SPECIALIA

A Note on Solutions Governing the Origin of Polytropes

In this note the author intends to give an entirely different proof, which is more logical, of his recent result that the origin of polytropes, whatever be the index, is governed by solutions of the LANE-EMDEN equation for either $n = 0$ or $n = -1$[1].

At the origin of the polytropes, dP/dr and $d\varrho/dr$ vanish: that is, at the origin, P and ϱ are not functions of r. Equations governing the hydrostatic equilibrium suggest that at any point in the configuration, where P and ϱ are related, both P and ϱ are functions of r simultaneously. Hence, at the origin, P and ϱ are independent of each other; but a polytropic model, in which P and ϱ are not related, cannot have any physical validity. This makes it clear that, at the origin, $P = K\varrho^{1+1/n}$ can be relevant only for such limiting values of n for which P and ϱ tend to become independent of each other. Thus, whatever be the index of the polytrope, the arrangement of solutions at the origin will be given by solutions for either n tending to zero or for n tending to -1.

If we consider the fundamental equation in terms of r and P, then solutions for $n = -1$ will govern the origin for the simple reason that for $n = 0$, P cannot be finite. For similar reasons if we consider the structure in $(r; \varrho)$-plane, solutions for $n = 0$ will govern the origin[2].

Zusammenfassung. Es wird bewiesen, dass für den Ursprung von Polytropen nur Lösungen der EMDEN-Gleichung vom Index 0 oder -1 sind.

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Molecular Compounds Without Chemical Bonding

When benzene is added to a solution of nickel cyanide in aqueous ammonia containing acetic acid, a precipitate of the composition $[Ni(CN)_2 \cdot NH_3 \cdot C_6H_6]$ is formed[1]. Other examples of these addition compounds are those formed between nickel cyanide-ammonia complex $[Ni(CN)_2 \cdot NH_3]$ and molecules of aniline ($C_6H_5NH_2$), pyridine (C_5H_5N), pyrrole (C_4H_5N) and thiophene (C_4H_4S). Contrary to the statement of HOFMANN and KÜSPERT[1], we have found that phenol and furan do not form clathrates with nickel cyanide-ammonia complex[2].

A single crystal X-ray investigation was undertaken on the benzene clathrate[3]. The large distance between the carbon atoms of benzene and the atoms of the caging material was interpreted to mean that the organic molecules are not bonded but are simply caged in the crystal lattice.

We present here the IR-spectroscopic evidence that the organic molecules are just trapped in the cavities provided by the nickel cyanide-ammonia lattice and there is no chemical bonding between the guest and the host molecules.

The absorption frequencies of benzene attributed to in-plane vibrations are identical in clathrate and the pure liquid (or gas) but those attributed to out-of-plane vibrations are different (more or less shifted e.g. 675 cm^{-1} band of liquid benzene appears at 706 cm^{-1} in benzene chathrate). This is the only indication of interaction between the clathrated molecule and the nickel cyanide-ammonia lattice.

It can be stated that the clathrate bands with large shifts correspond to bands which in pure components or in a solvent show large shifts in comparison with gaseous molecules. For example, in benzene clathrate the wave number of A_{2u} out-of-plane band is 706 cm^{-1}; 687 cm^{-1} in the solid state, and 675 cm^{-1} in the vapour or liquid state. Similarly, in pyrrole clathrate $[Ni(CN)_2 \cdot NH_3 \cdot C_4H_5N]$ the wave number of the B_2 out-of-plane ν_{21} is 552 cm^{-1}; 561 cm^{-1} in the liquid state and 475 cm^{-1} in the vapour state. Hence the magnitudes of these shifts in clathrate bands in comparison with the bands in pure compounds are of the same order as the magnitudes of the shifts in liquid or solid spectra as compared with the gaseous spectra. It is, therefore, suggested that the forces which may be causing the minor shifts in clathrate spectra are of the same kind as the forces which cause the shifts in liquid or solid spectra, i.e. van der Waals forces.

LORENZELLI and ALEMAGNA[4] recently gave a broad band near 110 cm^{-1} in liquid pyrrole. They assigned this band to an intermolecular vibration involving complexes bound through hydrogen bonds. The pyrrole clathrate

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[3] J. H. RAYNER and H. M. POWELL, J. chem. Soc. 319 (1952).

[4] V. LORENZELLI and A. ALEMAGNA, C. r. hebd. Séanc. Acad. Sci., Paris *257*, 2977 (1963).

shows no band in the 100–150 cm^{-1} region. The absence of this 110 cm^{-1} band in pyrrole clathrate suggests that no such hydrogen bonds are present in pyrrole clathrate and also no such bonding is involved between the pyrrole molecule and the neighbouring N–H groups of the host lattice (because the hydrogen bonds assumed by LORENZELLI and ALEMAGNA[4] involve the hydrogen atoms of the N–H groups in liquid pyrrole).

Further support for the absence of chemical bonds between caged molecules and the host complex came from the magnetic moment studies[5]. The constancy of the magnetic moment of the nickel atoms in nickel cyanide-ammonia clathrates suggests that the included organic molecules are not joined by chemical bonds with the nickel atoms. They are 'housed' in the host cavities due to van der Waals forces.

SNYDER[6], and FRITZ et al.[7] reported the IR-spectra of $Cr(C_6H_6)_2$ and $(C_6H_6)Cr(Co)_3$ compounds, respectively. In these complexes, the benzene molecules are coordinated to metal atoms through π-bonding[8,9]. These π-compounds show large shifts from the gaseous or liquid benzene bands which are not seen in the benzene clathrate (Table).

Therefore, the IR-spectroscopic study shows that benzene and other enclosed molecules in nickel cyanide-ammonia complex are not linked to the nickel atom through a chemical bond. HARADA[12], and MIYOSHI and co-workers[13] calculated the force constants for the fundamental out-of-plane vibrations of benzene. The force constants in the clathrates were found to be larger than the values in the gaseous benzene. This increase in the force constants was attributed to the electron-cloud repulsion between the cage-former and the enclosed molecules.

Since the ionic radius ('crystal radius' of PAULING) of the Ni^{++} (0.72 Å) is very nearly the same as those of Mn^{++} (0.80 Å), Fe^{++} (0.76 Å), Co^{++} (0.74 Å) and Zn^{++} (0.74 Å)[14,15]; these metallic ions may replace Ni^{++} without appreciable alteration in the tetragonal structure of clathrate compounds. The parameters (a and c) of the resulting clathrates may be slightly different from the nickel cyanide-ammonia-benzene clathrate. These minor differences in the lattice constants will result from the differences among the ionic radii of the respective metal ions and also from the differences in molecular volumes of the captured molecules.

Zusammenfassung. Die Infrarotspektren der Einschlussverbindungen

$[Ni(CN)_2(NH_3)(C_6H_6)]$ und $[Ni(CN)_2(NH_3)C_4H_5N]$

wurden untersucht und mit den Spektren von gasförmigen und flüssigen C_6H_6 bzw. C_4H_5N verglichen.

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The frequencies (cm^{-1}) of benzene in different compounds

Gaseous C_6H_6 ref. [10]	Liquid C_6H_6 ref. [11]	$Cr(C_6H_6)_2$ ref. [6]	$(C_6H_6)Cr(Co)_3$ ref. [7]	C_6H_6 clathrate BHATNAGAR	Assignment
675	675	796	784	706 s, i	$\nu^{11}(A_{2u})$
1010	1010	–	–	–	$\nu^{12}(B_{1u})$
1309	1309	–	–	1318 w	$\nu^{14}(B_{2u})$
1146	1148	–	–	1148 s, m	$\nu^{15}(B_{2u})$
405	404	–	–	408 m	$\nu^{16}(E_{2u})$
975	969	–	–	986 s, m	$\nu^{17}(E_{2u})$
3068	–	3047	2931	ca. 3021 vw	$\nu^{18}(E_{1u})$
1482	1479	1430	1445	1477 s, i	$\nu^{19}(E_{1u})$
1037	1035	1002	1016	1035 s, i	$\nu^{20}(E_{1u})$

s, strong; i, intense; w, weak; m, medium; vw, very weak.

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[16] Present address: Faculté des Sciences de Toulouse, École nationale supérieure de Chimie, 38, rue des 36 Ponts, Toulouse (France). – Clathrate work was carried out under a research grant by University of Western Australia. Nickel cyanide-ammonia clathrates were further investigated by the author at the Punjab University (Chandigarh, India), University of Rome (Rome, Italy) and Fisk University (Nashville, Tennessee, USA).

Avilamycin[1]

Aus Kulturlösungen des Actinomycetenstammes ETH 23575 (= NRRL 2860), der der Art *Streptomyces viridochromogenes* zugehört[2], haben wir durch Extraktion mit Äthylacetat, Chromatographie an Aluminiumoxid und Kristallisation aus Aceton-Äther ein farbloses Antibioticum mit Smp. 188–189°, das Avilamycin, isoliert. Auf Grund der Mikroanalysen, die am besten mit einer Formel $C_{63}H_{94}O_{35}Cl_2$ (Ber. C 51,01 H 6,36 Cl 4,78% Mol.-Gew. 1482: gef. C 51,24 H 6,53 Cl 4,93%, Mol.-Gew. durch Dampfdruckosmometrie 1324) vereinbar sind, des UV-Absorptionsspektrums in Feinsprit (λ_{max} 214 und 288 nm, $\log\varepsilon$ 4,12 bzw. 2,89) und des IR-Absorptionsspektrums wurde vermutet, dass das Avilamycin mit den Antibiotica Curamycin[3] oder Exfoliatin[4] identisch sein könnte. Ein direkter Vergleich durch Papierchromatographie und Dünnschichtchromatographie zeigte aber einen deutlichen Unterschied. Papierchromatographie mit Formamid als stationärer und Chloroform-Benzol 7:3 als mobiler Phase, Rf-Werte: Avilamycin 0,70, Curamycin 0,60, Exfoliatin 0,58; bei der bioautographischen Entwicklung mit *Bacillus*

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