

Figure 1. Differential scanning calorimetric thermogram of liquid glutaronitrile solidified by cooling: (a) at 2.5°/min; (b) at 20°/min; (c) at 30°/min; and (d) by quenching on liquid nitrogen.

These ranged from 244 cal/mole for samples quenched in liquid nitrogen to 134, 65, 12, 18, and 1.5 cal/mole at cooling rates of 30, 20, 10, 5, and 2.5°/min, respectively. We failed to observe any reversibility in the transition from crystal II to crystal I.

Calculations by Wulff and Westrum indicate that the vibrational and rotational contributions to entropy are greater for the TG than the GG conformation.⁵ The observed exothermic transitions from metastable crystal II to crystal I, which is in the GG conformation,^{2,5} thus give additional support to the assignment² of the TG conformation to the metastable crystal. However, the assignment of the metastable modification solely to the TG conformation remains to be established, in view of the dependence of the exothermic heats on the cooling rate.

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A Note on the Principle of Corresponding States

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As the nature of the molecular interactions in argon, krypton, and xenon satisfies the restrictive conditions required by the statistical-mechanical derivation of

the law of corresponding states,¹ their thermodynamic properties have extensively been used to test the validity of this law.² Reducing factors are derived from both critical constants and molecular parameters.²⁻⁴ The properties considered in this note are the second virial coefficient and the viscosity coefficient at low pressure reduced in terms of the parameters of the Kihara pair potential⁵ $U = U_0 [(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6]$, where U_0 is the minimum of the potential which occurs at ρ_0 . The intermolecular separation ρ is defined as the shortest distance between the outer surface of the cores. The given equation is valid for $\rho \geq d$, where d is the core diameter. For smaller values of ρ , $U \geq \infty$. The reduced expression for the second virial coefficient B is then $B^*(T^*) = B(T^*)/2\pi/3\rho_0^3$, where $T^* = Tk/U_0$. Myers and Prausnitz⁶ have made a similar study for the second virial coefficient, but the experimental data now available, mainly at low temperatures,⁷ allow a more precise check on the corresponding states behavior. No transport property has previously been studied on a corresponding states basis, although calculations on argon only have been done by Barker, *et al.*⁸ The core size we use is not an extra adjustable parameter but is independently fixed⁹ by the equation $X = 7.0\omega + 0.24$, where X is a core parameter related to the mean curvature, M_0 , of the core, and ω is the acentric factor introduced by Pitzer.¹⁰ The heavy rare gases (Ar, Kr, Xe) have $\omega = 0$ and for a spherical core $M_0 = 2\pi d$, so that the simple relationship $d = 0.08\rho_0$ results. We thus obtain a two-parameter potential function as required by the theory.¹

Parameters were obtained by simultaneous fitting of both second virial and viscosity coefficient data by automatic computation. We minimized the root mean square deviation between theoretical and experimental values of both properties. Results are shown in Table I and full details are given in ref 11.

Although the general quality of the Kihara potential was studied elsewhere,¹¹ the theoretical curve is drawn

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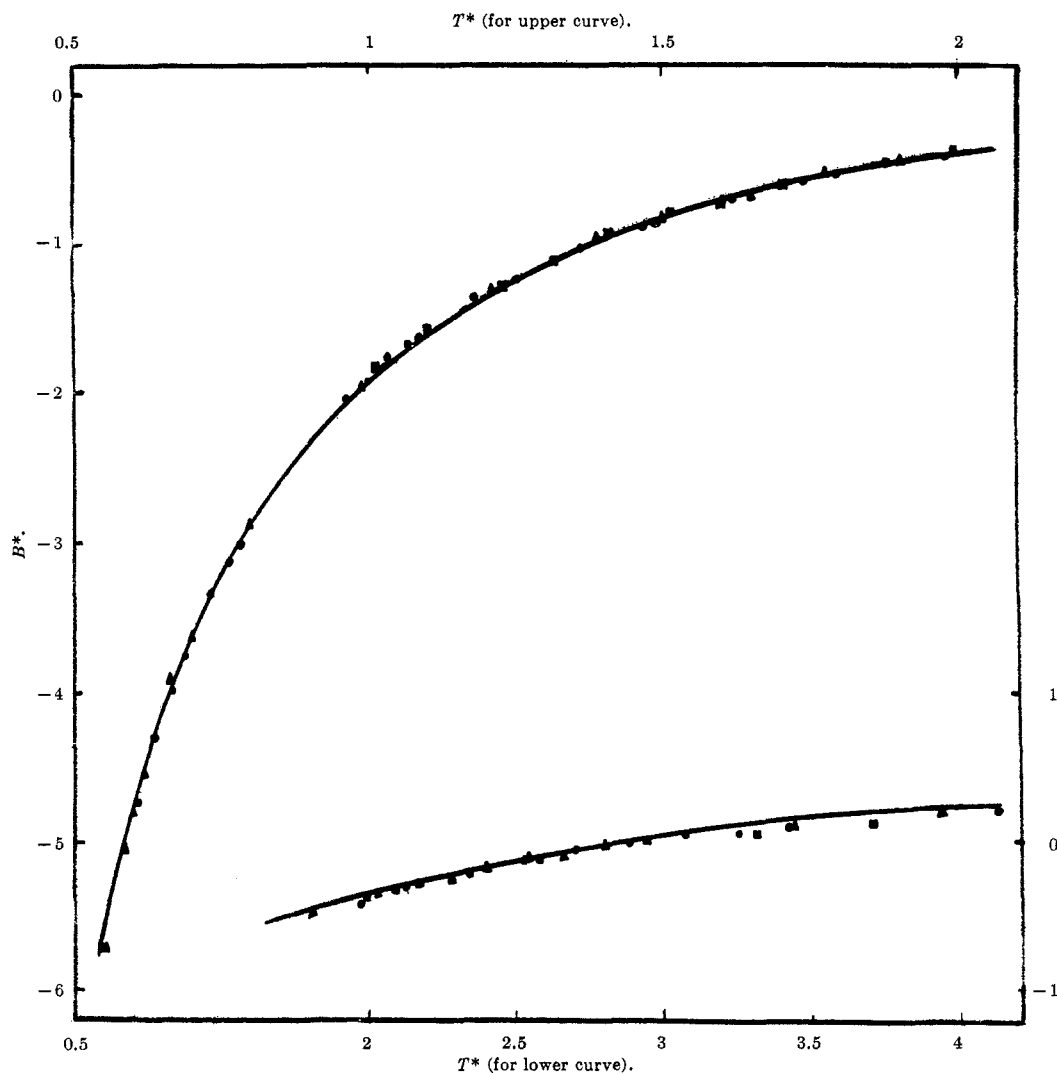


Figure 1. Reduced second virial coefficient: ●, argon; ▲, krypton; ■, xenon.

Table I: Parameters of the Kihara Pair Potential

	U_0/k , °K	ρ_0 , A	d , A	Standard deviations	
				$\eta \times 10^7$ (mT) ^{1/2}	$B(T)$, Å ³ /mole- cule
Argon	138.0	3.482	0.279	0.39	1.60
Krypton	196.1	3.735	0.299	0.07	3.9
Xenon	263.6	4.078	0.326	0.03	1.1

in Figure 1 to show the excellent agreement with the experiment over the entire range of temperature of $B^*(T^*)$. Figure 1 clearly shows that the corresponding states behavior is closely followed by the second virial coefficient of Ar, Kr, and Xe. The reduced viscosity coefficient $\eta^* = \eta R_0^2 / \sqrt{mU_0}$ is shown in Figure 2. Here $R_0 = 2^{-1/6} \rho_0 + d$ is the collision diameter and m is the

mass of the molecule. The recent data on Kr are included;¹² this allows a comparison on a larger temperature range than was previously possible.² The agreement between theory and experiment is again very good and it is seen that the principle of corresponding states is also followed by the property. Levelt³ has made a careful study of the compressibility of argon and xenon and concluded that it is impossible to represent the experimental $B-T$ curve of argon and xenon by means of a Lennard-Jones 6-12 potential within experimental accuracy. These curves however can be brought into coincidence by means of two reduction factors for temperature and density. The PV/RT isotherm for argon may also be transformed into the compressibility isotherm of xenon by multiplying by

(12) D. G. Clifton, *J. Chem. Phys.*, **38**, 1123 (1963).

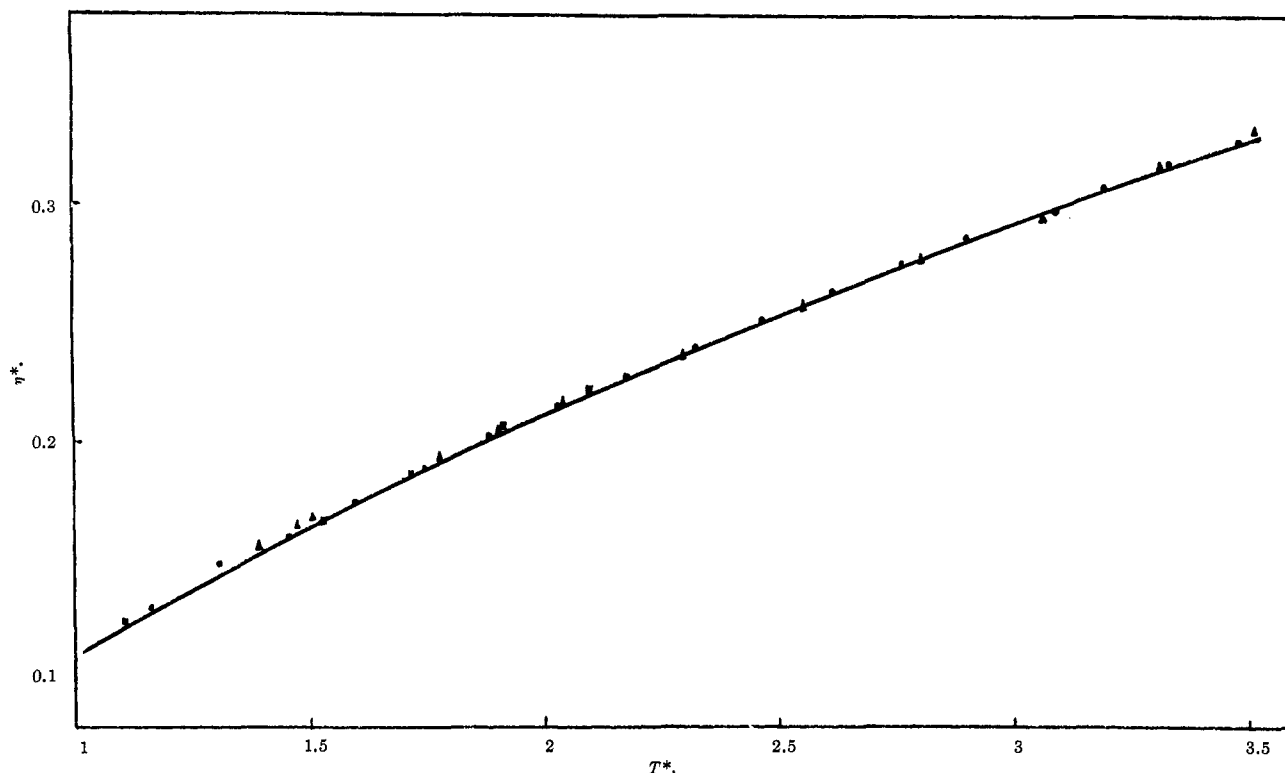


Figure 2. Reduced viscosity coefficient: ●, argon; ▲, krypton; ■, xenon.

scale factors. Levelt found the "ideal scale factors",³ *i.e.*, best set of scale factors, to be 1.931 for the temperature and 0.633 for the density. The ratios of the reduction factors in terms of the molecular parameters are shown in Table II.

Table II: Ratio of Reduction Factors

	Levelt		Present work		"Ideal"	
	Temp	Density	Temp	Density	Temp	Density
Param Xe	1.889	0.595	1.910	0.623	1.931	0.633
Param Ar						

It is seen that the ratios we obtain are much closer to the ideal ones than Levelt's. In order to obtain coincidence of the reduced isotherms, one should modify one set of parameters by about 1% in the temperature scale factor and by 0.6% in the density scale factor, values which are scarcely larger than the expected uncertainties of the parameters. Consequently, if the assumption of the pairwise additivity of the potential is valid, one expects that if the isotherms of argon and xenon are reduced with our set of molecular parameters they should come much closer to each other

than if reduced with the Lennard-Jones 6-12 potential parameters, so that the compressibility factor of these gases can also be correlated using the principle of corresponding states.

Effect of Solvent on the Entropy of the Tris-(1,10-phenanthroline)iron(III)-(II) System

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The partial molal entropy change occurring during a reversible electron transfer in solution can be obtained experimentally through measurement of a cell potential as a function of temperature. A compilation of temperature coefficients for a number of aqueous electrode potentials has been made by deBethune and Loud.¹ These data indicate that for systems in which the

(1) A. J. deBethune and N. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," C. A. Hampel, Publisher, Skokie, Ill., 1964.