When the equilibrium decomposition pressure is sufficiently close to the saturation pressure, so that adsorption is considerable, equilibrium may be facilitated among solid phases. However, when the dissociation pressure of water is very small compared to that of the saturated solution, the attainment of macroscopic equilibrium may be excessively slow, and a rather definite metastable equilibrium can exist as a consequence.

When very fine particles are themselves nonvolatile, and lack a reconstituting mechanism, such as some equilibrium volatile compound which can transport material from them, they can only be expected to give equilibrium results consistent with their own free energy. At sufficiently high temperatures, sintering will produce macroscopic properties but the $Mg(OH)_2$ dissociation pressure would reach considerable values at temperatures below those required to sinter the MgO produced. We conclude that many measurements on systems involving equilibrium between gases and dry solid phases should be accepted with considerable caution in correlating thermodynamic data.

Summary

It is shown that the true dissociation pressure in the reaction $Mg(OH)_2(cry.) = MgO(cry.) + H_2O(g)$, as determined from the third law of thermodynamics, is some 130% higher than accurately measured values which were reproducible to 0.1%.

The above result is attributed to the colloidal nature of the magnesium oxide produced under equilibrium conditions.

Giauque and Archibald have shown previously that the third law gives accurate agreement with the measured equilibrium pressures, when the entropy and heat content are measured on the actual finely divided magnesium oxide in equilibrium. Thus the colloidal particles approached essentially zero entropy at very low temperatures and evidently approximated a perfect crystalline structure.

For the finely divided material obtained during equilibrium dissociation, MgO(cry.) = MgO (finely divided); $\Delta H_{25} = 888$ cal. mole.$^{-1}$

It is concluded that neither reproducibility of equilibrium measurements based on approach from each side nor agreement with the third law of thermodynamics, can be accepted as proof that an equilibrium corresponds to the thermodynamic properties of macrocrystalline phases.

It seems impossible to escape the conclusion that many equilibrium measurements involving gases and finely divided dry solid phases, produced by the evolution of gases, or formed by reaction with gases, do not correspond to the properties of macroscopic materials.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Infrared Spectrum of Dimethylcadmium

BY H. S. GUTOWSKY[1]

In a previous publication,[2] the infrared and Raman spectra of dimethylmercury and dimethylzinc were presented and interpreted as supporting a linear C–M–C structure of D_{3h}' symmetry, with essentially free internal rotation of the methyl groups. Similar data for dimethylcadmium are of interest in verifying this interpretation and in providing force constants which, with those for mercury and zinc, afford a basis for relating molecular properties to atomic parameters of the Group IIb metals.

Experimental

Preparation of Sample.—Attempts to produce dimethylcadmium by heating dimethylmercury with cadmium metal were unsuccessful. The sample used was prepared by Mr. A. R. Bader, under the direction of Professor E. G. Rochow, from cadmium iodide and methylmagnesium bromide in ether solution. Their coöperation in furnishing the sample is gratefully acknowledged. It was purified by bulb to bulb distillation in a vacuum system until it was infrared spectroscopically free from ether.

Infrared Spectrum.—The region from 430 to 650 cm.$^{-1}$ was observed with a KRS-5 prism in conjunction with a lithium fluoride mirror using the Harvard spectrometer.[3] The gaseous sample of dimethylcadmium was at its room temperature vapor pressure of 3.6 cm., in a 30-cm. cell with potassium bromide windows. The region from 625 to 5000 cm.$^{-1}$ was run at the same pressure in a 5-cm. sodium chloride cell on a Baird Associates spectrometer. The observed spectrum is summarized in Table I. Its general appearance is similar to that of dimethylzinc,[2] with the exception that the structure of the bands at 1140 and 1305 cm.$^{-1}$ in dimethylcadmium is not nearly as distinct as the corresponding bands in dimethyl zinc.

Frequency Assignment

A generally satisfactory frequency assignment has been made, using D_{3h}' symmetry. The Raman data of Fehér, Kolb and Leverenz[4] are in-

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[2] H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

[3] For a detailed listing of pertinent literature and the general methods used in this investigation see ref. (2).

[4] F. Fehér, W. Kolb and L. Leverenz, *Z. Naturforsch.*, **2a**, 454 (1947).

TABLE I

INFRARED AND RAMAN SPECTRA OF DIMETHYLCADMIUM AND THE ASSIGNMENT OF VIBRATIONAL FREQUENCIES[a]

Infrared (g), ν cm.$^{-1}$	Raman[4] (l), Δν cm.$^{-1}$	Assignment	Species for combinations	Calcd. freq. of combinations, ν cm.$^{-1}$
	150 $(^1/_2?)$	ν_{11}		
	$\begin{matrix}464\\468\end{matrix}\left(\left.\begin{matrix}\text{20b}\\\text{2?}\end{matrix}\right\}0.29\right)$	ν_3		
	520 $(^1/_2$ b)	? (ν_7)		
538 (8)		ν_7		
	642 (3sb, 0.77)	ν_{14}		
705 (10)		ν_{10}		
	934 (00)	$2\nu_3$	A_1'	930
	1129 (8sb, 0.32)	ν_2		
1140 (5)		ν_6		
1305 (6)		$\nu_2 + \nu_{11}$; $2\nu_{14}$	E'; $A_1' + A_2' + E'$	1279, 1284
1325 (4)		$\nu_3 + \nu_{10} + \nu_{11}$	$A_1' + A_2' + E'$	1320
1350 (2)		$\nu_{10} + \nu_{14}$	$A_1'' + A_2'' + E''$	1347
	1384 (00b)	ν_{13}		
1435 (1)	1448 (00)	ν_9		
1620 (1)		$\nu_3 + \nu_6$	A_2''	1605
	2103 $(^1/_2)$	$\nu_{10} + \nu_{13}$	$A_1'' + A_2'' + E''$	2089
2230 (2)	2218 $(^1/_2)$	$\nu_{10} + \nu_{11} + \nu_{13}$	$A_1'' + A_2'' + 3E''$	2239
	2658 (00)	$\nu_2 + \nu_{11} + \nu_{13}$	$A_1' + A_2' + E'$	2663
	2691 (00)	$\nu_7 + \nu_9 + \nu_{10}$	$A_1'' + A_2'' + E''$	2684
2840 (6)		$\nu_9 + \nu_{13}$	$A_1'' + A_2'' + E''$	2832
(2895)	2876 (3)	ν_8		
2900 (9)		ν_8; P branch ν_5		
	2904 (4, pol.)	ν_1		
(2920)		ν_5		
2940 (7)		R branch ν_5		
	2963 $(^1/_2)$	ν_{12}		
3530 (0)		$\nu_8 + \nu_{14}$	$A_1'' + A_2'' + E''$	3517

[a] The numbers after the band frequencies are relative apparent intensities. The appearance and polarization are indicated for the Raman lines by the letters s (scharf), b (breit) and a second set of numbers.

cluded in Table I as well as the infrared observations and the details of the frequency assignment. The infrared band intensities listed are merely relative values. The numerals in parentheses after the Raman line frequencies are intensity and polarization, respectively. The assignment of fundamental frequencies is summarized in Table II.

The Raman active A_1' fundamental frequencies are readily assigned as the three strongest lines which are polarized. The infrared active A_2'' fundamentals ν_6 and ν_7 are obtained by comparison with the corresponding A_1' frequencies. The E'' Raman active fundamentals are selected from the remaining unassigned lines. 2963 cm.$^{-1}$ is assigned as ν_{12} since it does not overlap the C–H stretching frequencies in the infrared spectrum. In the CH_3 deformation region the Raman line at 1448 cm.$^{-1}$ coincides with the infrared band at 1435 cm.$^{-1}$ so they are assigned as ν_9, which leaves the 1384 cm.$^{-1}$ line as ν_{13}. ν_{14} is taken to be the Raman line at 642 cm.$^{-1}$ as this value is intermediate between the corresponding values for dimethylmercury and dimethyl zinc. Moreover, there are no other unassigned lines in the expected frequency range. The polarization value of 0.77 given for this line is sufficiently close to the depolarized value that this assignment is not precluded. The E' fundamentals are both infrared and Raman active and ν_8 is assigned as the coincidence in frequencies at about 2885 cm.$^{-1}$. The intense infrared band at 705 cm.$^{-1}$ is undoubtedly ν_{10}, and the only observed frequency low enough to be the C–Cd–C bending frequency, ν_{11}, is the doubtful 150 cm.$^{-1}$ line reported by Kolb and Leverenz.[4]

The remaining bands are interpretable as combinations or overtones with the exception of the weak Raman line at 520 cm.$^{-1}$. Assuming this line to be real, it might be the asymmetric skeletal stretching frequency, ν_7, the selection rule prohibiting its appearance in the Raman spectrum being relaxed by Coriolis interaction with the skeletal bending ν_{11}. The relatively high intensity of the infrared bands at 1305 and 1325 cm.$^{-1}$ is a bit surprising for combinations but their assignment as fundamental frequencies is not supported by any other considerations.

Normal Coördinate Analysis and Force Constants

Valence-type force constants have been determined from the above frequency assignment following the symmetry coördinate methods of Wilson[5] and using the *G* and diagonal *F* matrices

[5] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1949); **9**, 76 (1941).

TABLE II

FUNDAMENTAL FREQUENCIES AND FORCE CONSTANTS OF DIMETHYLCADMIUM

	D_{3h}'		Obs.	Comp.	% Dev.	F_{ii}
A_1'	C–H stretching	ν_1	2904 cm.$^{-1}$	2882 cm.$^{-1}$	−0.76	4.79×10^5
	CH_3 bending	ν_2	1129	1131	[a]	0.36×10^{-11}
	C–Cd–C R, P stretching	ν_3	465	470	+1.06	2.05×10^5
A_1''	Torsion	ν_4	..	..	....	....
A_2''	C–H stretching	ν_5	(2920)	2886	−1.15	4.79×10^5
	CH_3 deformation	ν_6	1140	1140	[a]	0.375×10^{-11}
IR, ∥	C–Cd–C stretching	ν_7	538	535	[a]	2.05×10^5
E′	C–H stretching	ν_8	2885	2922	+1.29	4.55×10^5
R	CH_3 deformation	ν_9	1441	1441	[a]	0.549×10^{-11}
IR, ⊥	CH_3 rocking	ν_{10}	705	705	[a]	0.334×10^{-11}
	C–Cd–C bending	ν_{11}	150	150	[a]	0.368×10^{-11}
E″	C–H stretching	ν_{12}	2963	2921	−1.42	4.55×10^5
	CH_3 deformation	ν_{13}	1384	1384	[a]	0.505×10^{-11}
R	CH_3 rocking	ν_{14}	642	642	[a]	0.277×10^{-11}

[a] Used in computing force constants.

FORCE CONSTANTS DERIVED FROM F_{ii}

f_r	4.63×10^5 dynes/cm.	$d^2f_{\alpha\alpha}$	$0.003 + 10^{-11}$ dyne cm./radian
f_{rr}	0.08	$d^2f_{\beta\beta}$	− .036
f_η	2.05	$d^2(f_{\alpha\alpha_2} + f_{\beta\beta_2})$	.029
d^2f_α	0.530×10^{-11} dyne cm./radian	$d^2(f_{\alpha\alpha_2} - f_{\alpha\alpha'_2})$	.022
d^2f_β	0.270	$d^2(f_{\beta\beta_2} - f_{\beta\beta'_2})$	.029
D^2f_γ	0.368		

given previously[2] for a linear CH_3–M–CH_3 molecule. These force constants, as given in Table II, are in terms of the internal coördinates α, β, γ, r and η which are defined as small displacements in the H–C–H, H–C–Cd, C–Cd–C bond angles and the C–H, C–Cd bond lengths, respectively. In the computations, tetrahedral angles were assumed for the methyl groups and 1.10 Å. was adopted as the C–H bond distance, *d*. No measurement of the C–Cd bond distance, *D*, appears to be available, so a value estimated from the covalent radii to be 2.15 Å. was used.

The F_{ii} values in Table II are the numerical values used in the diagonal *F* matrices for the various factors in computing the frequency of the corresponding vibration. No attempt was made to introduce off-diagonal terms in the *F* matrix. The values of the force constants given in terms of the internal coördinates are derived from F_{ii} using the relations previously reported[2]; the numerical values for the C–H stretching, f_r and f_{rr}, and the H–C–H angle distortion, d^2f_α, are also adopted from the previous work.

Discussion

Configuration and Internal Rotation.—On the basis of the evidence reported herein for dimethyl cadmium and the earlier data[2] for dimethylmercury and dimethylzinc, it appears that the dimethyl compounds of the group IIb metals have a linear C–M–C skeleton. Moreover, there are sufficient coincidences between the infrared and Raman frequencies assigned as E′ fundamentals to confirm the nonexistence of the staggered orientation of the methyl groups; such a D_{3d} configuration would have a center of symmetry and the fundamentals could be active only in either the infrared *or* Raman spectrum. The simplest interpretation of all the spectral data is in terms of either an eclipsed D_{3h} orientation of the methyl groups or a D_{3h}' model in which the methyl groups are free to rotate internally about the C–M bonds. Inasmuch as the staggered configuration is generally considered[6,7] to be the stable form when there is hindrance to internal rotation, it appears that a more or less free internal rotation exists in these dimethyl compounds. The application of an empirical inverse fifth power law[6] to the potential restricting the internal rotation suggests the barrier to such rotation is of the order of 15 cal./mole. The theoretical calculations of Lassettre and Dean[7] give a value of 31 cal./mole for the barrier to internal rotation in dimethyl acetylene; this indicates the possibility of a somewhat higher barrier in the metal alkyls than the 15 cal./mole from the empirical calculation. In any event, the spectral results are in general accord with the calculated barriers; both suggest that hindrance to internal rotation in these compounds is slight at most.

Force Constants and Electronegativities of the Group IIb Metals.—In Table III there are summarized the force constants directly related to the C–M bonds in the Group IIb dimethyl alkyls. A number of more or less empirical expressions have been proposed, relating bond stretching force constants, bond lengths, position in the periodic table, type of compound, and similar parameters. In this connection, it is of some

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(6) J. G. Aston, S. Iserow, G. J. Szasz and R. M. Kennedy, *J. Chem. Phys.*, **12**, 336 (1944).

(7) E. N. Lassettre and L. B. Dean, Jr., *ibid.*, **17**, 317 (1949).

TABLE III

C-M FORCE CONSTANTS FOR THE GROUP IIb DIMETHYL ALKYLS

	$Zn(CH_3)_2$	$Cd(CH_3)_2$	$Hg(CH_3)_2$	
f_η	2.39×10^5	2.05×10^5	2.45×10^5	dynes/cm.
d^2f_β	0.274×10^{-11}	0.270×10^{-11}	0.359×10^{-11}	dyne cm/radian
D^2f_γ	0.276×10^{-11}	0.368×10^{-11}	0.457×10^{-11}	dyne cm/radian

interest to consider the recent extensive discussion by Gordy[8] who proposed the equation $k = aN(X_AX_B/d^2)^3/^4 + b$. k is the bond stretching force constant in 10^5 dynes/cm.; a and b are empirical constants with the values 1.67 and 0.30 for stable molecules in their normal covalent state; N is the bond order; X_A and X_B are the electronegativities of the bonded atoms; and d is the bond length in angstroms. Electronegativities are given in Table IV for zinc, cadmium and mercury, computed with this equation using the f_η force constants in Table II and also the force constants of the dihalides from their Raman spectra in solution.[9,10] Included for comparison are the electronegativities proposed by Gordy[8] from the force constants in the diatomic hydrides and also values suggested by Haissinsky[11] from thermal data. While some of the differences between the computed electronegativities may result from the approximation of several of the bond lengths, the differences between the values from the alkyls and those from the halides and hydrides are too large not to be real.

TABLE IV

ELECTRONEGATIVITIES OF ZINC, CADMIUM AND MERCURY COMPUTED FROM THE BOND STRETCHING FORCE CONSTANTS IN THE DIMETHYL ALKYLS AND THE DIHALIDES

A/B	Zn		Cd		Hg		
	d^a_{Zn-A}	X_{Zn}	d^a_{Cd-A}	X_{Cd}	d_{Hg-A}	X_{Hg}	$X_Å$
C,Å	2.05	2.22	2.15	1.93	[b]2.20	2.66	2.55
Cl	2.13	1.14	2.23	0.72	[c]2.28	2.24	2.97
Br	2.23	1.08	2.33	0.89	[c]2.38	2.13	2.75
I	2.40	..	2.50	0.91	[c]2.55	1.73	2.45
Gordy[8]		1.2		1.1		1.0	
Haissinsky[11]		1.5		1.5		1.9	

[a] Bond lengths are estimated from convalent radii by comparison with the corresponding compounds of mercury. [b] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, 58, 2036 (1936). [c] H. Braune and S. Knoke, *Z. physik. Chem.*, B23, 163 (1933).

Part of the disagreement may lie in the bond order. For the alkyls, hyperconjugation of the methyl groups could increase the bond order from 1.0 to perhaps as high as 1.2. This is still inadequate to bring the corresponding electronegativities into agreement with the values from the halides and hydrides. The thermal electronegativities of Haissinsky[11] differ from the alkyl values by a fairly narrow range, from 0.43 to 0.76 indicating the force constants could be fitted fairly well by Gordy's equation, with a different value of *b* or else a bond order of about 1.4. However, it is particularly difficult to reconcile the very wide scatter of electronegativity values for mercury without introducing an excessive number of new empirical constants.

Summary

1. The infrared spectrum of dimethylcadmium is reported and a frequency assignment proposed. Valence-type force constants are computed from a normal coördinate analysis. The results support a linear C–Cd–C structure of D_{3h}' symmetry with free internal rotation of the methyl groups, consistent with similar conclusions made previously for dimethylzinc and dimethylmercury.

2. A comparison of electronegativity values computed from the bond stretching force constants in the dimethyl alkyls and dihalides of the Group IIb metals, using an empirical relation proposed by Gordy, suggests the difficulty of applying the relation to additional types of compounds.

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[8] W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946). Citations of earlier work are given in this reference.

[9] S. Venkateswaran, *Proc. Ind. Acad. Sci.*, **1**, 851 (1935).

[10] K. W. F. Kohlrausch, "Ramanspectren," Edwards Brothers, Inc., Ann Arbor, Michigan, 1945, p. 75.

[11] M. Haissinsky, *J. phys. radium.*, **7**, 7 (1946).