta = 1$ is assumed, Eq. (15) give

$$\xi = \left[\frac{\sqrt{\sigma_{11}\sigma_{22}}}{(\sigma_{11} + \sigma_{22})/2}\right]^6 \frac{\sqrt{h\nu_1 h\nu_2}}{(h\nu_1 + h\nu_2)/2}, \tag{17}$$

i.e. ξ is given by the ratio of geometric to arithmetic mean of the σ's to the 6th power times the ratio of geometric to arithmetic mean of the characteristic energies. It is, therefore, very important to have good σ-values for making predictions on the unlike interaction. As a fit on the liquid density gives only a combination of σ and the elongation L, one may say that a lot depends on choosing the correct molecular model. The criteria for a good molecular model are the correct temperature dependence of the vapour pressure and a $h\nu/I$ ratio near two [4].

Correlation Formulae for Excess Properties

Following the pioneering work of *Singer* and *Singer* [28], we can give now correlation formulae for the excess properties for equimolar mixtures of 1CLJ + 2CLJ molecules (details will be published elsewhere). As indicated in Ref. [4] we start to calculate the properties of 1CLJ + 1CLJ mixture, and then elongate the one molecule in such a way, that vapour pressure and orthobaric density remain the same. Therefore, input parameters are then 1CLJ ε and σ and the non-sphericity parameter α connected to the elongation L by

$$\alpha = (1 + L)(2 + L)/(2 + 3L - L^3). \tag{18}$$

The excess properties of a *Lorentz-Berthelot* (LB, i.e. $\xi = 1.0$, $\eta = 1.0$) mixture 1CLJ + 1CLJ are for $\varepsilon_{12}/k = 133.5$ K, $\sigma_{12} = 3.596$ Å and equimolar composition, using the abbreviations

$$\delta = (\varepsilon_{22}/\varepsilon_{12} - 1)\sqrt{\varepsilon_{12}/\varepsilon_{22}}$$

and $\mu = (\sigma_{22}/\sigma_{12} - 1)$: (19)

$$g^E/\mathrm{J\,mol^{-1}} = 2\,980\,\delta^2 - 1\,300\,\mu^2 - 9\,050\,\delta\mu;$$
$$h^E/\mathrm{J\,mol^{-1}} = 2\,060\,\delta^2 + 3\,600\,\mu^2 - 12\,350\,\delta\mu; \tag{20}$$
$$v^E/\mathrm{cm^3\,mol^{-1}} = -17.2\,\delta^2 - 20.9\,\mu^2 + 27.0\,\delta\mu.$$

If molecule 2 is now elongated to a non-sphericity parameter α, the following increments have to be added:

$$\begin{aligned}\Delta g^E/\mathrm{J\,mol^{-1}} = &-2\,950\frac{(\alpha-1)^{3/2}}{1+15(\alpha-1)^{3/2}} + 7\,070\,\delta\frac{\alpha-1}{\alpha\left(1+25(\alpha-1)^{1/2}\right)} + \\ &+ 120\,190\,\mu\frac{\alpha-1}{\alpha\left(1+25(\alpha-1)^{1/2}\right)} - \\ &- 1\,274\,615\,\delta\mu\left[\frac{\alpha-1}{\alpha\left(1+25(\alpha-1)^{1/2}\right)}\right]^2\end{aligned} \tag{21}$$

$$\begin{aligned}\Delta h^E/\mathrm{J\,mol^{-1}} = &-5\,000\frac{(\alpha-1)^{3/2}}{1+15(\alpha-1)^{3/2}} + 7\,244\,\delta\frac{\alpha-1}{\alpha\left(1+5(\alpha-1)^{1/2}\right)} + \\ &+ 116\,170\,\mu\frac{\alpha-1}{\alpha\left(1+15(\alpha-1)^{1/2}\right)} - \\ &- 841\,535\,\delta\mu\frac{(\alpha-1)^2}{\alpha^2\left(1+5(\alpha-1)^{1/2}\right)\left(1+15(\alpha-1)^{1/2}\right)}\end{aligned} \tag{22}$$

$$\begin{aligned}\Delta v^E/\mathrm{J\,mol^{-1}} = &-11.12\frac{(\alpha-1)^{3/2}}{1+15(\alpha-1)^{3/2}} + 4.836\,\delta(\alpha-1)^{3/2} + \\ &+ 18.42\,\mu\frac{(\alpha-1)^{1/2}}{1+(\alpha-1)^{1/2}} - 6.8\,\delta\mu\frac{(\alpha-1)^{1/2}}{1+(\alpha-1)^{1/2}}\end{aligned} \tag{23}$$

For ξ and η values different from unity the following increments have to be added:

$$\Delta g^E/\mathrm{J\,mol^{-1}} = 3\,400(1-\xi) - (\eta-1)\left(900 + 2\,400(\alpha-1)^{1/2}\right) \tag{24}$$
$$\Delta h^E/\mathrm{J\,mol^{-1}} = 5\,000(1-\xi) + (\eta-1)\left(400 - 3\,700(\alpha-1)^{1/2}\right) \tag{25}$$
$$\Delta v^E/\mathrm{cm^3\,mol^{-1}} = 6(1-\xi) + (\eta-1)\left(50 - 13.2(\alpha-1)^{1/2}\right) \tag{26}$$

When the actual mixture has ε_{12} and σ_{12} values different from 133.5 k and 3.596 Å, all g^E and h^E-terms have to be multiplied by $\varepsilon_{12}/133.5\,k$ and all v^E-

terms by $(\sigma_{12}/3.596)^3$. The resultant excess properties are for a reduced temperature $kT/\varepsilon_{12} = 0.72659$. The excess *Gibbs* energy can be easily extrapolated to another experimental temperature by using h^E. The temperature dependence of h^E is usually not very serious. The temperature dependence of v^E, however, can be remarkable. Denoting the reduced experimental temperature T^*, the following procedure has been used to calculate v^E for T^*:

For the 1CLJ + 1CLJ LB-mixture,

$$v^E(T^*) = v^E(0.72659)\left(1 + 2\frac{T^* - 0.72659}{1.30 - T^*}\right) \tag{27}$$

For all other v^E-terms:

$$\Delta v^E(T^*) = \Delta v^E(0.72659)\left(1 + 0.8\frac{T^* - 0.72659}{1.30 - T^*}\right) \tag{28}$$

The Pair Potential of Nitric Oxid Monomer and Dimer

As the nitric oxid dimer should be treated as 2CLJ, it is natural to describe the monomer by an 1CLJ model. The experiences with nitrogen and oxygen have shown that for these relatively weak anisotropies the description by an 1CLJ is permissible.

Next we have to collect the experimental facts which are helpful for the evaluation of the potential parameters. For the liquid, the ratio of monomer to dimer is known by a magnetic susceptibility technique [21]. At 115.76 K, the mole fraction of dimer amounts to $x_D = 0.9328$. The molar volume of the (mainly dimeric) mixture is at this temperature [2] $v = 23.179\,\mathrm{cm^3\,mol^{-1}}$. The vapour pressure is $p_\sigma = 0.051$ MPa [2, 3]. The vapour phase is mainly monomeric, as the second virial coefficient is (slightly extrapolated value [2]) not more negative than $B = -275.3\,\mathrm{cm^3\,mol^{-1}}$. Furthermore, we note that for the monomer the polarisability is $\alpha = 1.71 \cdot 10^{-24}\,\mathrm{cm^3}$, and the ionization potential $I = 9.25$ to 9.5 eV [22, 23].

First of all, we will estimate the vapour pressure of (fictitious) pure monomeric NO. Assuming that there is no $(NO)_2$ in the vapour, we have

$$0.051 = (1 - x_D)\,\gamma_m\,(p_{om}/\mathrm{MPa})\,e^{p_{om}B/RT}, \tag{29}$$

were the fugacity coefficient is approximated by

$$\varphi_{om} = e^{p_{om}B/RT}. \tag{30}$$

The activity coefficient γ_m is set equal to 1.165 on account of a calculation dealt with later. This gives for the fictitious vapour pressure of monomeric liquid $p_{om}/\mathrm{MPa} = 0.8255$. Comparison with the vapour pressure of O_2

(0.7925 MPa) and N_2 (2.0215 MPa) shows that ε_{NO} is much nearer to ε_{O_2} than to ε_{N_2}. The detailed assignment depends on the value of σ, for which we have no densities. Therefore, we can only determine σ via Eq. (13a), choosing a suitable value for the characteristic energy $h\nu$. As this energy should be about twice the ionization potential (in fact a bit more than twice because we treat NO as 1CLJ), we choose $(h\nu)_{NO} = 20$ eV. This leads, together with the vapour pressure given above, to $\varepsilon/k = 125$ K and $\sigma = 3.1715$ Å (for the corresponding parameters of O_2 and N_2 cf. Table 1). The small value for σ is remarkable, but this is backed by the small critical volume $v_c = 58\,\mathrm{cm^3\,mol^{-1}}$ (to be compared with $v_c = 76.4\,\mathrm{cm^3\,mol^{-1}}$ for O_2 and $v_c = 90.1\,\mathrm{cm^3\,mol^{-1}}$ for N_2 [24]).

Now the assumption of purely monomeric vapour can be reinvestigated. The potential parameters give for the second virial coefficient at 115.76 K a theoretical value of $B = -113\,\mathrm{cm^3\,mol^{-1}}$. As the *Lennard-Jones* potential tends to give too positive second virial coefficients at low temperatures, a value of the dimerization constant of $K_p/\mathrm{MPa^{-1}} = -(B-113)/RT = 0.169$ would be an upper limit. This value is comparable to the value deduced by *Guggenheim* [25] from his correlation of second virial coefficients (when corrected for his non-understandable factor of 4) ($K_p/\mathrm{MPa^{-1}} = 0.174$) and also to an evaluation from heat of vapourization [26] and slope of the vapour pressure curve [3] (which gives, along the lines of Ref. [27], $K_p = 0.152\,\mathrm{MPa^{-1}}$), but does not confirm the argument put forward by *Scott* [24]. For the partial vapour pressure of the dimer at 115.76 K, a value of $p_D = 0.00043$ MPa follows, which is less than one percent of the total pressure measured at this temperature. Thus our assumption of purely monomeric vapour is within the error of the chosen characteristic energy.

The assignment of the potential parameters ε, σ, L for the dimer has to take into account the small vapour pressure and the given molar volume of

Table 1. *Potential parameters of* O_2, N_2, NO, CH_4, Kr *as 1CLJ and of* $(NO)_2$ *as 2CLJ and equivalent 1CLJ*

Substance	$\dfrac{\varepsilon/\mathrm{K}}{k}$	σ/Å	L
O_2	122.67	3.3718	
N_2	100.31	3.6065	
NO	125.00	3.1715	
CH_4	149.92	3.7327	
Kr	164.11	3.6221	
$(NO)_2$	125.00	3.506	0.62
	247.35	4.1491	

the liquid. We assume the site parameter ε to be the same as for the monomer and adjust L to the small vapour pressure of the fictitions pure dimer, p_{od}/MPa = 0.000462. It should be noted that the vapour pressure (for constant site parameters ε and σ) decreases from $L = 0.79$ to $L = 0.59$ by a factor of 15, according to the Tables of Ref. [12] and [13]. Thus a small amount of dimerization in the gas phase is connected with a relatively short bond length of the dimer bond (in the absence of effects from polar forces).

In the present case, for a correct order of magnitude of p_{od}, the elongation L should not be much above $L = 0.59$. For a more detailed statement, the σ-parameter has to be determined. The experimental volume $v = 23.179\,\mathrm{cm^3\,mol^{-1}}$ is connected to the volumes of monomer and dimer by

$$v = (x_d v_d + x_m v_m + v^E)/(1 + x_d) \tag{31}$$

Inserting the volume of monomer according to the potential parameters, $v_m = 25.805\,\mathrm{cm^3\,mol^{-1}}$, and v^E from the calculation given in the next section (which is $v^E_{0.5} = -0.665\,\mathrm{cm^3\,mol^{-1}}$, and approximately $v^E_{0.9328} = -0.167\,\mathrm{cm^3\,mol^{-1}}$), the volume of the dimer is determined to be $v_d = 46.348\,\mathrm{cm^3\,mol^{-1}}$. This gives $L = 0.62$ and $\sigma = 3.506\,\text{Å}$. The resulting $l = 2.17\,\text{Å}$ is only slightly smaller than the experimental N—N distance (2.23) [29].

It is remarkable that σ of one site in dimeric $(NO)_2$ is so much bigger (about ten per cent) than σ of the monomeric NO. Probably it has to do with the fact that NO is less spherical than N_2, and that $(NO)_2$ has an almost rectangular structure [29]. Apparently, for the density in monomeric NO the smallest dimension of the molecule is most important, whereas the rotation of the dimeric molecule around the axis of smallest moment of inertia coincides almost with the end-over-end rotation of the NO group [30]. It would be worth while to reconsider the monomer-dimer mixture of nitric oxide as soon as 2 CLJ + 4CLJ mixtures can be treated.

The Excess Properties of Nitric Oxid Mixtures

Table 1 gives a summary of the potential parameters of the components of interest. The properties of nitric oxid mixtures are then calculated as pseudoternary mixtures [30], with activity coefficients γ_i of the species formulated according to the simple *Porter* ansatz, as e.g.,

$$\ln \gamma_1 = \alpha_{12} x_2^2 + \alpha_{1B} x_B^2 + x_2 x_B (\alpha_{12} + \alpha_{1B} - \alpha_{2B}). \tag{32}$$

The interaction parameters α between monomer (1), dimer (2) and second component (B) are calculated from the equimolar excess properties of the binaries, e.g.

$$\alpha_{12} = 4\, g^E_{12,0.5}/RT \tag{33}$$

For determining the mole fractions of monomer and dimer in the pseudoternary mixture of given formal mole fraction X_B, the thermodynamic dimerisation constant has to be formulated in activities:

$$K = \frac{x_2 \gamma_2}{(x_1 \gamma_1)^2} = 154.175\,(T = 115.76\,\mathrm{K}) \tag{34}$$

In addition, one has the relations

$$X_B = \frac{x_B}{1 + x_2}, \quad x_1 + x_2 + x_B = 1. \tag{35}$$

The activity coefficients of the components φ_i follow via

$$\varphi_A = x_1 \gamma_1 / (x_1^\circ \gamma_1^\circ X_A) \tag{36}$$

$$\varphi_B = x_B \gamma_B / X_B, \tag{37}$$

where the superscript o refers to pure component A.

The excess properties of the binaries are given in Table 2. The temperature was always set to 115.76 K. The excess properties of the nitric oxide mixtures (at equimolar formal composition, $X_A = X_B = 0.5$) are presented in Table 3. For g^E, the calculation followed the scheme of Eqs. (30)–(35), for h^E the calculation used the equimolar binary data $h_{0.5}^E$ via

$$\begin{aligned} h^E = {} & [4\,x_1 x_2 (h_{0.5}^E)_{12} + 4\,x_1 x_B (h_{0.5}^E)_{1B} + \\ & + 4\,x_2 x_B (h_{0.5}^E)_{2B}]/(1 + x_2) - \\ & - 2\,x_1^\circ x_2^\circ (h_{0.5}^E)_{12}/(1 + x_2^\circ) + \\ & + \Delta h^\circ [x_2/(1 + x_2) - 0.5\,x_2^\circ/(1 + x_2^\circ)], \end{aligned} \tag{38}$$

where

$$\Delta h^\circ = R T^2\, \partial \ln K / \partial T. \tag{39}$$

Table 2. *Excess properties for equimolar composition for the fictitious binary systems of* NO *and* $(NO)_2$ *with* Kr, CH_4, N_2. g^E/J mol^{-1} *and* v^E/cm^3 mol^{-1} *are calculated for* $T = 115.76$ *K,* h^E/J mol^{-1} *is given for* T/K *indicated in parenthesis*

System	ξ	η	g^E	h^E	v^E
NO + Kr	0.96557	1.00143	85.9	123.6 (104.07)	0.078
NO + CH_4	0.95789	1.00172	81.3	164.9 (99.47)	0.254
NO + N_2	0.94935	1.00158	181.7	319.5 (81.36)	—0.727
NO + $(NO)_2$	1.00075	0.99885	42.1	—50.0 (127.78)	—0.665
$(NO)_2$ + Kr	0.98856	1.00019	73.0	54.2 (146.39)	—0.219
$(NO)_2$ + CH_4	0.98586	1.00033	152.3	107.9 (139.92)	—0.592
$(NO)_2$ + N_2	0.9771	0.99966	524.6	342.4 (114.45)	—3.354

The parameters ξ and η give the deviations from the *LB*-combining rule (Eq. 16)

Table 3. *Calculated excess properties for 115.76 K and equimolar composition for the real binary mixtures of nitric oxid with* Kr, CH_4, N_2 *in comparison with experimental values*

System	$g^E/\mathrm{J\,mol^{-1}}$ calc	$g^E/\mathrm{J\,mol^{-1}}$ exp	$h^E/\mathrm{J\,mol^{-1}}$ calc	$h^E/\mathrm{J\,mol^{-1}}$ exp	$v^E/\mathrm{cm^3\,mol^{-1}}$ calc	$v^E/\mathrm{cm^3\,mol^{-1}}$ exp
nitric oxid + Kr	244.3	389.9[a]	138.6	—	—0.077	0.451
+ CH_4	292.3	426.6[b]	211.4	—	—0.289	—
+ N_2	524.5	491.2[c]	456.0	475	—1.950	—

No temperature correction has been applied for h^E

[a] *Ref.* [2]

[b] For $T = 111.2\,\mathrm{K}$, Ref. [1] (g^E calculated without correction for the non-ideality of the gas phase)

[c] For $T = 114.7\,\mathrm{K}$, Ref. [3]

An analogous formula applies to v^E. The experimental value [21] for $\partial \ln(x_2^\circ/x_1^{\circ 2})/\partial T$ has to be corrected for $\partial \ln(\gamma_2^\circ/\gamma_1^{\circ 2})/\partial T$ by means of the h_{12}^E-value given in Table 2. The result is $\Delta h^\circ = —14890\,\mathrm{J\,mol^{-1}}$. The calculated value of Δv°, using the molar volumes of dimer and monomer in the preceding section, is $\Delta v^\circ = —5.262\,\mathrm{cm^3\,mol^{-1}}$. As the term within the brackets in the fourth line of eqn. (36) contributes only between —0.006 and —0.016, most of v^E and an appreciable part of h^E comes from the non-ideal behaviour of the binaries.

The comparison between calculated and experimental excess properties in Table 3 shows that the calculation gives a reasonable trend, but fails in some details. The values of g^E are too low for the Kr and the CH_4 system, and a bit too high for the N_2 system. But the order is produced correctly. The only serious failure concerns the v^E value of the Kr system. Though the calculation gives the smallest negative value for this system, the discrepancy is still $0.5\,\mathrm{cm^3\,mol^{-1}}$.

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