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Liquid-Vapor Isotope Fractionation Factors in Argon-Krypton Binary Mixtures[*]

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ABSTRACT

An equilibrium isotope effect has been studied as a continuous function of the potential field acting on the atom undergoing isotopic exchange. This has been accomplished through a study of the liquid vapor isotope fractionation factors for both $^{36}Ar/^{40}Ar$ and $^{80}Kr/^{84}Kr$ in a series of binary mixtures which span the range between the pure components at 117.5°K. The $^{36}Ar/^{40}Ar$ fractionation factor increases (linearly) from ($\ln\alpha$) 2.49×10^{-3} in pure liquid argon to 2.91×10^{-3} in an infinitely dilute solution in liquid krypton. Conversely, the $^{80}Kr/^{84}Kr$ fractionation factor decreases (linearly) from ($\ln\alpha$) 0.98×10^{-3} in pure liquid krypton to 0.64×10^{-3} in an infinitely dilute solution in pure liquid argon. The mean force constants, $<\nabla^2 U>_c$, on both argon and krypton atoms in the mixtures are derived from the respective isotope fractionation factors. It is shown that the mean force constant on argon atoms in infinitely dilute solution in krypton is equal, within experimental error, to the mean force constant on krypton atoms in infinitely dilute solution in argon. The symmetry of the mixed force constants, $<\nabla^2 U_i>_j = <\nabla^2 U_j>_i$ indicates that the assumption of additive pair interactions is sufficient to treat $<\nabla^2 U>$. The latter is mainly a function of $U(r)$ in the range $0.90 r_{min} < r < 1.10 r_{min}$.

The mean force constants for argon and krypton as a function of composition have been calculated by a modified corresponding states theory which uses the pure liquids as input parameters. The modified corresponding states theory reproduces $<\nabla^2 U>$ for Kr over the entire concentration range, but leads to values of $<\nabla^2 U>(Ar)$ which are systematically higher than experiment. The discrepancy is 8% at $X_{Ar}=0$. A systematic set of calculations has been made of $<\nabla^2 U>(Ar)$ and $<\nabla^2 U>(Kr)$ as a function of composition using radial distribution functions generated by the Weeks-Chandler-Anderson perturbation theory. The calculated results for $<\nabla^2 U>(Kr)$ using the Lee-Henderson-Barker, Maitland-Smith, and Lennard-Jones potentials are in good agreement with experiment. None of these potentials give satisfactory agreement with the experimental values of $<\nabla^2 U>(Ar)$ in dilute solution in krypton. The discrepancy is ascribed to failure of the WCA method to predict g_{Ar-Kr}, the mixed radial distribution function, with sufficient accuracy close to the triple point of a fluid.

Introduction

The isotopic vapor pressure ratio or liquid-vapor separation factor of a monatomic substance is directly related to the mean square force or the Laplacian of the intermolecular potential.[1-3] The isotope separation factor is a sensitive probe of the steepness of the repulsive part of the potential;[4] liquid pressures are sensitive to the collision diameter; while the internal energy is sensitive to the potential well depth. The vapor pressure ratios and separation factors have been measured for the pure rare gases Ne, Ar and Kr to study properties of the liquid state and test various intermolecular potentials.[4] To calculate the mean square force in a fluid from the intermolecular potential, it is necessary to know the radial distribution function. Experimental values of the latter when combined with a wide variety of reasonable potential functions give values of the mean square force as a function of temperature in poor agreement with experiment. On the other hand, numerical calculation of the radial distribution functions by molecular dynamics, integral equations and perturbation methods do give quantitative agreement with experimental values when one uses good intermolecular potentials for monatomic substances.[4] The criterion for a good potential is one that is in good agreement with experimental values for such diverse properties as gas viscosity, virial coefficients of the gas, molecular beam scattering, energy levels of the dimer, liquid pressure and energy of vaporization.

In the general theory of equilibrium isotope effects, the difference in chemical and physical properties of isotopes is to first order a product of $(\hbar/kT)^2$, a mass factor, and a difference in values of $\langle \nabla^2 U \rangle$, the Laplacian of the potential energy, in the two chemical species or phases in the equilibrium. The mass factor is $(\frac{1}{m'} - \frac{1}{m})$, where m' and m are atomic masses of the light and heavy isotope respectively, and is therefore independent of phase or chemical combination.[5] Equilibrium isotope effects are then a linear function of $\langle \nabla^2 U \rangle_a$ minus $\langle \nabla^2 U \rangle_b$, the difference in the Laplacian of the potential energies of the two species or phases. These are discontinuous functions when the systems are chemical compounds or pure phases. The study of a series of mixtures opens the possibility of varying $\langle \nabla^2 U \rangle$ in a continuous fashion from its value in a pure component to a completely different one. An example of the latter is the potential energy between unlike pairs in a mixture. No such study of a systematic variation of $\langle \nabla^2 U \rangle$ has been carried out to date.

We have chosen for the study the $^{36}Ar/^{40}/Ar$ and $^{80}Kr/^{84}Kr$ liquid-vapor isotope fractionation factors in argon-krypton mixtures. As a complement to the data in hand on the isotopic fractionation factors of the pure components, there is a rich literature on the thermodynamic properties of the mixtures[6] potential energy functions for the pure components and pairs,[7-10] and statistical mechanical theories of the mixtures.[11-16] The measurements cover the entire composition range at the convenient temperature of 117.5° K. Limitations of equipment and precision in measurement preclude a measurement at this time of the temperature coefficient of $\langle \nabla^2 U \rangle$ in this mixture.

Isotope Separation Factor in a Multicomponent Mixture

In this section we give an extension of the statistical
thermodynamic relationship of the liquid-vapor isotope fraction
factor in a pure phase [16,17] to a multicomponent mixture.

The partition function of a system of N dependent monatomic
particles can be expanded about its classical value to give[1,18,19]

$$\ln Q = \ln Q_{cl} - \hbar^2 \overline{\chi}_2 + \ldots \tag{1}$$

where Q_{cl} is the classical partition function. When the
potential energy, U, is of the order of kT, then

$$\overline{\chi}_2 = \frac{1}{24}(kT)^{-2} \sum_{i}^{N} \frac{1}{m_i} <(\nabla^2 U)_i> \tag{2}$$

where m_i is the atomic mass of the i'th atom. In general
$U = U(x_1, x_2 \ldots x_{3N})$. If U is several fold larger than kT,
Eq. (2) can be modified by the method of Bigeleisen and Ishida.[20-22]
The Helmholtz free energy associated with the partition function
given by Eqs. (1) and (2) is

$$A = A_{cl} + \frac{1}{24} \frac{\hbar^2}{kT} \sum_{i}^{N} \frac{1}{m_i} <(\nabla^2 U)_i> \tag{3a}$$

$$A = A_{cl} + \frac{1}{24} \frac{\hbar^2}{kT} \sum^{r} \frac{N_i}{m_i} <(\nabla^2 U)_i> \tag{3b}$$

where the sum over r runs over the number of distinct components in the phase. The classical Helmholtz free energy is

$$A_{cl} = \Sigma n_i \overline{A}_{icl} = \Sigma n_i (\overset{\circ}{A}_{icl} + RT\ln x_i) + (A_e)_{cl} \qquad (4)$$

where $\overline{A}_{icl}$ and A°_{icl} are partial molal and standard partial molal Helmholtz free energies respectively in the classical limit; n_i is the number of moles of species i whose mole fraction in the mixture is x_i. $(A_e)_{cl}$ is the excess free energy of mixing in the classical limit. From the equilibrium condition $\mu_{i(1)} = \mu_{i(g)}$ and the thermodynamic relation $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$, we obtain from Eq'(s) (3) and (4) under the assumptions $A^{\circ}_{icl} = A^{\circ}_{jcl}$, $\frac{\partial (A_e)_{cl}}{\partial n_i} = \frac{\partial (A_e)_{cl}}{\partial n_j}$ and $U_i = U_j$ when i and j are isotopes of a given element[23]

$$\ln \alpha = \ln [(x_i/x_j)_g / (x_i/x_j)_1] = \frac{1}{24} \left(\frac{\hbar}{kT}\right)^2 \left(\frac{1}{m_i} - \frac{1}{m_j}\right) \times$$

$$[<(\nabla^2 U_i)>_1 - <(\nabla^2 U_i)_g>] \qquad (5)$$

Equation (5) is identical in form with that derived for a single chemical component system.[17] In the one component system $<(\nabla^2 U)_i>_{1,c}$ is only a function of temperature; in the multi-component system it is also a function of composition. In the

approximation of pair interactions $<(\nabla^2 U)_i>$ can be related to the two body potential by

$$<(\nabla^2 U)_i> = 4\pi \sum_k^r \rho_k \int g_{ik} r^2 \nabla^2 U_{ik} \, dr \tag{6}$$

where k designates the chemical component, ρ_k is the number density of the k'th component $(\rho_k = x_k \rho_m)$, and U_{ik} is the two body potential between components i and k.   The calculation of g_{ik} from U_{ik} is discussed later.

Experimental

The cryostat and the measuring devices for pressure and temperature have been described previously[17]. The sample temperatures were measured by a platinum resistance thermometer which had been calibrated to ± 0.02° K. Samples of the liquid and vapor can be withdrawn through capillary tubes extending into the liquid and vapor phase respectively. Alternatively vapor phase samples can be isolated from sections of the circulation line external to the cryostat. Chemical analyses of the liquid and vapor phases were made mass spectrometrically. Isotope ratios of the vapor phase and the tank sample were made on our Nuclide 6-60-RMS isotope ratio mass spectrometer. The isotopic composition of the liquid phase differs by a small amount from that of the tank sample and was calculated through

a material balance correction to the latter. This procedure leads to more reproducible values for the isotopic composition of the liquid phase than our sampling procedure.

The argon-krypton sample mixtures were separated into pure components for isotopic analysis. The separation procedure has been described previously.[24] The argon and krypton samples were research grade from Matheson.

Kr-Ar mixtures of the desired composition were prepared by injecting known quantities of Ar into the calorimeter which contained a known quantity of Kr.

The liquid mixture was stirred by a gas circulating pump [25] which has two compartments separated by a stainless steel bellow. An external magnet drives the bellows back and forth. Uni-directional continuous flow of the gas is achieved by a pair of three-way solenoid valves. The flow rate was about 15cc/min.

Results

Natural argon contains 0.34% ^{36}Ar, 0.06% ^{38}Ar and 99.6% ^{40}Ar. It is convenient to measure the ^{36}Ar/(^{38}Ar + ^{40}Ar) ratio. Since ^{38}Ar is a minor constituent compared with ^{40}Ar and its fractionation factor is small, the system can be treated as a two component mixture of ^{36}Ar and ^{40}Ar. Natural krypton has isotopes ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr and ^{84}Kr. The most abundant nuclide is ^{84}Kr (56.9%). It is convenient for us to measure the ratio $N_{80}/(N_{82} + N_{83} + N_{84} + N_{86})$ where

N_A is the number of krypton atoms of mass A. We define an observed fractionation factor α_{Kr} (obs)

$$\alpha_{Kr}(obs) = \frac{[N_{80}/(N_{82} + N_{83} + N_{84} + N_{86})]_g}{[N_{80}/(N_{82} + N_{83} + N_{84} + N_{86})]_l} \tag{7}$$

and the $^{80}Kr/^{84}Kr$ fractionation factor as

$$\alpha_{Kr} = (N_{80}/N_{84})_g/(N_{80}/N_{84})_l \tag{8}$$

Then

$$\alpha_{Kr} = \alpha_{Kr}(obs) \frac{(1 + \frac{N_{82}}{N_{84}} + \frac{N_{83}}{N_{84}} + \frac{N_{86}}{N_{84}})_g}{(1 + \frac{N_{82}}{N_{84}} + \frac{N_{83}}{N_{84}} + \frac{N_{86}}{N_{84}})_l} \tag{9}$$

The liquid-vapor fractionation factor of krypton of mass A against ^{84}Kr is of the form

$$(N_A/N_{84})_g/(N_A/N_{84})_l = 1 + (\frac{1}{m_A} - \frac{1}{84})a \tag{10}$$

The quantity a can be related to the $^{80}Kr/^{84}Kr$ fractionation factor, α_{Kr}

$$a = \frac{(80)(84)}{(84-80)} (\alpha_{Kr} - 1) \tag{11}$$

combination of Eq's (7-11) leads to

$$\alpha_{Kr} = \alpha_{Kr}(\text{obs}) \frac{[1 + \sum_{A=82,83,86} (\frac{N_A}{N_{84}})_1 (1 - \frac{80}{m_A} (\frac{84-m_A}{84-80}))]}{[1 + \sum_{A=82,83,86} (\frac{N_A}{N_{84}})_1 (1 - \frac{80}{m_A} (\frac{84-m_A}{84-80}) \alpha_{Kr}(\text{obs}))]} \tag{12}$$

Since $(N_A/N_{84})_1$ is almost identically that of natural abundance krypton, we can insert the natural abundance values for N_A/N_{84} into Eq. (12) and obtain

$$\alpha_{Kr} = 1.7056 \, \alpha_{Kr}(\text{obs})/(1.7114 - 0.0059 \, \alpha_{Kr}(\text{obs})) \tag{13}$$

The liquid-vapor fractionation factors calculated from the measured isotope ratios are given in Table I and shown in Fig. 1. The values for pure Ar and pure Kr in Fig. 1 are taken from previous work from our laboratory.[17,24]

To derive the values of $<\nabla^2 U)_i>_1$ from the observed fractionation factors and Eq. (5), we have calculated $<(\nabla^2 U)_i>_g$ for the mixtures using the Percus-Yevick equation to calculate the

radial distribution function in the gas from several potentials.[7-10]
The correction to $<(\nabla^2 U_i)>_l$ from $<(\nabla^2 U_i)>_g$ at 117° K is of the
order of five per cent.[26] The experimentally determined values
of $<(\nabla^2 U)_{Ar}>$ and $<(\nabla^2 U)_{Kr}>$ as a function of composition are
tabulated in Table II and shown in Figs. 2 and 3.

For the case of argon, $<(\nabla^2 U)_{Ar}>$, increases from its value
of 8580 ± 350 erg cm^{-2} in pure argon to 9960 ± 375 erg cm^{-2} in an
infinitely dilute solution of krypton solvent at 117.5° K.
Conversely $<(\nabla^2 U)_{Kr}>$ decreases from its value 15570 ± 350 erg cm^{-2}
in pure krypton to $10,800 \pm 750$ erg cm^{-2} in an infinitely dilute
solution in pure argon. Within experimental error, $<\nabla^2 U)_{Ar}>$ at
$X_{Ar} = 0$ is equal to $<(\nabla^2 U)_{Kr}>$ at $X_{Kr} = 0$. This result indicates
that the assumption of additive pair potentials should be
adequate for the treatment of the mean force constants
of the two chemical components in the mixtures.

Discussion

Corresponding States Approach

In this section we develop a corresponding states approach for $<(\nabla^2 U)_{Ar}>$ and $<(\nabla^2 U)_{Kr}>$ as a function of composition and compare the results with our experiments. The basis for the corresponding states approach to the equation of state is the assumption that the potential energy has a universal form. With the approximation of pair potentials, we write

$$U_{ij} = \epsilon_{ij} R_{ij} (r/r_{mij}) \tag{14}$$

where ϵ_{ij} is the depth of the pair potential and r_{mij} is the value of r at the minimum. The corresponding states assumption, $R_{11} = R_{12} = R_{22}$, then gives $g_{11}(r^*) = g_{12}(r^*) = g_{22}(r^*)$, where $r^* = r/r_{mij}$. It then follows that

$$\frac{<\nabla^2 U^*>_{11}}{\rho^*} = \frac{<\nabla^2 U^*>_{12}}{\rho^*} = \frac{<\nabla^2 U^*>_{22}}{\rho^*} \qquad \text{where the subscripts}$$

denote the respective pair potentials. Finally, one gets for $<(\nabla^2 U)_i>$, the mean force constant on the i'th chemical species in a two component mixture

$$<\nabla^2 U_i> = 4\pi\rho_M \, [x_1 \epsilon_{i1} r_{mi1} + x_2 \epsilon_{i2} r_{mi2}] \; x$$

$$\int g(r^*) r^{*\,2} (\nabla^2 U^*) dr^* \tag{15}$$

where ρ_M is the density of the mixture. The ratio of the mean force constants for the two components in their respective pure states, $<(\nabla^2 U^\circ)_i>$, is

$$\frac{<(\nabla^2 U^\circ)_{Kr}>}{<(\nabla^2 U^\circ)_{Ar}>} = \left(\frac{\rho_{Kr}}{\rho_{Ar}}\right) \frac{\epsilon_{KrKr} r_{mKrKr}}{\epsilon_{ArAr} \; r_{mArAr}} \qquad (16)$$

The experimental determinations of $<(\nabla^2 U^\circ)_{Kr}>$[24] and $<\nabla^2 U^\circ)_{Ar}>$[17,27] give 1.83 for the left hand side of Eq. (16) or 1.88 for the ratio of (ϵr) parameters in Eq (16). The ratio of the product $\epsilon_{11} r_m$ for krypton to that of argon is calculated to be 1.51, 1.48, and 1.50 from the Lee, Henderson, Barker,[7] Maitland-Smith,[9,10] and Kim-Gordon[18] potentials directly. Clearly, the corresponding states approach cannot be used without further refinement. From Eq. (16) it follows that $<\nabla^2 U^{\circ *}>$, the reduced mean force constant is a universal constant. We have found this conclusion to be invalid. In a similar way we find it is impossible to reproduce simultaneously the variation of both $<(\nabla^2 U)_{Ar}>$ and $<(\nabla^2 U)_{Kr}>$ over the entire composition range through Eq (15).

We have shown experimentally that $\frac{1}{\rho} <\nabla^2 U^\circ>$ is independent of temperature from the triple point to $(.9)(T/T_c)$ where T_c is the critical temperature. However, $\frac{1}{\rho} <\nabla^2 U^{\circ *}>$ varies from substance to substance. It is possible to modify the theorem

of corresponding states for $\langle\nabla^2 U\rangle$ by the introduction of a scaling factor, b, in the vicinity of the first peak of the radial distribution function. We shall use this approach to examine the variation of $\langle\nabla^2 U\rangle_i$ in a two component mixture. We write

$$g_{11} = b^{\frac{1}{2}} g_{12} = b g_{22} \qquad (0.9 < r^* < 1.3) \qquad (17)$$

Introduction of the scaling factor, b, into Eq. (8) leads to the following correction to Eq (15)

$$\langle(\nabla^2 U)_1\rangle = 4\pi\rho_M[x_1 \epsilon_{11} r_{m11} + b^{-\frac{1}{2}} x_2 \epsilon_{12} r_{m12}] \quad x$$

$$\int g^* r^{*2} \nabla^2 U^* dr^* \qquad (18a)$$

$$\langle(\nabla^2 U)_2\rangle = 4\pi\rho_M[b^{-\frac{1}{2}} x_1 \epsilon_{12} r_{m12} + b^{-1} x_2 \epsilon_{22} r_{m22}] \quad x$$

$$\int g^* r^{*2} \nabla^2 U^* dr^* \qquad (18b)$$

The values of $\langle(\nabla^2 U^\circ)_{Ar}\rangle$ and $\langle(\nabla^2 U^\circ)_{Kr}\rangle$ at 117.5° K lead to the value $b(117^\circ$ K$) = (g_{ArAr}/g_{KrKr}) = 0.80$. The scaling factor b should be relatively insensitive to temperature.

For the calculation of $\int g^* \nabla^2 U^* r^{*2} dr^*$ one can use either molecular dynamics, the WCA perturbation theory or good experimental data on liquid argon and a self consistent set of potential parameters as given in Table III. Comparison of the modified corresponding states approach with experiment is shown in Figs. 2 and 3. Agreement with experiment is excellent for $<(\nabla^2 U)_{Kr}>$; however, the calculated value of $<(\nabla^2 U)_{Ar}$ in pure krypton is about 9% larger than the experimental value.

Calculation of $<(\nabla^2 U)_i>$ by the WCA Perturbation Theory

The Weeks-Chandler-Andersen (WCA)[28] method has been shown by comparison with molecular dynamics calculations to give good values of the radial distribution function of a pure liquid at high density. We have shown that WCA calculated radial distribution functions give good values for $<\nabla^2 U^\circ>$ for argon and krypton over a wide temperature range for a number of reasonable potentials.[29] These include the familiar Lennard Jones (12 - 6), Lee-Henderson-Barker,[7] and Maitland-Smith[9,10] potentials. In this section we shall utilize these potentials to calculate the g_{11}, g_{12}, and g_{22} radial distribution functions by an extension of the WCA method to two component mixtures.

The WCA method approximates the repulsive part of the potential by

$$U_{eff}(r) = U_{ij}(r) + \epsilon_{ij} \qquad r \leq r_{mij}$$
$$\tag{19}$$
$$= 0 \qquad r > r_{mij}$$

where $U_{eff}(r)$ is the effective WCA potential, ϵ is the well depth and $U(r)$ is any reference potential. The radial distribution function g_{ij} is calculated from the relation

$$g_{ij}(r) = Y_{dij}(r) \exp(-U_{effij}/kT) \tag{20}$$

Lebowitz[13] has shown how to calculate y_{dij} for a two component
system of hard spheres using the Percus-Yevick equation for
mixtures. The effective hard sphere diameter, d_{ij}, is calculated
as a function of composition, $y_{dij} = y_{dix}(x_1, x_2)$, through the
WCA criterion.

$$\int_0^\infty y_{dij}[\exp(-U_{effij}/kT) - \exp(-U_d/kT)]r^2 dr = 0 \qquad (21)$$

where U_d is the hard sphere potential. The effective hard
sphere diameters for Ar - Kr mixtures at 117^a K are given as a
function of composition in Table IV. We now calculate
$<(\nabla^2 U)_i>$ as a function of composition through Eq (6) from the
radial distribution functions given by Eq (20). Three potential
functions, L-J, LHB, and MS, have been used. The results are
compared with experiment in Table II and Figs. 2 and 3. We
have also calculated the mean potential energy, $<U>$, of
mixture

$$<U_i> = \sum_{ij} x_i x_j <U_{ij}> \qquad (22)$$

for the three potential functions. The mean pair potential
is given by

$$<U_{ij}> = 2\pi\rho \int_0^\infty g_{ij}(r) U_{ij}(r) r^2 dr \qquad (23)$$

The values of the mean potential energy of the mixture given in Table V show that there is little difference in this quantity at $117°$ K for the three potentials. In Table VI we compare the mean potential energy for the L-J(12-6) potential calculated by the WCA method with that calculated by the Monte Carlo method[15] for Ar-Kr mixtures at $116°$ K. We also give calculations of <U> from the free energies of the mixtures by Lee and Levesque[11] calculated by the WCA method. The agreement between all three calculations is within one per cent. The present direct calculations of <U> by the WCA method are in somewhat better agreement with the Monte Carlo values than those calculated through the free energy.

The calculated values of $<(\nabla^2 U)_{Kr}>$ are in good agreement with experiment over the entire composition range for the L-J, L-H-B, and M-S potentials. On the other hand all of these potentials give values of $<(\nabla^2 U)_{Ar}>$ significantly larger than the experimental value at $x_{Ar} = 0$. We attribute this discrepancy to the failure of the WCA method to calculate g_{Ar-Kr} with sufficient accuracy at low mole fractions of argon, where the solvent krypton is just above its triple point. The calculation of g_{Ar-Kr} probably improves as one gets away from the triple point. Thus the calculated value of $<(\nabla^2 U)_{Kr}>$ in pure argon at $117°$ K is in good agreement with experiment. It appears that the WCA method for the mixed radial distribution

function close to the triple point is inadequate particularly in the vicinity of the first peak. There is also a discrepancy between the $\langle U_{Ar-Kr} \rangle$ value calculated by the WCA compared with the Monte Carlo method at low mole fraction Ar (cf Table VI). It is much smaller than the discrepancy in $\langle (\nabla^2 U)_{Ar-Kr} \rangle$ since the latter is a much more sensitive function of the radial distribution function in the region $\sigma < r < r_{min}$ than is $\langle U_{Ar-Kr} \rangle$.

Captions

Fig. 1. $(^{36}Ar/^{40}Ar)$ and $(^{80}Kr/^{84}Kr)$ liquid-vapor fractionation
factors in a series of argon-krypton binary
mixtures at 117.5° K.

Fig. 2. $<(\nabla^2 U)_{Ar}>$ (erg cm^{-2} mole^{-1}) as a function of mole
fraction of argon (x_{Ar}) dissolved in liquid
krypton. ⊙ experimental data, ···· least square
line, —··— modified corresponding states
calculation, —·—WCA calculation using the
Maitland-Smith potentials, ——— WCA calculation using
the Lennard-Jones potentials, and — — — WCA
calculation using the Lee-Henderson-Barker potentials.

Fig. 3. $<(\nabla^2 U)_{Kr}>$ (erg cm^{-2} mole^{-1}) as a function of mole
fraction of krypton (x_{Kr}) dissolved in liquid
argon. ⊙ experimental data, ···· least square
line, —··—modified corresponding states
calculation, —·—WCA calculation using the
Maitland-Smith potentials, —— WCA calculation
using the Lennard-Jones potentials, and — — — WCA
calculation using the Lee-Henderson-Barker
potentials.

Table I

Liquid-Vapor Isotope Separation Factors in

Ar-Kr Mixtures at 117.5° K

Mole Fraction of Argon (Liquid)	$10^3 \ln\alpha_{Ar}$ [a]	$10^3 \ln\alpha_{Kr}$ [b]
0.103	2.87 ± 0.04	0.979 ± 0.022
0.210	2.82 ± 0.13	0.942 ± 0.057
0.310	2.73 ± 0.08	0.885 ± 0.059
0.614		0.736 ± 0.036
0.790		0.742 ± 0.022

a $(^{36}Ar/^{40}Ar)_g / (^{36}Ar/^{40}Ar)_l$

b $(^{80}Kr/^{84}Kr)_g / (^{80}Kr/^{84}Kr)_l$

Table II

Mean Force Constants, $\langle\nabla^2 U\rangle$, for Argon and Krypton

in Binary Mixtures of Argon-Krypton

Liquid at 117.5° K. (in erg cm^{-2})

(A) Argon

x_{Ar}	$\langle(\nabla^2 U)_{Ar}\rangle_{obs}$[a]	$\langle\nabla^2 U\rangle_{L-H-B}$	$\langle\nabla^2 U\rangle_{M-S}$	$\langle\nabla^2 U\rangle_{L-J}$
0.0		12708	13118	13534
0.1	9820 ± 140	(12411)	(12881)	(13174)
0.2	9680 ± 460	12115	12643	12813
0.3	9420 ± 260	(11711)	(12390)	(12340)
0.4		11307	11937	11867
0.6		10402	11547	10830
0.8		9494	10838	9807
1.0	8580 ± 350[b]	8646	8735	8864

(B) Krypton

x_{Ar}	$\langle(\nabla^2 U)_{Kr}\rangle_{obs}$[a]	$\langle\nabla^2 U\rangle_{L-H-B}$	$\langle\nabla^2 U\rangle_{M-S}$	$\langle\nabla^2 U\rangle_{L-J}$
0.0	15570 ± 350[c]	14540	15191	15070
0.1	15530 ± 950	(14177)	(14750)	(14668)
0.2	15080 ± 910	13813	14309	14265
0.3	14220 ± 930	(13327)	(13862)	(13737)
0.4		12841	13415	13208
0.6	11990 ± 570	11760	12454	12049
0.8	12170 ± 350	10678	11396	10904
1.0		9969	10243	9848

a $\langle \nabla^2 U \rangle_{obs} = [\langle \nabla^2 U \rangle_l - \langle \nabla^2 U \rangle_g]_{obs} + \langle \nabla^2 U \rangle_{gas}$ (cal)

b J. T. Phillips, C. U. Linderstrom-Lang and J. Bigeleisen, J. Chem. Phys. <u>56</u>, 5053 (1972).

c M. W. Lee, D. M. Eshelman and J. Bigeleisen, J. Chem. Phys. <u>56</u>, 4585 (1972).

Table III

Potential Parameters

(A) L-H-B - Potential [a]

	Ar-Ar	Ar-Kr	Kr-Kr
$\epsilon/k(^{\circ}K)$	142.10	163.87	201.31
$r_m(\text{Å})$	3.7612	3.8807	4.0078
$\sigma(\text{Å})$	3.3605	3.4674	3.5799
A_o	0.27783	0.28134	0.23526
A_1	-4.50431	-4.48103	-4.78686
A_2	-8.33122	-8.25965	-9.2
A_3	-25.2696	-25.7037	-20
A_4	-102.0195	-105.4810	-60
A_5	-113.25	-113.19	-114
C_6	1.10727	1.11090	1.06324
C_8	0.16971	0.16968	0.17012
C_{10}	0.01361	0.01356	0.01425

(B) M-S - Potential [b]

	$n(r)$	$\epsilon/k(^{\circ}K)$	$r_m(\text{Å})$
Ar-Ar	$-3.310(\frac{r}{r_m})^2 + 20.571(\frac{r}{r_m}) - 2.657$	142.5	3.75
Ar-Kr[*]	$-1.655(\frac{r}{r_m})^2 + 15.586(\frac{r}{r_m}) + 0.1715$	168.5	3.885
Kr-Kr	$10(\frac{r}{r_m}) + 3$	199.2	4.02

Table III (continued)

(C) L-J (12-6)[c]	ϵ/k (°K)	r_m(Å)	σ(Å)
Ar-Ar	119.8	3.822	3.405
Ar-Kr*	140.68	3.965	3.533
Kr-Kr	165.20	4.108	3.660

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a $$\frac{V}{\epsilon} = \left\{ \sum_{i=0}^{5} A_i \left(\frac{r}{r_m} - 1\right)^i \right\} e^{12.5\left(1 - \frac{r}{r_m}\right)} - \sum_{j=0}^{2} \frac{C_{2j+6}}{0.01 + \left(\frac{r}{r_m}\right)^{2j+6}}$$

b $$\frac{V}{\epsilon} = \frac{6}{n(r)-6} \left(\frac{r}{r_m}\right)^{-n(r)} - \frac{n(r)}{n(r)-6} \left(\frac{r}{r_m}\right)^{-6}$$

c Special case of M-S potential, $n(r) = 12$

* Average value of Ar-Ar and Kr-Kr

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}}, \qquad r_{m12} = (r_{m11} + r_{m22})/2$$

Table IV. Effective Hard Sphere Diameters (Å)

x_{Ar}	L-J (12,6)		L-H-B		M-S	
	d_{ArAr}	d_{KrKr}	d_{ArAr}	d_{KrKr}	d_{ArAr}	d_{KrKr}
0.0	3.45796	3.75300	3.42859	3.69553	3.50831	3.69717
0.2	3.45847	3.75351	3.42898	3.69585	3.50888	3.69763
0.4	3.45916	3.75416	3.42951	3.69630	3.50948	3.69810
0.6	3.45996	3.75489	3.43013	3.69681	3.51001	3.69856
0.8	3.46080	3.75562	3.43079	3.69734	3.51058	3.69903
1.0	3.46161	3.75630	3.43143	3.69785	3.51115	3.69949

Table V

Average Potential Energy, $\langle U \rangle$, of Liquid Ar-Kr Mixtures

at 117.5° K (in K cal/mole) along the Saturation Line

x_{Ar}	$- \langle U \rangle_{L-H-B}$	$- \langle U \rangle_{L-J}$
0.0	2.091	2.031
0.2	1.905	1.863
0.4	1.714	1.685
0.6	1.526	1.504
0.8	1.349	1.327
1.0	1.187	1.158

Table VI

Comparison of the Internal Energies at $115.8°$ K of Liquid Ar-Kr Mixtures

Calculated by the Monte Carlo and WCA Methods

x_{Ar}	Vcc/mole	$-\langle U_{ij}/RT\rangle MC$			$-\langle U_{ij}/RT\rangle WCA$		
		(1,1)	(1,2)	(2,2)	(1,1)	(1,2)	(2,2)
0.25	33.22	5.28	6.88	9.12	5.28	6.98	9.15
0.398	32.96	5.18	6.99	9.13	5.31	7.02	9.20
0.5	32.82	5.28	6.96	9.14	5.31	7.04	9.21
0.602	32.76	5.24	7.03	9.15	5.31	7.03	9.20
0.75	32.77	5.26	7.01	9.12	5.30	7.00	9.26

$$\langle U/RT\rangle = \sum_{i,j} x_i x_j \langle U_{ij}/RT\rangle$$

x_{Ar}	$-\langle U\rangle MC(j\ mole^{-1})$	$-\langle U\rangle WCA(WCA\ (j\ mole^{-1})$	$-\langle U\rangle Lee,\ Levesque(j\ mole$
0.25	7733	7792	7656
0.398	7206	7258	7154
0.5	6841	6883	6870
0.602	6473	6499	6459
0.75	5929	5954	5944

Table VI (continued)

	ε/k	σ	r_m
1 - 1	119.8	3.405	3.822
1 - 2	141.4	3.519	3.950
2 - 2	167.0	3.633	4.078

References

1. K. F. Herzfeld and E. Teller, Phys. Rev. $\underline{54}$, 912 (1938).

2. J. Bigeleisen, J. Chem. Phys. $\underline{34}$, 1485 (1961).

3. I. Oppenheim and A. S. Friedman, J. Chem. Phys. $\underline{35}$, 35 (1961).

4. J. Bigeleisen, M. W. Lee, and F. Mandel, Acc. Chem. Res. $\underline{8}$, 179 (1975).

5. J. Bigeleisen and M. G. Mayer, J. Chem. Phys. $\underline{15}$, 261 (1947).

6. R. H. Davies, A. G. Duncan, G. Saville, and L. A. K. Stavely, Trans. Faraday Soc. $\underline{63}$, 855 (1967).

7. J. K. Lee, D. Henderson and J. A. Barker, Mol. Phys. $\underline{29}$, 429 (1975).

8. Y. S. Kim and R. G. Gordon, J. Chem. Phys. $\underline{61}$, 1 (1974).

9. G. C. Maitland and E. B. Smith, Mol. Phys. $\underline{22}$, 861 (1971).

10. D.W. Gough, E. B. Smith, and G. G. Maitland, Mol. Phys. $\underline{27}$, 867 (1974).

11. L. L. Lee and D. Levesque, Mol. Phys. $\underline{26}$, 1351 (1973).

12. G. J. Throop and R. J. Bearman, J. Chem. Phys. $\underline{44}$, 1423 (1966).

13. J. L. Lebowitz, Phys. Rev. II, $\underline{133}$, A895 (1964).

14. G. J. Throop and R. J. Bearman, J. Chem. Phys. $\underline{42}$, 2838 (1965).

15. I. R. McDonald, Mol. Phys. $\underline{23}$, 41 (1972).

16. J. Bigeleisen, J. Chem. Phys. $\underline{39}$, 769 (1963).

17. J. T. Phillips, C. Linderstrom-Lang and J. Bigeleisen, J. Chem. Phys. $\underline{56}$, 5053 (1972).

18. E. Wigner, Phys. Rev. $\underline{40}$, 749 (1932).

19. J. E. Mayer and W. Band, J. Chem. Phys. $\underline{15}$, 141 (1947).

20. J. Bigeleisen and T. Ishida, J. Chem. Phys. 48, 1311 (1968).

21. T. Ishida, W. Spindel and J. Bigeleisen, Advances in
    Chemistry 89, 192 (1969).

22. G. Janscó, G. Nemeth and B. Gellai, Chem. Phys.
    Letters, 2, 314 (1970).

23. The physical approximations in these assumptions are
    discussed in ref. 1, 2, 16 and 17.

24. M. W. Lee, D. M. Eshelman and J. Bigeleisen, J. Chem. Phys.
    56, 4585 (1972).

25. F. J. Torre, D. M. Eshelman, M. W. Lee, P. Neufeld and
    W. Watson, Rev. Sci. Inst. 47, 1142 (1976).

26. F. Mandel, J. Chem. Phys. 57, 3929 (1972).

27. M. W. Lee, S. Fuks and J. Bigeleisen, J. Chem. Phys. 53, 4066
    (1970).

28. J. D. Weeks, D. Chandler and H. C. Anderson, J. Chem. Phys.
    54, 5237 (1971).

29. M. W. Lee and J. Bigeleisen (accompanying manuscript).