

Transport Properties Experimental Data as a Probe to Test the Suitability of ESMSV and MSV Potentials: Neon + Noble Gas Systems

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Ng, Lee and Barker (J.Chem. Phys. 61, 1996 (1974)) have recently proposed very sophisticated multiparametric unlike pair potential energy functions for Ne+Ar, Ne+Kr and Ne+Xe systems. Recent data over a wider temperature range for viscosity, diffusion and thermal diffusion have prompted us to examine those portions of Ng-Lee-Barker (NLB) potentials which are sensitively influenced by these transport properties data. The overall satisfactory agreement, except some fine tuning required in certain portions of the potentials, between the theoretical predictions and the experimental data establishes the validity of the method used by Ng, Lee and Barker.

Ng, Lee and Barker (J.Chem.Phys. 61, 1996 (1974)) propuseram, recentemente, funções muito sofisticadas de energia potencial de múltiplos parâmetros para moléculas não semelhantes do tipo Ne+Ar, Ne+Kr e Ne+Xe. A disponibilidade de recentes dados sobre viscosidade, difusão e difusão térmica numa faixa maior de temperatura leva-nos a examinar

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aquelas partes dos potenciais de Ng - Lee - Barker (NLB) que são sensivelmente influenciados por estas propriedades de transporte. A concordância muito satisfatória, exceto pequenos ajustamentos necessários em certas regiões de potenciais, entre predições teóricas e dados experimentais estabelece a validade do método usado por Ng, Lee e Barker.

1. INTRODUCTION

The methods¹ have been developed whereby elastic scattering cross-section data can be inverted without any preassumptions about the form of the potential energy functions. The procedures directly yield the numerical values of the potential energy between a pair of atoms or molecules. This Inversion procedure requires very high grade experimental data for velocity spread, angular spread etc. Until the resolution of the measurements is improved to the required degree we will have to depend on the conventional techniques employed for the analysis of the scattering data. In this method a model is assumed to represent the interactions (like-like or unlike), depending upon the case under considerations between the molecular systems and the χ^2 - dispersion is minimized so that the calculations agree with the experimental results. The realisticness of the assumed model depends upon the amount of the theoretical informations used in its construction. Now, that fairly accurate short-range and long-range potential energy values for various systems of interest have become available, one can construct a reasonable semi-empirical model. The latter can be further refined by the analysis of the scattering, spectroscopy, solid state, liquid state and bulk property data. The experienced worker in this field have realized, through the repeated and step wise fine tuning of this assumed model, that the stage can be reached when analysis becomes model independent. By the latter we mean that the slight changes in the parameters of the model result in comparatively appreciable disagreement between experimental results and the calculations. Thus, a "unique" set of parameters is possible and can be achieved. We can further elucidate this by citing below a few instances where it has actually occurred.

Lee and coworkers² have recently measured the low energy differential cross-sections for the systems Ne+Ar, Ne+Kr and Ne+Xe. Through

the analysis of these results along with the diffusion and virial data they have been able to suggest semi-empirically derived unlike-atom interatomic potential energy functions. These are highly flexible and complicated functions as compared to (n-6) series of models to which they³ had fitted their earlier scattering results on these very systems. Not surprisingly the parameters defining the well-depths and their positions for these two sets of models lie within the error of the individual determinations. The same is true for the values of these parameters for the same-systems as determined by Hogervorst⁴ via the analysis of his highly accurate diffusion data on the L-J (12-6) and exp-6 models. All these above mentioned sets of potential parameters are directly determined for the unlike molecule interactions without any recourse to the combination rules. Thus, though the various potential energy functions may differ in the details and the realisticness as embedded in their semi-empiricism, but their essential and physically realizable parameters (ϵ , α , r_m etc) once fine tuned with the aid of the experimental data, can be regarded with confidence. This may be reworded by stating that the potential parameters thus determined may be treated as model independent and bear a good degree of "uniqueness". Judging from the serious efforts of various groups of theoreticians and experimentalists in the area of intermolecular forces, it may not be long before one would be able to test degree of uniqueness in the nature of the presently available sets of potential parameters (e. g. the ones discussed above) against the corresponding values determined from the *ab initio* calculations and the inversion of the experimental data.

In the present article we plan to study the recently proposed potential energy functions for Ne+Ar, Ne+Kr and Ne+Xe systems due to Ng, Lee and Barker². Our efforts will be mainly directed to examine the suitability of those portions of these potential energy functions which are influenced by the transport properties. We would also make comparisons with a Morse - 6 potential for Ne+Ar as suggested by Konowalow and Zakheim⁵. The salient features of the specific potentials which will be the subject of the present study are mentioned below.

2. THE POTENTIALS

1. Exponential - Spline - Morse - Spline - van der Waals (ESMSV)² potential for Ne + Ar systems and Morse - Spline - van der Waals (MSV)² potentials for Ne + Kr and Ne + Xe systems:

The theoretical calculations for the potential energy values for Ne+Ar system in the short-range region are available. This repulsive part of the potential in Born-Mayer form is smoothly joined by an exponential spline to a Morse-function. For Ne+Kr and Ne+Xe Morse-function replaces the above mentioned Born-Mayer plus exponential spline function portion in the absence of the rigorous repulsive energy calculations. The purely attractive portions of all three potential energy functions have the same functional forms. The Morse-function which defines the bowl part of the well is smoothly connected to a cubic spline function which in turn is joined to the multipole expansion series of the van der Waals interactions. The latter involves accurately determined values of the C_6 and C_8 coefficients. Thus the piece-wise, Exponential - Spline - Morse - Spline - van der Waals (ESMSV) potential for Ne+Ar and the Morse-Spline -van der Waals (MSV) type potentials for Ne+Kr and Ne+Xe can be written in the reduced form as below:

$$f(X) = V(r)/\epsilon, \quad X = r/r_m, \quad c_n = \frac{C_n}{\epsilon r_m^n}$$

$$f = A \exp\{-\alpha(X-1)\}, \quad (\text{Born - Mayer}) \quad 0 < X < X_1$$

$$f = \exp(a_1 + (X-X_1) \{a_2 + (X-X_2) \{a_3 + (X-X_1)a_4\}\})$$

$$(\text{exponential spline function}) \quad X_1 < X < X_2,$$

$$f = \exp\{-2\beta(X-1)\} - 2 \exp\{-\beta(X-1)\}$$

$$(\text{Morse-function}) \quad X_2 \leq X \leq X_3$$

$$f = b_1 + (X-X_3) \{b_2 + (X-X_4) \{b_3 + (X-X_3) b_4\}\}$$

$$(\text{cubic spline function}) \quad X_3 < X < X_4$$

$$f = -c_6 X^{-6} - c_8 X^{-8} - c_{10} X^{-10} \quad ,$$

$$\text{(van der Waals)} \quad X_4 \leq X < \infty$$

The sensitivity of the fast oscillations in the scattering data to the position of r_m and the low energy small angle differential cross-sections sensitivity to the slope of outer attractive wall of the potential well help not only in reducing the number of free parameters but at the same time impose a physically viable restraint on the optimization of ϵ and β . Lee and co-workers² have skillfully exploited the analysis of the virial and diffusion data on these systems to choose the slope of the repulsive limbs to supplement the information afforded by the scattering cross-section measurements. On account of certain misprints and the changes in the values of the parameters⁶ for some of these systems in the original article authored by Ng, Lee and Barker², we have decided to redo the diffusion calculations. Except these changes the reader is advised to refer to the original work² to look for the details of the fitting procedure.

2.2. Morse - 6 Potential for Ne + Ar System⁵

Konowalow and Zakheim⁵ developed a hybrid Morse - 6 potential given by

$$\phi_{12}(r) = 4\epsilon(y^2 - y) \quad r \leq q_0 \quad (1)$$

$$\phi_{12}(r) = -C_6 r^{-6} \quad r \geq q_0 \quad (2)$$

where $y = \exp C(1-r/\sigma)$, and q_0 is the separation at which the curves (1) and (2) intersect, σ is the separation at which the potential energy values change sign and ϵ is the value of the energy at which the potential energy minimum occurs. Two of the disposable parameters C , a and ϵ are adjusted by equating the repulsive part of the Morse-Potential to the theoretical repulsion expressed in the Born-Mayer form, that is

$$A \exp(-\lambda r) = 4\epsilon y^2$$

The theoretical expression involved is the TFD repulsion of Gaydaenko and

Nikulin⁷. The dispersion coefficient, C_6 , is consistent with the calculations of Langhoff and Karplus⁸. Finally, the remaining parameter is determined by fitting the potential to experimental second virial coefficient data. The potential parameters are:

$$\begin{aligned}
 A(e^2 a_0^{-1}) &= 77.785 \quad , \quad \lambda(a_0^{-1}) = 1.990 \quad , \\
 C_6(e^2 a_0^5) &= 21,4 \quad , \quad \epsilon/k (K) = 70.096 \quad , \\
 C &= 5.6903 \quad \sigma(A^0) = 3.0270 \quad , \\
 r_m(A^0) &= 3.3958 \quad \text{and} \quad q_0(A^0) = 4.2703
 \end{aligned}$$

3. EXPERIMENTAL DATA

3.1. Viscosity

Kestin et al.⁹ Have reported η_{mix} and pure component value η_1 and η_2 for Ne + Ar^{9a} and Ne + Kr^{9b} systems over a temperature range of 300 - 1000 K using an oscillating disc viscometer. Since η_{mix} is not directly relatable to the unlike molecule interactions so they have derived the so called interaction Viscosity, η_{12} , from their η_{mix} , η_1 and η_2 values. Like the interaction second virial coefficient the η_{12} is defined as the viscosity of a hypothetical gas whose molecules obey the force law between a molecule of component 1 and a molecule of component 2. Kestin and Mason¹⁰ have accomplished the derivation of η_{12} values by formulating a semi-empirical extended law of corresponding states and applying sophisticated numerical-graphical data fitting procedures to adjust the effective scaling parameters for their semi-empirical correlations. Kestin et al.⁹ have claimed an accuracy of $\pm 0,4\%$ for Ne+Kr on their thus derived η_{12} values. Nain and Aziz¹¹ have elucidated elsewhere the merits and demerits of Kestin-Mason procedure and disagree with their rather conservative estimate of the accuracy of their⁹ data. We treat Kestin et al.'s η_{12} data accurate within one percent and the most accurate yet available in the literature.

There exist no such direct measurements for η_{12} on Ne+Xe sys-

tem. To generate data for this system Kestin and Mason¹⁰ determined scaling parameters for their viscosity correlation through the analysis of the diffusion data which were limited in their temperature range (200 - 600K) and were not very accurate. Nain and Aziz¹¹ have determined a better set of effective scaling parameters for the Kestin-Mason correlation using the recent and more accurate diffusion data available over a fairly wide temperature range (400-1400 K) due to Hogervorst⁴. Thus, Kestin-Mason correlation in conjunction with these parameters¹¹ is used to generate a set of interaction viscosity data for the Ne + Xe system.

3.2. Diffusion

Van Heijningen *et al*¹³, using a two chamber cell have measured the diffusion coefficient, D_{12} , for these systems at four temperatures in the region (90 - 400 K). Hogervorst, using a cataphoresis technique (cataphoretic segregation in a d.c. discharge) has also measured diffusion coefficient for Ne + Ar, Ne + Kr and Ne + Xe systems over a temperature range of (300 - 1400 K). Both sets of data are quoted to an accuracy of $\pm 0.5 - 1.0\%$.

Diffusion data derived from empirically determined universal functionals proposed by Kestin and Mason¹⁰, and Marrero and Mason¹² in the form of an extended law of corresponding states are also tested against the predictions of the Ng, Lee and Barker Potentials². We include them here for the sake of completeness and not for a detailed analysis because of the far more accurate experimental data on diffusion being available in the overlapping temperature range due to Van Heijningen *et al* and Hogervorst. The error band associated with the derived data of Kestin and Mason¹⁰ are $\pm 3\%$. For the limited temperature range of 300 - 1400 K we cannot provide error limits for the data of Marrero and Mason¹² with certainty but would estimate them bearing the same uncertainty limits as those for the Kestin and Mason's derived data.

3.3. Thermal Diffusion

Thermal diffusion factors, α_T , for these systems have been determined experimentally both as a function of temperature and composi-

tion. The sources of these data are numerous and are listed in table 1 along with the temperature and composition ranges studied by various workers¹⁴⁻²³. The accurate limits on the older data are undefined but the data after 1950 can be treated to be accurate within $\pm 5 - 7\%$. The experimental techniques employed are either the Trennschaukel or the conventional two-bulb apparatus.

4. RESULTS AND DISCUSSION

For Ne + Ar, Ne + Kr and Ne + Xe systems there is reasonable amount of data available on the transport properties extending from very low to high temperatures. Low temperature transport properties are more useful than low temperature second virial coefficients in the evaluation of the pair potential energy function, because (1) transport coefficients are more easily measurable in the laboratory (2) the quantum effects at low temperatures are not as important and (3) low temperature transport coefficients can be directly related to the magnitude of the dispersion coefficient C_6 and hence to the potential energy at long range. The dependence of transport coefficients on the potential at large separations is a consequence for their being weighted averages of angles of deflections of colliding atoms. More weight is given to slow atoms at low temperatures which pass at large separations.

High temperature transport properties and high temperature second virial data are useful in sampling the repulsive wall of the potential. For example, viscosity provides information on the position and diffusion and thermal diffusion give information on the slope of the repulsive limb²⁴⁻²⁶.

Little information is provided by transport properties in the intermediate region and unfortunately *ab initio* calculations are prohibitively difficult to perform in this region.

It must be borne in mind that nothing definite can be inferred regarding the superiority of one potential over another if the predictions of both lie within the experimental error bands.

System	Temperature or Temperature Range (K)	Heavier component Composition or Composition Range (per cent)	P O T E N T I A L S			RMS Deviations	Reference Experimental Data
			Ne	Heavier Component	Ne + Heavier Component		
Ne+Ar	327	40 - 80	ESMSV III	ξSBN	HLB	.00144	Atkins, Bastick and Ibbs (1939)
			ESMSV III	EFW	N'E H	.00142	do
			SPSL	EFW	N'E H	.00188	do
			MDM	ξSBN	N'E	.00191	do
Ne+Ar	117-585	48.80	ESMSV III	ξSBN	NLB	.00215	Grew (1947)
			ESMSV III	EFW	NLB	.00216	do
			SPSL	EFW	NLB	.00197	do
			MDM	ξSBN	NLB	.00196	do
Ne+Ar	73-1167	48.0	ESMSV III	ESBFW	NLB	.00259	Grew, Johnson and Neal (1954)
			ESMSV III	BFW	NLB	.00257	do
			SPSL	BFW	NLB	.00265	do

Table I - α_T data¹⁴⁻²³ and RMS deviations between experimental data and theoretical predictions based on "Three Potential Calculations" for Ne + Ar, Ne + Kr and Ne + Xe systems.

System	Temperature or Temperature Range (K)	Heavier component Composition or Composition Range (per cent)	P O T E N T I A L S			RMS Deviations	Reference Experimental α_T Data
			Ne	Heavier Component	Ne+Heavier Component		
Ne + Ar	73-1667	48.0	MDM	ESBFW	NCB	.00277	do
Ne + Ar	318.6	30-80	ESMSV III	ESBFW	NLB	.01787	Saxena, Nain and Saxena (1968)
			ESMSV III	BFW	NLB	.01784	Nain and Saxena (1969)
			SPSL	BFW	NLB	.01729	do
			MDM	ESBFW	NLB	.01730	do
Ne + Ar	79-267	0.83	ESMSV III	ESBFW	NLB	.00307	Grew and Wakeham (1971)
			ESMSV III	BFW	NLB	.00307	do
			SPSL	BFW	NLB	.00369	do
			MDM	ESBFW	NLB	.00373	do
Ne + Ar	70-267	4.90	ESMSV III	ESBFW	NLB	.00085	Grew and Wakeham (1971)
			ESMSV III	BFW	NLB	.00085	do

Table 1 - Continued

System	Temperature or Temperature Range (K)	Heavier component Composition or Composition Range (per cent)	P O T E N T I A L S			RMS Deviations	Reference Experimental α_T Data
			Ne	Heavier Component	Heavier Component		
Ne+Ar	70-267	4.90	SPSL	BFW	NLB	.00143	do
			MDM	ESBFW	NLB	.00147	do
Ne+Ar	75-267	50.0	ESMSV III	ESBFW	NLB	.00158	Grew and Wakeham(1971)
			ESMSV III	BFW	NLB	.00158	do
			SPSL	BFW	NLB	.00142	do
			MDM	ESBFW	NLB	.00141	do
Ne+Ar	82-267	89.92	ESMSV III	ESBFW	NLB	.00397	Grew and Wakeham (1971)
			ESMSV III	BFW	NLB	.00397	do
			SPSL	BFW	NLB	.00396	do
			MDM	ESBFW	NLB	.00394	do
Ne+Kr	327	40-80	ESMSV III	GMS	NLB	.01631	Atkins, Bastick and Ibbs (1939)

Table 1 - Continued

System	Temperature or Temperature Range (K)	Heavier Component Composition or Composition Range (per cent)	P O T E N T I A L S			RMS Deviations	Reference Experimental Data α_T
			Ne	Heavier Component	Ne+Heavier Component		
Ne+Kr	327	40-80	ESMSV III	LHB	NLB	.01630	do
			ESMSV III	BWLSL	NLB	.01631	do
			MDM	GMS	NLB	.01619	do
Ne+Kr	117-585	47.0	ESMSV III	GMS	NLB	.00149	Grew (1947)
			ESMSV III	LHB	NLB	.00148	do
			ESMSV III	BWLSL	NLB	.00149	do
			MDM	GMS	NLB	.00174	do
Ne+Kr	318.5	20-73	ESMSV III	GMS	NLB	.02059	Mathur, Joshi and Saxena (1967)
			ESMSV III	LHB	NLB	.02058	
			ESMSV III	BWLSL	NLB	.02058	
			MDM	GMS	NLB	.02072	

Table 1 - Continued

System	Temperature or Temperature Range (K)	Heavier Component Composition or Composition Range (per cent)	POTENTIALS			RMS Deviations	Reference Experiments α β
			Ne	Heavier Component	Ne+Heavier Component		
Ne+Xe	327	40-80	ESMSV III	BWLSL	NLB	.02861	Atkins, Bastick and Ibbes (1939)
Ne+Xe	185-585	45.80	ESMSV III	BWLSL	NLB	.00799	Grew (1947)
Ne+Xe	300-700	10.0	ESMSV III	BWLSL	NLB	.01284	Heymann and Kistemaker (1959)
		1.0	ESMSV III	BWLSL	NLB	.03152	
		0.1	ESMSV III	BWLSL	NLB	.03676	
		0.01	ESMSV III	BWLSL	NLB	.03730	
		0.001	ESMSV III	BWLSL	NLB	.03735	
		0.00001	ESMSV III	BWLSL	NLB	.03736	
		0.000000	ESMSV III	BWLSL	NLB	.03736	
Ne+Xe	318.6	10-80	ESMSV III	BWLSL	NLB	.01671	Saxena, Nair and Saxena (1965) Nair and Saxena (1966)

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System	Temperature or Temperature Range (K)	Heavier Component Composition or Composition Range (per cent)	P O T E N T I A L S			RMS Deviations	Reference Experimental Data ^{α} T
			Ne	Heavier Component	Ne+Heavier Component		
Ne+Xe	328	0.1-95.6	ESMSV III	BWLSL	NLB	.00359	Taylor, Weissman, Haubauck and Pickett (1969)
	373	0.1-95.7	ESMSV III	BWLSL	NLB	.00276	
	473	0.1-95.4	ESMSV III	BWLSL	NLB	.00118	
	573	0.1-95.6	ESMSV III	BWLSL	NLB	.00401	
	673	0.1-95.5	ESMSV III	BWLSL	NLB	.00834	
	773	0.1-95.6	ESMSV III	BWLSL	NLB	.00184	
	873	0.1-95.3	ESMSV III	BWLSL	NLB	.00124	
Ne+Xe	311	1.30 and 99.0	ESMSV III	BWLSL	NLB	.01086	Rutherford (1971)

Table 1 - Continued

4.1. Viscosity

The temperature range (300 - 1000 K) over which the experimental data exist for the Ne + Ar and Ne + Kr systems would be sensitive to the low repulsive energy portion of the potential curve. This supplements the low energy low angle differential elastic scattering data for these systems. Deviation curves are displayed in figure 1 as a function of temperature. Kestin et al's viscosities are accurately reproduced both by the ESMSV potential for the Ne + Pr system and by the MSV potential for

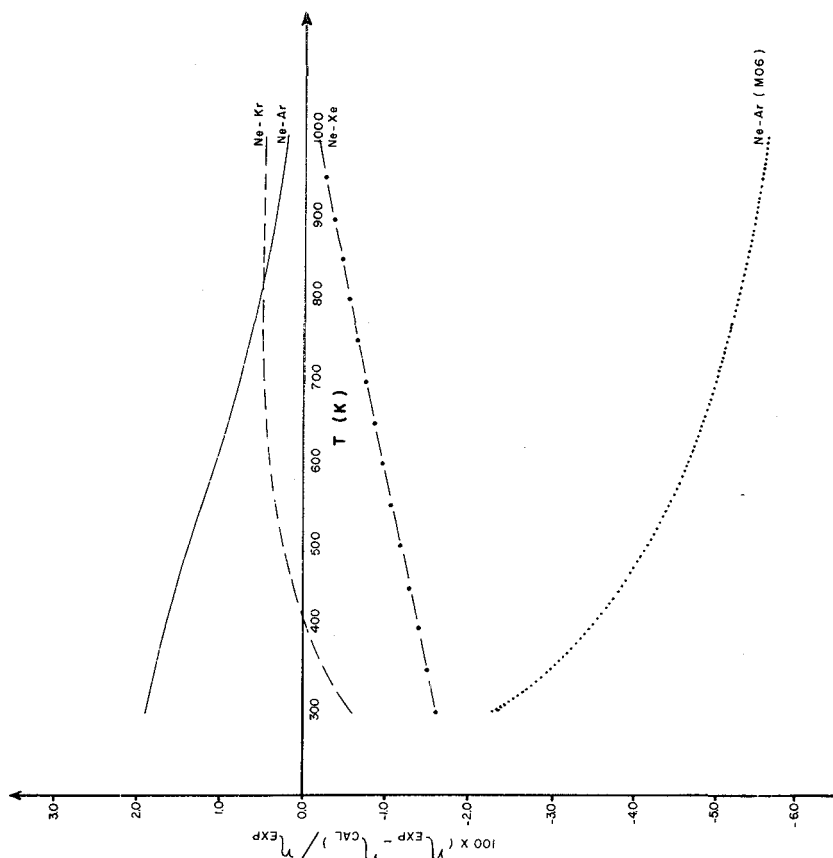


Fig.1 - Deviation Curves between the prediction of the Chapman-Enskog theory²⁷ based on the NLB potentials² and the experimental data on viscosity due to Kestin et al.⁹ For Ne+Ar and Ne+Kr systems. For Ne+Xe system the viscosity values generated by KM correlation¹⁰ based on the Parameter of Nain and Aziz¹¹ are treated as experimental data. M06 potential⁵ predictions for Ne+Ar system and their deviation from the experimental data⁹ are also displayed.

the Ne + Kr system. For Ne + Ar the exponential spline function in the repulsive limb of the ESMSV potential seems to have slightly too steep a slope below about 450 K.

There are no directly measured viscosities available for Ne + Xe. Kestin et al.⁹ and Kestin and Mason¹⁰ have semi-empirically derived a correlation for interpolating (where data exist) and extrapolating (where data do not exist) the interaction viscosities for all the binary noble gas mixtures. This correlation¹⁰ (KM) holds good between $1 < T^* < 90$, where $T^* = (T/\epsilon/k)$. The (ϵ/k) and a values are tabulated by Kestin and Mason¹⁰ for a number of systems. We have examined the consistency between the Ne + Ar, Ne + Kr and Ne + Xe systems. We tested the Ne + Ar predictions in the temperature range 100 - 4500 K. The calculated viscosities from both these methods agree within $\pm 1.5\%$ in the range 450 - 4000 K. Below 450 K and above 4000 K the KM predictions are higher than those from the ESMSV potential and range from about 1.8 - 2.3% for this system for Ne + Kr we compared the KM and MSV based predictions for the interaction viscosity in the temperature range of 100 - 7000 K and found an agreement between them within $\pm 1.5\%$ in the range 250 - 5800 K. Below 250 K the viscosities calculated from MSV potential are higher by 1.7% to 5.0% and above 5800 K are lower by 1.6% to 2.0% than those calculated from the KM correlation.

In case of Ne + Xe where this comparison extends from 300 to 8000 K the values predicted by KM correlation are consistently higher, by 2.3 - 12.0%, than those calculated from the MSV type Ne + Xe potential. Nain and Aziz have shown that the present set of the effective scaling parameters determined by Kestin and Mason for their correlation are of doubtful validity in case of Ne + Xe and Ar + Xe systems. In addition, there are strong reasons to prefer the viscosity predictions of the MSV type Ne + Xe pair potential energy function over those of KM correlation because (1) MSV potential has a sounder theoretical base in its constructions as compared to the KM correlation. The effective scaling parameters of the latter do not bear much physical significance. (2) The MSV potential is fit to the scattering, virial and diffusion data for Ne + Xe system. Thus, one would expect reasonable predictions of the interaction viscosity values on the basis of the MSV potential for the Ne + Xe system, at least in the temperature range of the above data (scattering, virial

and diffusion). (3) In case of the KM correlation there were no viscosity data available on the Ne + Xe system to accurately determine the effective scaling parameters and to obtain these parameters Kestin and Mason have used not too accurate sets of diffusion data over a limited temperature range.

• Nain and Aziz¹¹ have recalculated the Ne + Xe parameters for the KM correlation using new more accurate data on diffusion due to Van Heijningen et al. and Hogervorst. These new scaling parameters do indeed make the predictions of the KM correlation for the interaction viscosities of the Ne + Xe system consistent with those of the MSV type potential of Ng, Lee and Barker². Thus, the predictions of the interaction viscosities based on the KM correlation are fairly consistent with those of the ESMSV (or MSV) potentials for the Ne + Ar and Ne + Kr systems over the temperature ranges 450 - 4000 K and 250 - 5800 K, respectively. The KM correlation predictions for Ne + Xe system again enhanced consistency with those of the NLB potentials, over the temperature ranges comparable to those of the other systems considered, when the parameters determined by Nain and Aziz¹¹ are used.

We have also performed the viscosity calculations for the Ne + Ar system on the basis of the M06 potential suggested by Konowalow and Zakheim⁵. The viscosity predictions for Ne + Ar on the basis of the M06 potential suggest that repulsive limb of this potential is definitely too soft to correctly reproduce the experimental data. However, M06 potential reproduces both the virial and the scattering data within the experimental error limits. We will defer further comment on this aspect of the M06 potential until we discuss it again in the succeeding section.

For all the potentials the third order Chapman-Enskog approximation to the coefficient of viscosity was calculated and then compared with the experiment.

Diffusion

Diffusion coefficients are more sensitive than the viscosity coefficients to the repulsive part of the potential function in a common

temperature range. Ng, Lee and Barker have used this characteristic of the diffusion data to sense the slopes of the repulsive limbs of their Ne + Ar, Ne + Kr and Ne + Xe potentials. We have reevaluated the diffusion coefficients, D_{12} , for these systems because of some misprints and mistakes in the potential parameters energy values for Ne + Ar and Ne + Xe in the article of Ng *et al.*². In comparing the predictions of these potentials besides the Hogervorst⁴ data we have included the Van Heijningen *et al.*'s¹³ low temperature and two sets of derived data^{10,12} as well.

In comparison to other transport properties, D_{12} is preferred for studying the unlike interactions on account of its dependence only on collisions between dissimilar molecules in the first order of the Chapman-Enskog theory²⁷ and its independence of composition.

Higher approximations to this property involve collisions between like molecules as well and result in a small composition dependent correction. Normally, with diffusion data accurate to $\pm 2 - 3\%$ it is sufficient to work with first order Chapman-Enskog theory²⁸. Hogervorst's data and Van Heijningen *et al.*'s data, however, have a stated accuracy of ± 0.5 to $\pm 1.0\%$. Under these circumstances, it is advisable to account for the actual dependence of D_{12} on composition embedded in higher order approximations. To do this, we have used the semi-empirical relation suggested by Mason and Marrero^{10,12}. The brief description of the method is given below:

$$\{D_{12}\}_1 = \frac{D_{12}}{1 + \Delta_{12}} \quad (3)$$

Where

$$\Delta_{12} = \xi (6 C_{12}^* - 5) \frac{ax}{1 + bx} \quad (4)$$

$\{D_{12}\}_1$ is the diffusion coefficient value calculated to the first approximation of the Chapman-Enskog theory²⁷, D_{12} is the higher order composition corrected diffusion coefficient, x is the mole fraction of the heavier component, ξ , a and b are constants. The values of ξ/k , ξ , a and b as suggested by Kestin and Mason are: for Ne + Ar 63.70, 1.2, 0.059 and 0.57 for Ne + Kr 87.81, 1.01, 0.12, 0.87 and for Ne + Xe 90.98, 1.25, 0.17 and 1.31, respectively. C_{12}^* can be determined from

$$C_{12}^* = 1 + \frac{1}{3} \frac{d \ln \Omega^{(1,1)*}(T^*)}{d \ln T^*} \quad (5)$$

with the use of the Kestin and Mason's universal functional¹⁰ for

$$\Omega^{(1,1)}(T^*) = \Omega_{11} = \exp \{0.347 - 0.444 (\ln T^*) + 0.093 (\ln T^*)^2 - 0.01 (\ln T^*)^3\}$$

we find

$$C_{12}^* = 0.852 + 0.062 \ln T^* - 0.010 (\ln T^*)^2, \quad 0.5 < T^* < 25 \quad (6)$$

Where $T^* = T/(\varepsilon/k)$. Equation (3) was employed in both sets of derived data for concentrations of heavier components as given by Hogervorst and Van Heijningen et al for their experimental data on Ne + Ar, Ne + Kr and Ne + Xe systems.

The RMS deviations between experimental and calculated D_{12} based on all potentials are listed in table 2. The percentage deviation plots as a function of temperature are displayed in figure 2.

Van Heijningen et al's low temperature data are excellently described for the Ne + Kr and Ne + Xe systems by the MSV type potentials well within the experimental error limits. Like in case of viscosity the Ne + Ar potential ESMSV seems to be too steep in the repulsive region sampled by the diffusion data in the temperature range 90 - 350 K.

Hogervorst's data are predicted reasonably well for all three systems except that the ESMSV potential for Ne + Ar seems to be slightly too soft above 1350 K and the HSV potential for Ne + Xe to be slightly too hard above 800 K. From our analysis of Hogervorst's data on other noble gas mixtures we feel that the estimates of his error bounds are little too conservative. Though his are the most accurate diffusion data yet available in the literature, our consistent experience with other systems suggests the error limits to be within $\pm 1.0 - 1.8\%$. If these error limits are accepted on Hogervorst's data then his data are fairly reasonably reproduced by the Ng, Lee and Barker potentials for Ne + Ar, Ne + Kr and Ne + Xe systems.

(K)	Ne + Ar			Ne + Kr			Ne + Xe		
	Experimen- tal	Calcula- ted	Difference %	Experimen- tal	Calcula- ted	Difference %	Experi- mental	Calcula- ted	Difference %
90.20	0.0371	0.0365	1.49	-	-	-	-	-	-
111.70	-	-	-	0.0443	0.0445	-0.44	-	-	-
169.30	0.1202	0.1168	2.85	0.0965	0.0959	0.63	0.0816	0.0813	0.31
231.10	-	-	-	-	-	-	0.1416	0.1416	0.00
295.0	0.316	0.311	1.68	0.2566	0.2573	-0.26	0.2184	0.2164	0.92
300.0	0.323	0.317	1.75	0.2624	0.262	-0.16	0.219	0.220	-0.33
350.0	0.421	0.414	1.71	0.342	0.342	-0.04	0.286	0.286	0.00
400.0	0.530	0.525	0.94	0.438	0.435	0.71	0.368	0.364	1.04
400.0	0.525	0.520	0.93	0.431	0.430	0.28	0.359	0.358	0.30

Table 2 - Experimental data^{4,13} and the theoretical predictions based on Chapman-Enskog theory for the diffusion coefficients for Ne + Ar, Ne + Kr and Ne + Xe systems.

T (K)	Ne + Ar			Ne + Kr			Ne + Xe		
	Experimen- tal	Calcula- ted	Difference %	Experimen- tal	Calcula- ted	Difference %	Experimen- tal	Calcula- ted	Difference %
450.0	0.635	0.636	-0.15	0.526	0.525	0.18	0.440	0.436	0.87
500.0	0.765	0.761	0.56	0.627	0.628	-0.10	0.523	0.520	0.52
550.0	0.892	0.894	-0.25	0.737	0.737	-0.05	0.615	0.610	0.80
600.0	1.045	1.036	0.83	0.850	0.854	-0.46	0.710	0.705	0.66
650.0	1.200	1.187	1.12	0.985	0.977	-0.79	0.810	0.806	0.52
700.0	1.355	1.345	0.74	1.098	1.107	-0.82	0.920	0.911	0.94
750.0	1.520	1.511	0.58	1.240	1.243	-0.26	1.025	1.022	0.30
800.0	1.675	1.685	-0.59	1.380	1.386	-0.41	1.155	1.137	1.53
850.0	1.870	1.866	0.20	1.530	1.534	-0.28	1.280	1.257	1.75

Ne + Ar				Ne + Kr			Ne + Xe		
T. (K)	Experimen- tal	Calcula- ted	Difference %	Experimen- tal	Calcula- ted	Difference %	Experimen- tal	Calcula- ted	Difference %
900.0	2.040	2.055	-0.73	1.690	1.689	0.70	1.405	1.382	1.60
950.0	2.230	2.251	-0.93	1.830	1.849	-1.05	1.535	1.512	1.50
1000.0	2.430	2.451	-0.97	2.010	2.015	-0.28	1.675	1.646	1.73
1050.0	2.620	2.664	-1.66	2.170	2.187	-0.81	1.815	1.784	1.68
1100.0	2.850	2.880	-1.06	2.350	2.365	-0.65	1.960	1.927	1.67
1150.0	3.090	3.104	-0.45	2.520	2.548	-1.13	2.110	2.075	1.68
1200.0	3.310	3.334	-0.73	2.710	2.737	-1.01	2.260	2.226	1.50
1250.0	3.540	3.571	-0.87	2.890	2.932	-1.44	2.410	2.381	1.18
1300.0	3.780	3.814	-0.90	3.110	3.131	-0.68	2.580	2.541	1.49

Table 2 - Continued

Ne + Ar				Ne + Kr			Ne + Xe		
T (K)	Experi- men- tal	Calcula- ted	Difference %	Experi- men- tal	Calcula- ted	Difference %	Experi- men- tal	Calcula- ted	Difference %
1350.0	4.000	4.064	-1.60	3.300	3.336	-1.10	2.750	2.705	1.63
400.0	4.240	4.320	-1.88	3.510	3.546	-1.04	2.920	2.873	1.60
RMS Deviations		0.80409		0.01675			0.0226		

Table 2 - Continued

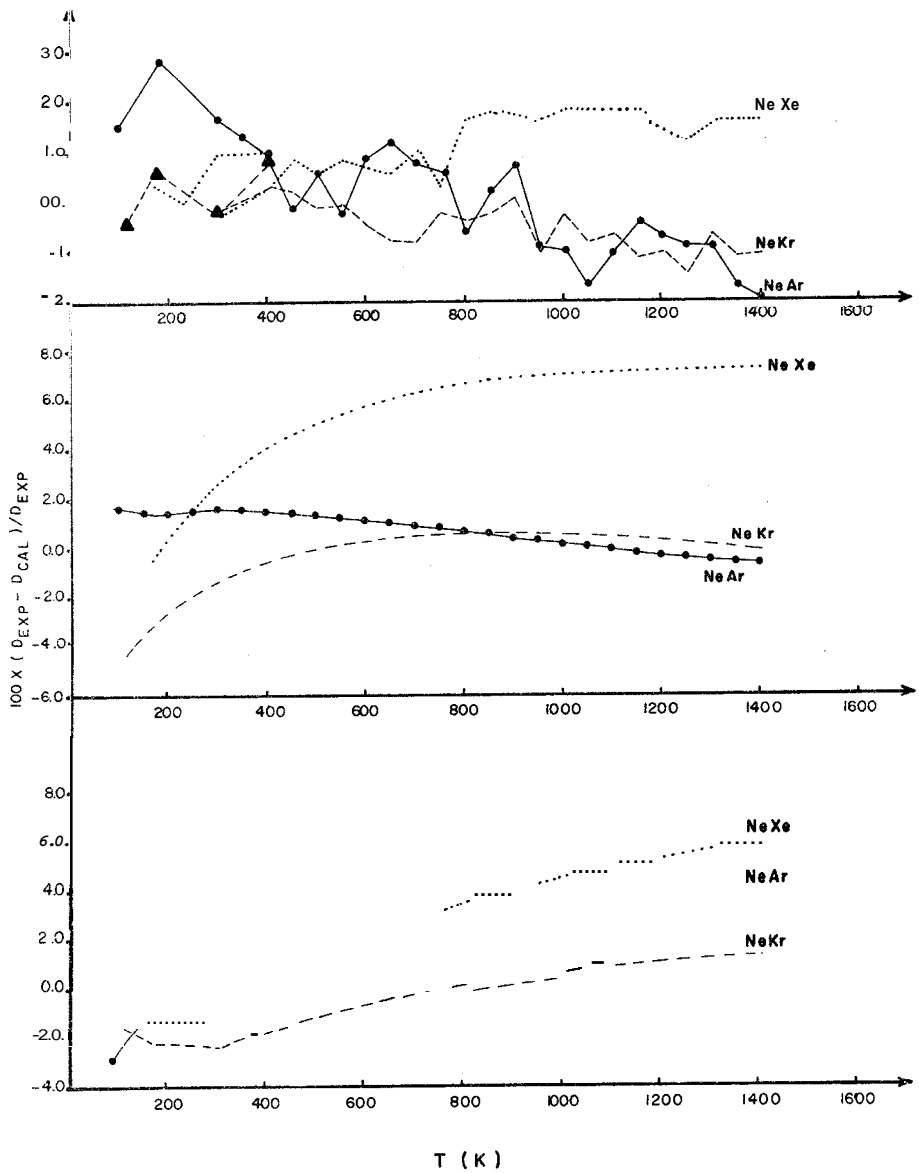


Fig.2 - Deviation curves between the predictions of the Chapman-Enskog theory based on the NLB potentials² and the experimental diffusion data due to: (upper) Van Heijningen *et al.*¹³ and Hogervorst⁴ (middle) generated using Marrero-Mason Correlation¹² (lower) generated using Kestin-Mason Correlation¹⁰

We have also tested the M06 potential⁵ in its ability to reproduce the available experimental data on diffusion for Ne + Ar system. Consistent with our conclusion drawn from the comparison between experimental and calculated viscosities the M06 potential⁵ is too soft in its repulsive limb to correctly reproduce the diffusion data on Ne + Ar. The magnitude of disagreement between calculated D_{12} values and the experimental data increases with temperature and reaches up to 40% at 1400 K.

Derived diffusion data from both the KM¹⁰ and Marrero-Mason¹² correlations for Ne + Ar and Ne + Kr systems are consistent with the predictions of the Ng-Lee-Barker (NLB) potentials², the predictions of the KM correlation being closer to those of the potentials². The KM correlation derived D_{12} and η_{12} values should be considered only above 300 K in view of the fact that it is the lowest temperature at which Kestin *et al* have reported their accurate viscosity data for these systems. They⁹ have used their viscosity data in adjusting the values of the effective scaling parameters for their correlation¹⁰. None of the correlations gives diffusion coefficient values in agreement to the predictions of the MSV potential for Ne + Xe.

We would like to discuss in bit of a detail an interesting observation here. As mentioned earlier the NLB potentials² for Ne + Ar, Ne + Kr and Ne + Xe were partly derived by using the experimental data on low energy molecular beam scattering, second virial coefficients and diffusion coefficients over a reasonably wide range of temperatures. Van Heijningen *et al*¹³ and Hogervorst⁴ have independently suggested some exp-6 and L-J (12-6) potential energy functions also for these systems using their diffusion data only. Konowalow and Zakheim have employed the virial data on Ne + Ar system to adjust its potential parameters and the well-depth, in particular. The parameters for all these potentials are listed in table 3. The repulsive limbs of the NLB potentials almost overlap with those of the exp-6 and L-J (12-6) potentials derived by Van Heijningen *et al* and Hogervorst for the Ne + Kr and Ne + Xe systems. The M06 potential reproduces the low energy elastic scattering data for the Ne + Ar system and thus making it markedly similar to the ESMSV potential in the well and the long-range regions. But as seen above, M06 is very poor in predicting viscosity and diffusion data on the Ne + Ar system and similarly Van Heijningen *et al*'s and Hogervorst's diffusion derived potentials

System	Lee & coworkers Potentials		Emsv or MSV	Brown and Munn	Srivastava and Srivastava		Hogervorst's D_{12}	
	LJ(12-6)	LJ(20-6)			D_{12} n_{12} LJ(12-6)	α_T	LJ(12-6)	Esp-6 $\alpha = 15.5$
Ne + Ar	64.464	75.328	71.94	78.95	64.5	69.5	64.5	64.5 (3.46)
	(3.48)	(3.48)	(3.43)	(3.30)	(3.4774)	(3.4426)	(3.47)	
Ne + Kr	73.155	76.225	74.47	90.54	67.5	63.5	71.5	71.5 (3.52)
	(3.60)	(3.60)	(3.58)	(3.43)	(3.6558)	(3.6940)	(3.62)	
Ne + Xe	73.155	75.328	74.98	99.23	-	-	73.0	73.0 (3.87)
	(3.90)	(3.85)	(3.745)	(3.63)	-	-	(3.88)	

Table 3 - The unlike potential energy parameters, ϵ/k and r_m (in brackets), determined by various groups of workers using different macroscopic properties and different potential energy functions.

are very poor in reproducing the virial and low energy elastic scattering data. The ϵ and r_m values of these variously derived potentials discussed in this paragraph are within each other's error of determination,

The discussion presented in the above paragraph essentially indicates that low energy elastic scattering data combined with the low temperature virial data cannot sample the entire potential energy curve "uniquely". The same is true when only the diffusion or viscosity data are employed in deriving the potentials (Van Heijningen et al and Hoger-vorst). Though we can arrive at the reasonably realistic values of ϵ and r_m within certain bounds employing the above two sets of data separately (for example low temperature virial and low energy elastic scattering data together, single transport property e.g. diffusion in the present case), the details of the entire energy curve remain undefined.

Thermal Diffusion

Thermal diffusion factor α_T , depends very sensitively and strongly on the unlike molecular interactions. The theoretical expression for α_T may be cast in the following form:

$$\alpha_T = (6C_{12}^* - 5)F(1 + K_{12})$$

The temperature dependence of α_T is largely due to the factor, $(6C_{12}^* - 5)$, which is only affected by the interactions between unlike molecules. The F factor is associated with the composition dependence and K_{12} with the higher order corrections. F and K_{12} are influenced by both like and unlike interactions but feebly depend on the temperature. Thus the temperature dependence of α_T is controlled essentially only by the unlike interactions. Though the diffusion coefficient shares this property, it lacks the same sensitivity as α_T . Now that the like-like interactions for the noble gases are quite accurately known, we may make use of not only the temperature but the composition dependence of the thermal diffusion factor also as a sensitive probe of the unlike interactions.

Three Potential Calculations of α_T

One approach to the calculation of α_T is to use the law of corresponding states and a set of combining rules where all the interactions are described by the same reduced potential energy functions. Alternatively, we may use three sets of collisional integrals, each derived from a potential specifically designed for the type of interactions involved. Neufeld and Aziz²⁹, and Nain and Aziz²⁴ have used this latter approach for the potential energy functions derived by Lee and coworkers for all three interactions in a mixture. Now, various groups of workers have independently proposed very realistic potentials for Ne, Ar, Kr and Xe systems. Thus, with the ESMSV² (Ne + Ar) potential, we will use ESMSV III³⁰, SPSL³¹ and MDM³² potentials for Ne + Ne, and BFW³³ and ESBFW³⁴ for Ar + Ar; with MSV² (Ne + Kr) potential we make use of the ESMSV III³⁰, SPSL³¹ and MDM³² potential for Ne + Ne, and GMS³⁵, LHB³⁶ and BWLSL³⁷ potentials for Kr+Kr; and with MSV² (Ne + Xe) potential we choose to couple ESMSV III³⁰ potential for Ne + Ne with the BWLSL³⁷ potential for the Xe + Xe system. We have shown a preference in the choice of the above Ne³⁰⁻³², Ar³³⁻³⁴, Kr³⁵⁻³⁷ and Xe³⁷ potentials above others available in the literature because their³⁰⁻³⁷ validity has been fairly well established.

The theoretical curves shown in figures are obtained without reference to corresponding states or combining rules. We used three independent sets of collision integrals (for example, Ne + Ne, Ar + Ar and Ne + Ar systems) each from a potential specifically designed for the type of interaction involved. Since α_T depends mainly on the unlike interactions these calculations are considered essentially as tests of the correctness of the NLB² potentials for Ne + Ar, Ne + Kr and Ne + Xe systems.

Unfortunately, accurate thermal diffusion data are very difficult to obtain. Hanley and Klein³⁸ have indicated that the thermal diffusion data in the temperature ranges $2 \geq T^* \geq 4$ can be used as a discriminator of potentials or to test the correctness of the various parts and the characteristics of a particular potential energy functions. For instance, high temperature data good to $\pm 5\%$ can be used to establish the slope of the repulsive wall of the potential and the low temperature data, in the vicinity of the α_T minimum, good to $\pm 20\%$ depends strongly on the width of the potential and the slope of the outer attractive wall.

Grew and Wakeham¹⁹ have measured low temperature α_T at four compositions for Ne + Ar system. They have reported the existence of a negative minimum at about 90.7 ± 4 K at all the four compositions while the ESMSV potential² predicts a positive minimum at about half the value of this temperature, as shown in figure 3. This discrepancy is hard to understand since the thermal diffusion factor at low temperatures is sensitive to the attractive well of the potential where the ESMSV potential for Ne + Ar, based on the theoretical and experimental information used in its construction, should be most accurate. Neufeld and Aziz²⁹ attributed the predictions of a similar positive minimum, on the bases of four realistic functional forms, to the breakdown of the corresponding states principle in case of thermal diffusion phenomenon. ESMSV reproduces the data of Grew and Wakeham very satisfactorily above the terminus of the right limb of the α_T minimum. The predictions of the ESMSV potential are consistent with the earlier data of Grew and coworkers¹⁵⁻¹⁶ as shown in figure 4. The absence of an experimental minimum at low temperatures in these data was mainly due to the lack of accuracy in the analysis of the experimental gas mixture composition as pointed out by Grew and Wakeham¹⁹. The composition dependence of α_T for Ne + Ar measured by Nain and Saxena¹⁷⁻¹⁸ at 318.6 K are excellently described by the ESMSV potential except one datum point at the lowest experimental Ar concentration. The comparison of these calculations with the experimental data is shown in Fig. 5.

The MSV potential² for Ne + Kr accurately reproduces the temperature dependence of α_T measured by Grew¹⁵. The experimental data do not go to low enough temperatures to verify the existence of the positive theoretical minimum in the vicinity of 50 K. The composition dependence of α_T for this system has been measured by Atkins *et al*¹⁴ (327 K) and by Mathur *et al*²⁰ (318.5 K). All three sets of data on Ne + Kr and the predictions of the MSV potential are displayed in figure 6 for comparison.

Recently available data on α_T measuring its temperature and composition dependence due to Taylor³⁴ and the low temperature diffusion data of Arora *et al*⁴⁰ for these systems have been analysed by Nain and Aziz⁴¹ separately in greater detail using other set of potentials for the pure components in the "three potential calculations" of thermal diffusion factor and the diffusion coefficients.

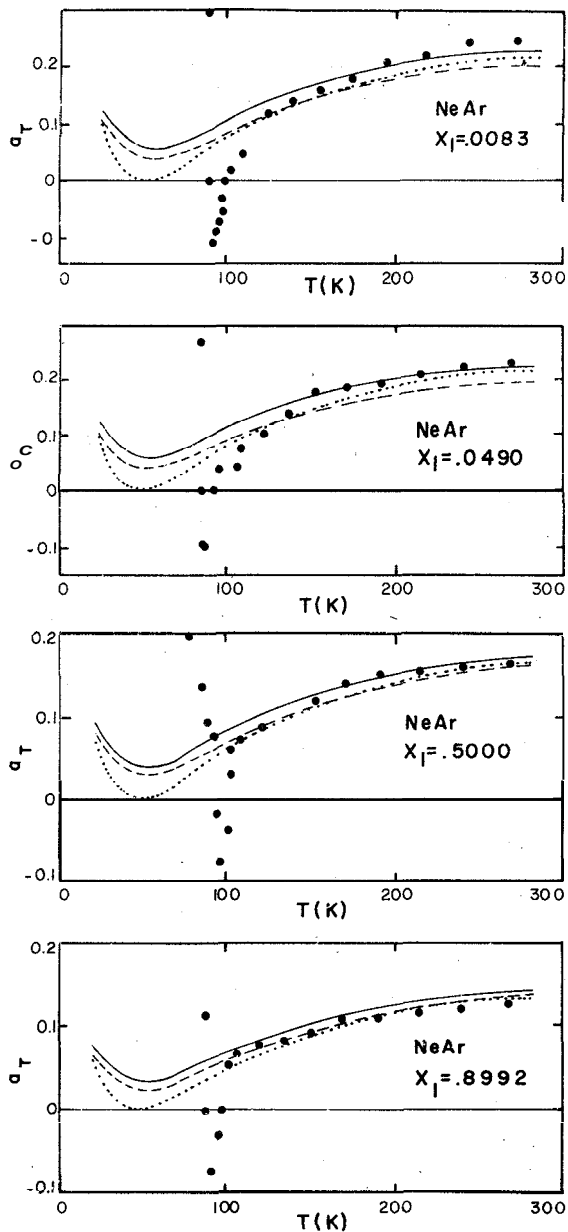


Fig.3 - Deviation curves between the predictions of the Chapman-Enskog theory based on the NLB potentials and the experimental thermal diffusion factor due to Grew and Wakeham¹⁹ for the Ne+Ar system. Continuous lines represent ESMSV III, ES3FW and NLB potential calculations while the broken line stands for the combination of SPSL, 3FW and NLB potentials and the dotted line for the combination of MDM, ES3FW and NLB potentials in all the figures based on the "three-potential calculations".

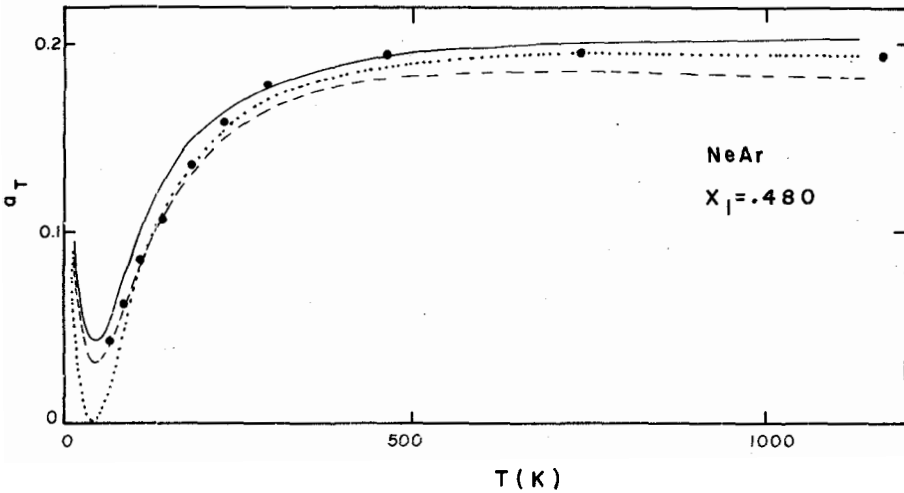
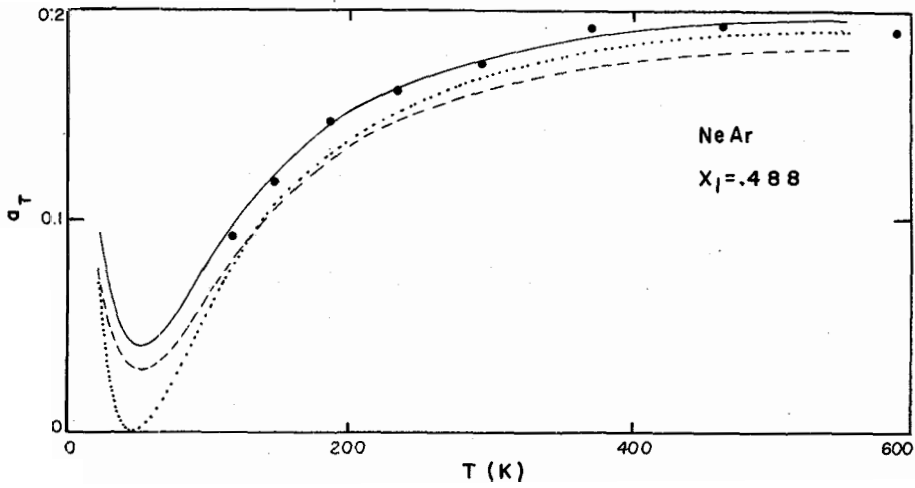


Fig.4 - Thermal diffusion "Three-potential Calculations" for Ne-Ar system compared with the experimental data of (upper) Grew¹⁵ and (lower) Grew, Johnson and Neil¹⁶.

Taylor et al²² have studied Ne + Xe experimentally both as a function of temperature and composition. The agreement between experimental data and the predicted α_T values of the basis of MSV potential is not always within the stated experimental error band though the similarity in the trends of their variations is quite marked. The same kind of qualitative comparison can be made between the data of Atkins et al¹⁴, Grew¹⁵⁻¹⁶, Nain and Saxena¹⁷⁻¹⁸, Heymann and Kistemaker²¹, and Ruther-

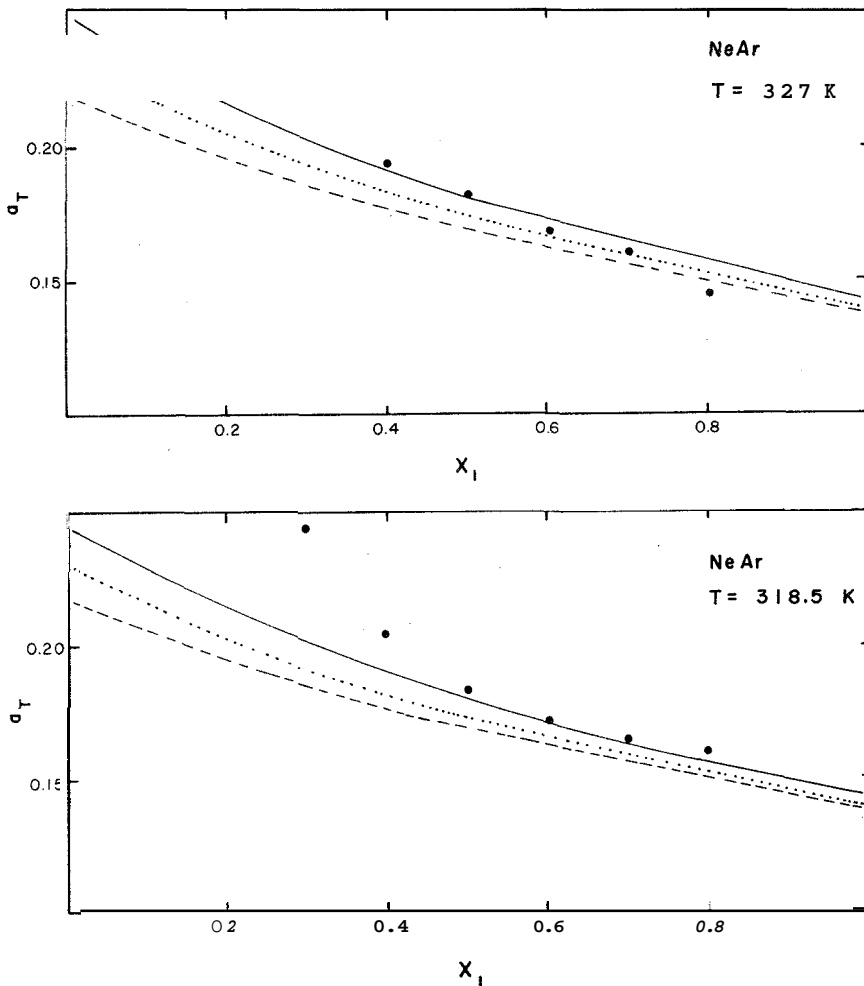


Fig.5 - Thermal diffusion "Three-potential Calculations" for Ne+Ar system compared with the experimental data of (upper) Alkins, Bastick and Ibbis¹⁴ and (lower) Nain and Saxena^{17,18}.

ford¹³, on one hand and the predictions based on the "three potential calculations" on the other. The predicted values are always higher than the experimental values of the thermal diffusion factor for all these sets of data^{14-18, 21-23} on the Ne + Xe system as shown in figures 7 to 10. Heymann and Kistemaker using the radiotracer technique have tried to establish the optimum concentration required for the radioactive component. As clear from the tabulations of table the radiotracer concentrations between .01 and .0001% render a_T values independent of the composition.

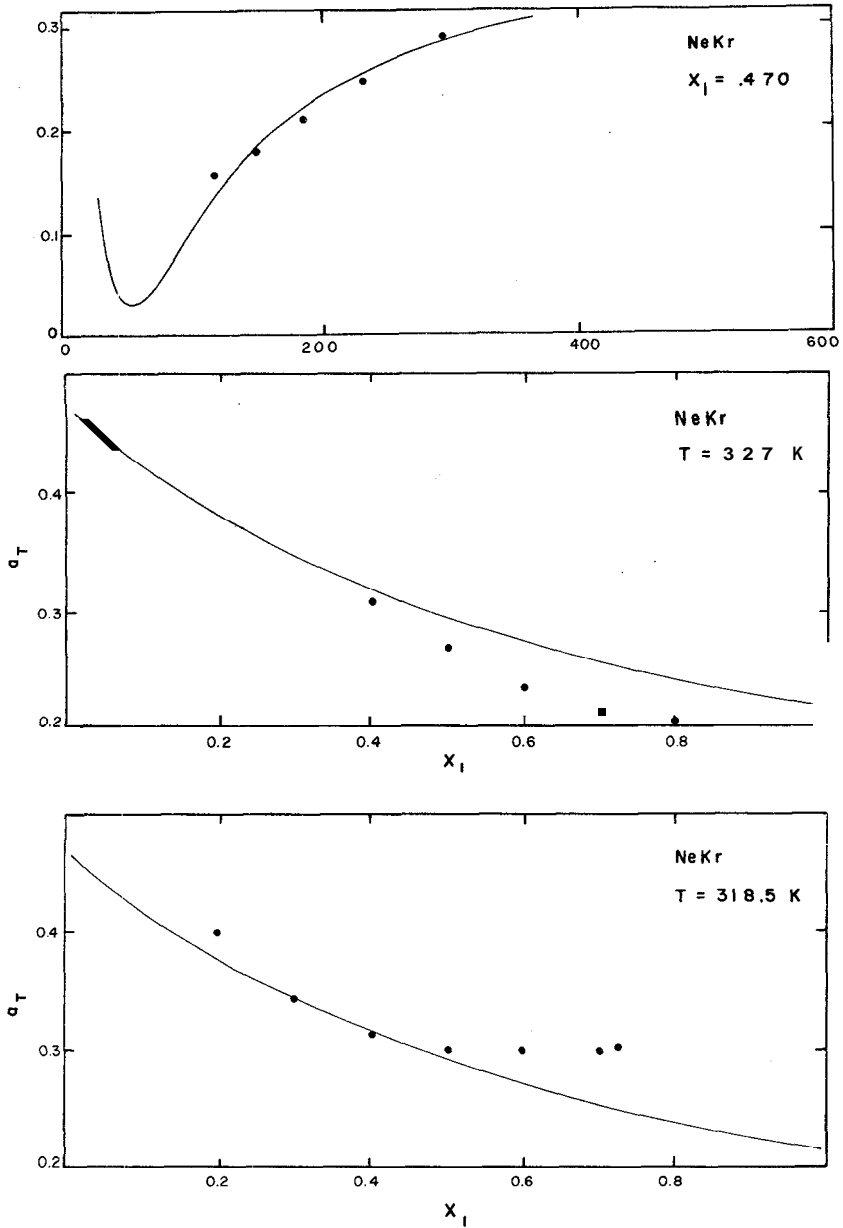


Fig.6 - Thermal diffusion "Three-potential Calculations" for the Ne+Kr system compared with the experimental data of (upper) Grew¹⁵, (middle) Alkins *et al.*¹⁴ and (lower) Mathur *et al.*²⁰. The three potential combination used for the display of the α_T calculations consists of ESHSV III, BWLSL and NLB potentials.

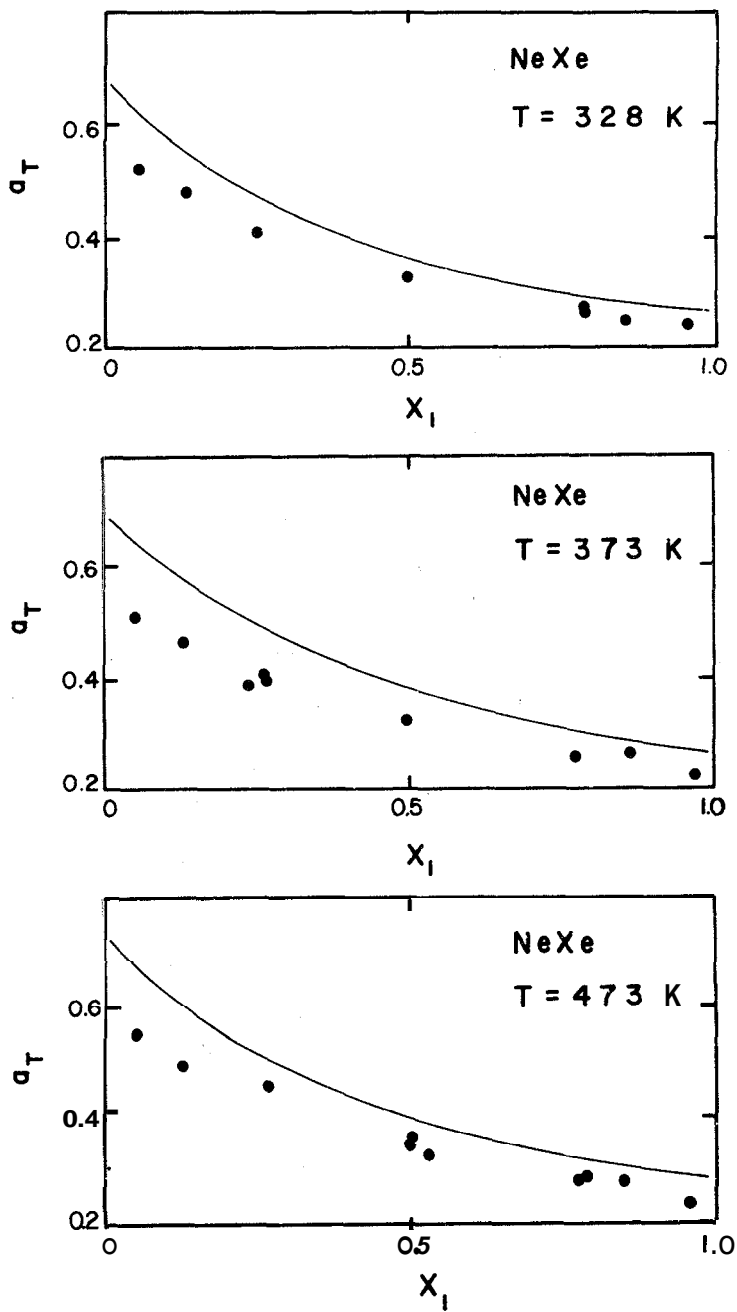


Fig.7 - "Three-potential Calculations" for the thermal diffusion factor on Ne+Xe system compared with the experimental data due to Taylor *et al.*²².The potentials used are ESMSV III, BWLSL and NLB.

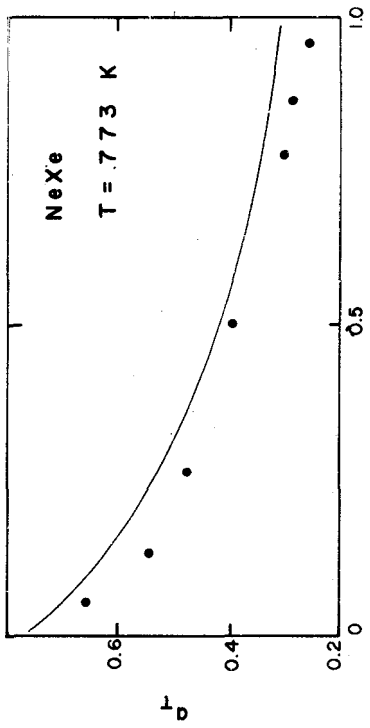
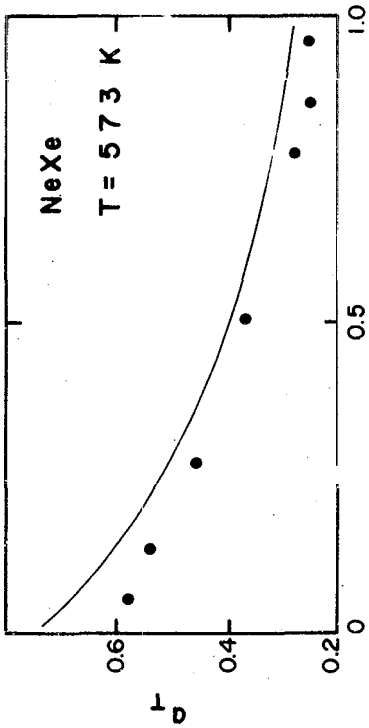
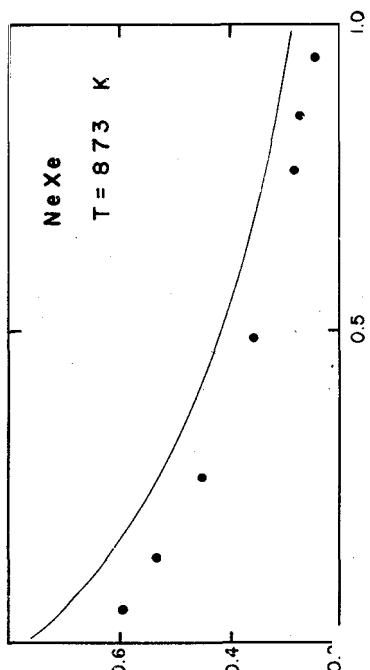
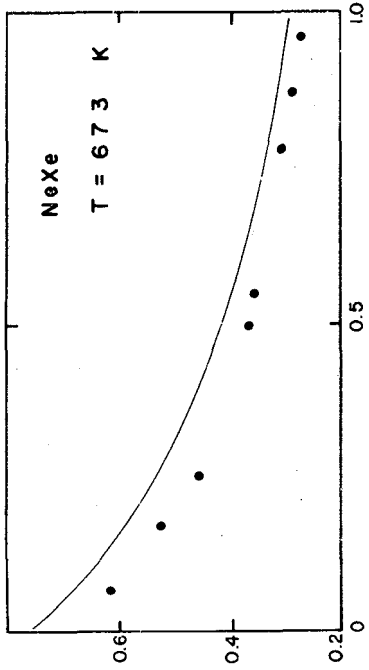


Fig. 8 - Continuation Fig. 7.

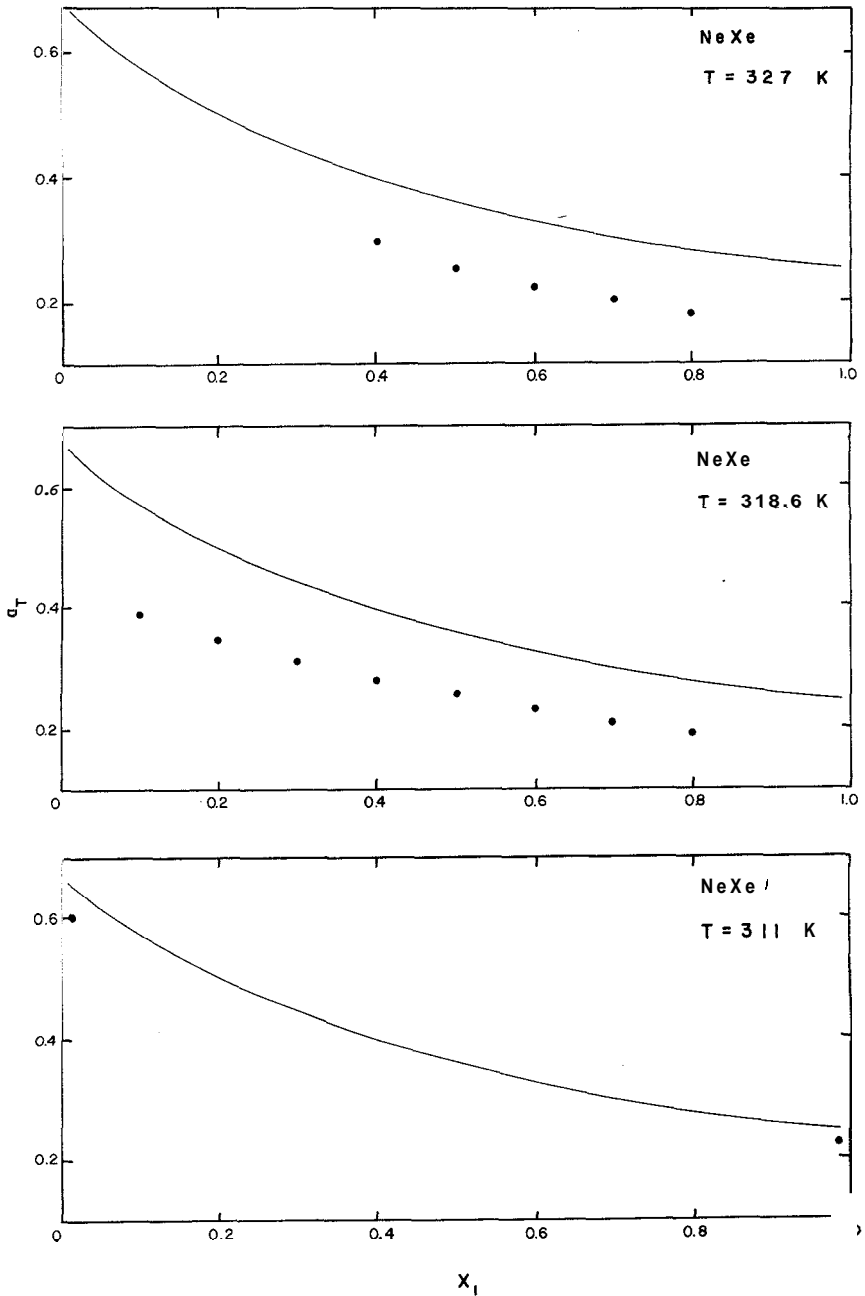


Fig.9 - "Three-potential Calculations" for the thermal diffusion factor on Ne+Xe system compared with the experimental data due to (upper) Alkins *et al*¹⁴, (middle) Nain and Saxena^{17,18} and (lower) Rutherford²³. Potentials used for these data are the same as in Fig.7.

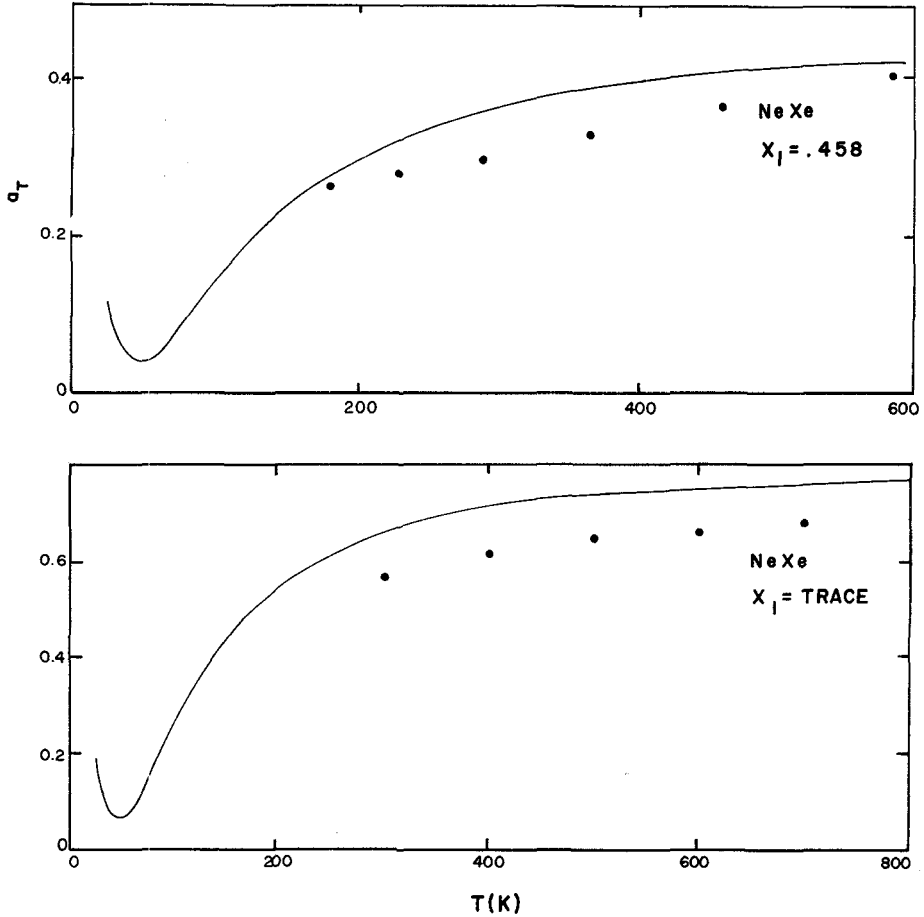


Fig.10 - "Three-potential Calculations" for the thermal diffusion factor on Ne+Xe system compared with the experimental data due to (upper) Grew^{15,16} and (lower) Heymann and Kistemäker²¹.

5. CONCLLSIONS

- 0) - Except some fine tunings required here and there the NLB potentials reproduced satisfactorily the experimental data on the transport properties of the Ne + Ar, Ne + Kr and Ne + Xe systems and can be used with confidence to generate data on these properties viz. interaction viscosity, diffusion, thermal conductivity and thermal diffusion. The parallel techniques used to propose unlike atom (molecula) potential energy functions for other gaseous mixtures stand a good chance of success.

- 02 - If the repulsive forces, as embedded in the constructions of the ESMSV (or MSV) potentials models are regarded to exactly describe the actual state of affairs then the temperature ranges for the validity of the KM correlation to predict interaction viscosity values accurately for these systems is found to be smaller than that recommended by Kestin and Mason. Therefore, caution should be exercised in the choice of the temperature ranges while extrapolating values using KM correlation.
- 03 - Using the interaction viscosity data generated by the NLB potentials for these systems over an extended range of temperature as mentioned above in 2.), the thermal conductivity and the diffusion data over the comparable temperature ranges can be extrapolated in conjunction with the Chapman-Enskog²⁷ theory which relates mathematically the various transport properties among themselves.
- 04 - To resolve the question of the positive theoretical minimum encountered in the Ne + Ar system, instead of a negative one as found experimentally¹⁹, more detailed experiments with better accuracy using the radiotracer technique are suggested to be performed in the lower temperature region.

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