

Excess Heats and Volumes of Mixing

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Citation: [The Journal of Chemical Physics](#) **22**, 955 (1954); doi: 10.1063/1.1740241

View online: <http://dx.doi.org/10.1063/1.1740241>

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Bending Fundamental of NO₂

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(Received March 5, 1954)

RECENTLY Moore has investigated the infrared spectrum of NO₂ under high dispersion in the 1.4–3.4 μ region.¹ The results of this work combined with those obtained from the bending fundamental yielded the ground-state parameters and a complete set of quadratic anharmonicity coefficients. The present paper communicates the results of the investigation under prism dispersion of the bending fundamental ν_2 .

Experimental.—The spectra were taken with a Perkin-Elmer Model 12C spectrometer equipped with NaCl and KBr prisms and a Baird Associates spectrophotometer with NaCl optics.

Commercial nitrogen dioxide was repeatedly redistilled until a crystalline white solid was obtained when the distillate was frozen in a trap immersed in a solid carbon dioxide-acetone mixture. To minimize overlapping absorption by the strong N₂O₄ band at 684 cm⁻¹ the absorption cells were held at 175 \pm 2°C.

The data obtained replotted on a linear frequency scale are given in Fig. 1. The positions of the Q branches are listed in the second column of Table I.

TABLE I. Rotational structure of the bending fundamental of NO₂.

Assignment PQ	Observed (cm ⁻¹)	Smoothed curve (cm ⁻¹)
10	639	639
9	647.5	647
8	656	656
7	(667)	666
6	676	677
5	688	688
4	700	700.5
3	714.5	714.5
2	730.5	728
1	742	743
RQ		
0	761	758.0
1	772.5	774.5
2	791.5	791.5
3	809	809
4	826.5	826.5
5	844	844
6	861	861
7	878.5	878.5
8	897	897

Discussion.—The electron diffraction investigation of NO₂² and the rotational structure of the bending mode indicate that nitrogen dioxide is very close to a symmetric top. Accordingly, the bending fundamental was analyzed to this approximation. To compensate partly for the deviation from a symmetric top the positions of the Q branches were plotted as a function of K and a smooth curve drawn through the points. The frequencies read from this smooth curve (column 3 of Table I) were then used to calculate the combination differences which are plotted as a function of K² in Fig. 2. The position of the band origin was de-

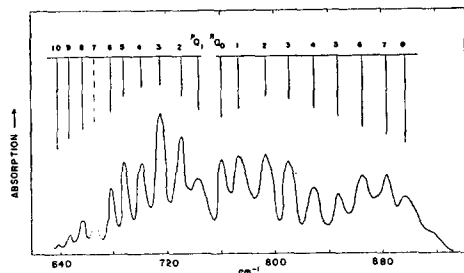


FIG. 1. The bending fundamental of NO₂. The background absorption near 880 cm⁻¹ is due to nitric acid, and the dashed part of the curve indicates region observed by CO₂.

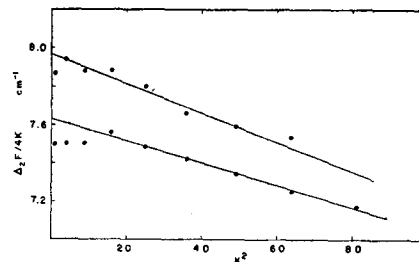


FIG. 2. Determination of the rotational constants of NO₂. The top curve refers to the upper state and the bottom curve refers to the ground state.

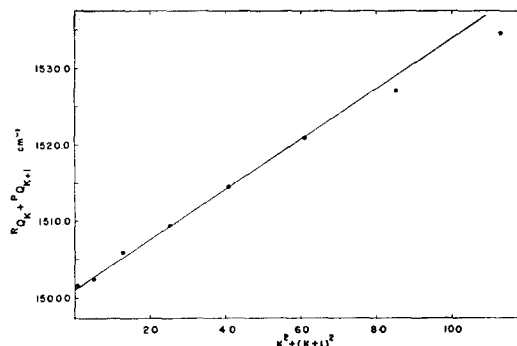


FIG. 3. Determination of the band origin for ν_2 of NO₂.

termined by plotting the sum $RQ_K + PQ_{K+1}$ versus $K^2(K+1)^2$ as illustrated in Fig. 3. The value of ν_0 as well as the constants ($A-B$) and D_K in both the upper and lower states are listed in Table II.

TABLE II. Rotational constants of NO₂ and band center for ν_2 .

$A'' - \tilde{B}'' = 7.63 \pm 0.05$ cm ⁻¹
$D_K'' = 2.9 \times 10^{-3}$ cm ⁻¹
$A' - \tilde{B}' = 7.97 \pm 0.05$ cm ⁻¹
$D_K' = 3.8 \times 10^{-3}$ cm ⁻¹
$(A' - \tilde{B}') - (A'' - \tilde{B}'')^a = 0.33$ cm ⁻¹
$\nu_0 = 750.6 \pm 0.3$ cm ⁻¹

^a From plot of $RQ_K + PQ_{K+1}$.

Since the data obtained in this investigation have been incorporated into a much more extensive paper on NO₂ by Moore,¹ it will suffice here to remark that the value of the small moment of inertia as obtained from ν_2 agrees well with that calculated from the structural parameters derived from the electron diffraction investigation.²

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¹ G. Moore, J. Opt. Soc. Am. 43, 1045 (1953).

² Claesson, Donohue, and Schomaker, J. Chem. Phys. 16, 207 (1948).

Excess Heats and Volumes of Mixing

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(Received March 11, 1954)

IN view of the recent letter of Thacker and Rowlinson,¹ it is noteworthy that many mixtures are known for which the excess enthalpy and volume of mixing have opposite signs. The purpose of this communication is to discuss briefly the data for some of these, examined by the writer,^{2,3} together with the data of Thacker and Rowlinson.

In an earlier discussion² the existence of three effects contributing to the volume change on mixing was demonstrated. One of these,

concerned with molecular packing, is absent when the component molecules are of similar sizes. Restricting this discussion to such mixtures, two effects remain. Scatchard⁴ has shown that the internal energy change on mixing ΔU is related to a volume change ΔV_f by

$$\Delta V_f = \kappa \Delta U, \quad (1)$$

where κ is the isothermal compressibility of the mixture. ΔV_f is therefore similar in sign to the energy and enthalpy of mixing. A further contribution ΔV_c arises from the differences between the compressibilities and cohesive energy densities, L , of the pure components and of the mixture. This can be expressed by²

$$\Delta V_c = v_1 v_2 (L_1 - L_2) (\beta_1 - \beta_2), \quad (2)$$

where v_1 and v_2 are the volume fractions of components 1 and 2 in the mixture, and β_1 and β_2 are the compressibilities of single or small groups of molecules of types 1 and 2 in the mixture. These are not susceptible to measurement or precise definition, but will clearly be smaller than the corresponding macroscopic compressibilities κ_1 and κ_2 . The simplest reasonable assumption is that for random mixing

$$\beta_1 = k\kappa_1, \text{ etc.}, \quad (3)$$

where the constant, k , has the same value for all substances. It is a matter of observation that when ΔV_c is large enough to be significant, it is always negative. When the component molecules are very unlike in molecular force fields, ΔV_c is numerically greater than ΔV_f , and the enthalpy and volume changes in an endothermal mixture have opposite signs.

By a suitable choice of the constant, k , the foregoing argument is placed on a basis for comparison with experiment. In Table I

TABLE I.

Mixture	$\frac{\Delta V_f}{\text{ml}}$	$\frac{\Delta V_c}{\text{ml}}$	$\frac{\Delta V_{\text{calc}}}{\text{ml}}$	$\frac{\Delta V_{\text{obs}}}{\text{ml}}$	$\frac{\Delta H_{\text{obs}}}{\text{cal}}$
Ethyl benzene + <i>o</i> -xylene	+0.0003	-0.0005	-0.0002	-0.0002	+0.075
Ethyl benzene + tetralin	+0.0004	-0.0009	-0.0005	-0.0007	+0.067
Ethyl benzene + dimethyl phthalate	+0.0036	-0.0061	-0.0025	-0.0024	+0.985
Ethyl benzene + diethyl phthalate	+0.0017	-0.0039	-0.0022	-0.0020	+0.371
Ethyl benzene + dipropyl phthalate	+0.0011	-0.0026	-0.0015	-0.0018	+0.200
Ethyl benzene + dibutyl phthalate	+0.0005	-0.0023	-0.0018	-0.0015	+0.045
1:3 Butanediol diacetate + dimethyl phthalate	+0.0005	-0.0028	-0.0023	-0.0012	+0.093
1:3 Butanediol diacetate + dimethylglycol phthalate	+0.0011	-0.0033	-0.0022	-0.0011	+0.356

data are given for eight mixtures, taken from references 2 and 3, which have approximately equal-sized component molecules and opposite signs for the heat and volume changes on mixing. The mixtures contain equal volumes of the two components. To calculate ΔV_c , k has been taken throughout as 0.4, a physically reasonable value. The calculation of ΔV_f has been described previously.⁵ ΔV_{calc} is the sum ($\Delta V_f + \Delta V_c$). Its good agreement with ΔV_{obs} should not be too highly stressed, as k was chosen to represent the data.

The calculation cannot be extended in such detail to the mixtures of Thaker and Rowlinson as the heats of mixing, though stated to be positive, are not available. An estimate of ΔV_f has been made by combining (1) with the Hildebrand regular solution equation,⁶

$$\Delta V_f = \kappa v_1 v_2 (L_1^{\frac{1}{3}} - L_2^{\frac{1}{3}})^2. \quad (4)$$

Calculation of ΔV_c has been carried out using for *n*-pentane and *n*-hexane the cohesive energies compiled by Hildebrand and Scott,⁶ and isothermal compressibilities derived from adiabatic compressibilities⁷ (i.e., C_6H_{12} $\kappa = 177 \times 10^{-6}$ megabar⁻¹, C_6H_{14} $\kappa = 146 \times 10^{-6}$ megabar⁻¹). Volume fractions have been taken as 0.5 as this will be near the composition for maximum contraction.^{1,2} Similar calculations for three mixtures examined at 0°C by Mathot and Desmyter⁸ have also been made. 180×10^{-6} megabar⁻¹ was taken

for the compressibility of neopentane; the other compressibilities were obtained as before.⁵ These calculated values of ΔV are compared with the observed values in Table II. The agreement is

TABLE II.

Mixture	$\frac{\Delta V_f}{\text{ml}}$ Eq. (4)	$\frac{\Delta V_c}{\text{ml}}$	$\frac{\Delta V_{\text{calc}}}{\text{ml}}$	$\frac{\Delta V_{\text{obs}}}{\text{ml}}$	H_{obs}
Ethyl benzene + <i>n</i> -pentane	+0.0044	-0.0093	-0.0049	-0.0052	+ive
Ethyl benzene + <i>n</i> -hexane	+0.0028	-0.0050	-0.0022	-0.0013	+ive
<i>o</i> -xylene + <i>n</i> -pentane	+0.0048	-0.0148	-0.0100	-0.0063	+ive
Neopentane + benzene	+0.0104	-0.0170	-0.0066	-0.0048	+ive
Neopentane + cyclohexane	+0.0038	-0.0074	-0.0036	-0.0105	+ive
Neopentane + carbon tetrachloride	+0.0070	-0.0130	-0.0060	-0.0049	+ive

satisfactory, considering the uncertainty in ΔV_f from (4). This equation will usually underestimate ΔV_f ,^{3,5} and this is supported by the fact that ΔV_{calc} is usually larger than ΔV_{obs} , except for neopentane + cyclohexane where the divergence is surprisingly large.

Consideration of the physical relation between cohesive energy density and compressibility in terms of molecular force and volume parameters shows that the behavior of ($\Delta V_f + \Delta V_c$) for various mixtures follows closely the predictions of Prigogine and Bellemans,⁹ based on the cell model for mixtures of molecules of slightly different sizes.

- ¹ R. Thacker and J. S. Rowlinson, *J. Chem. Phys.* **21**, 2242 (1953).
- ² P. Meares, *Trans. Faraday Soc.* **45**, 966 (1949).
- ³ P. Meares, *Trans. Faraday Soc.* **49**, 1133 (1953).
- ⁴ G. Scatchard, *Trans. Faraday Soc.* **33**, 160 (1937).
- ⁵ P. Meares, *Trans. Faraday Soc.* **45**, 1066 (1949).
- ⁶ J. H. Hildebrand and R. L. Scott, *Solubility of Non-electrolytes* (Reinhold Publishing Corporation, New York, 1950), 3rd edition.
- ⁷ W. Schaaffs, *Z. physik. Chem.* **194**, 28 (1944).
- ⁸ V. Mathot and A. Desmyter, *J. Chem. Phys.* **21**, 782 (1953).
- ⁹ I. Prigogine and A. Bellemans, *Faraday Soc. Disc.* **15**, 80 (1953).

Thermodynamic Functions of Hydrogen Isocyanate

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(Received March 18, 1954)

A LIKELY side reaction in a nitrogen-containing system at high temperatures is a radical combination according to



and for kinetic considerations the thermodynamic functions of hydrogen isocyanate are required. These can now be obtained statistically from known^{1,2} molecular parameters and vibrational frequencies, *viz.*, fundamentals $\omega = 572, 670, 797, 1327, 2274, 3531$ cm⁻¹, and moments of inertia $I \times 10^{40} = 0.9157, 76.36, 77.276$ g cm². The functions were calculated for an ideal gas of HNCO molecules at a total pressure of 1 atmos by using the familiar approximation of the harmonic oscillator and rigid rotator (Table I).

TABLE I. Calculated thermodynamic functions of ideal HNCO gas at 1 atmos.

$T^\circ\text{K}$	S°	$-(F^\circ - H^\circ)/T$	$(H^\circ - H^\circ_0)/T$	C_p°
298.16	56.92	48.14	8.78	10.73
300	56.97	48.19	8.78	10.75
400	60.26	50.81	9.45	12.08
500	63.06	52.98	10.08	13.12
600	65.54	54.88	10.66	13.93
800	69.72	58.08	11.64	15.19
1000	73.22	60.77	12.45	16.12
1200	76.23	63.10	13.13	16.84
1400	78.86	65.16	13.70	17.39
1500	80.06	66.12	13.94	17.61