

## Extension of Fowler's Treatment of Surface Tension to Physical Adsorption

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The change was reflected in the decrease of current being fed to the system. The portion of the discharge tube just above the electrode was much more sensitive to external radiation than any other portion of the tube. For optimum voltage setting the discharge could be totally inhibited by the external radiation and appeared as soon as the radiation was removed.

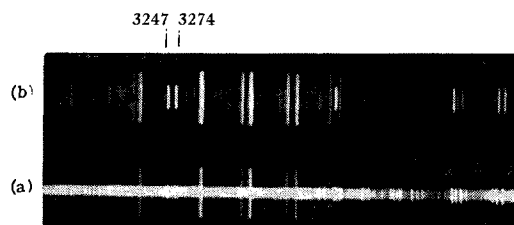


FIG. 1.

Plates (a) and (b) shows the spectra of the discharge with and without external radiation, for equal exposures. The decrease in intensity on irradiation is clearly noticeable. The superposed spectrum is of copper arc. The incandescent lamp itself gave a continuous spectrum.

\* This work was done at the Physical Laboratory, Council of Scientific and Industrial Research, Delhi, India.

### Ultrasonic Velocities of Sound in Some Liquid Metals\*

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May 31, 1949*

THE electronic pulse-circuit technique provides a new and valuable tool for the study of the elastic properties of solids and liquids. The application of this method for investigation of liquids at room temperature is well known.<sup>1</sup> The author has used this same technique for the study of metallic liquids up to 300–350°C under atmospheric pressure. So far, data have been obtained for the more readily available low melting metals—such as sodium, potassium, indium, and tin. Investigations of other low melting liquid metals (cadmium, bismuth, etc.), as well as of certain liquid metallic mixtures, are in progress.

Due to pulse distortions and loss of signal strength (attenuation and/or surface barriers) the precision of the velocity measurements is not better than  $\pm 1$  percent. However, in view of the absence of data for the elastic properties of the liquid metals in question, the results obtained should still prove valuable. More unfortunate is the fact that this uncertainty makes an accurate determination of temperature coefficients impossible. Such coefficients are given below with due reservation.

In Table I are given the results obtained for the ultrasonic velocities,  $u$ , in the mentioned liquid metals at their melting points. Data obtained for mercury at 50° and 150°C are given for comparison.

TABLE I. Sound velocities and temperature coefficients.

Metal	$t^\circ\text{C}$	$u$ (m/sec.)	$du/dt$ (m/sec. deg., approx.)
Na	98	$2395 \pm 25$	-0.3
K	64	$1820 \pm 20$	-0.5
In	156	$2215 \pm 20$	-0.5
Sn	232	$2270 \pm 20$	-0.7
Hg	50	$1440 \pm 10$	-0.7
Hg	150	$1370 \pm 10$	

TABLE II.

Metal	$T^\circ\text{K}$	$\rho$ (g/cm <sup>3</sup> )	$\alpha \times 10^{-4}$	$C_p$	$k_S \times 10^6$ (bar <sup>-1</sup> )	$C_p/C_v$	$k_T \times 10^6$ (bar <sup>-1</sup> )
Na	371	0.930	2.8	7.5	$18.7 \pm 0.4$	1.12	21.0
K	337	0.835	2.9	7.7	$36.2 \pm 0.8$	1.11	40.3
In	429	7.0	1.2	7.0	$2.9 \pm 0.1$	1.12	3.2
Sn	505	6.99	1.0	6.6	$2.79 \pm 0.05$	1.11	3.1
Hg	323	13.47	1.82	6.6	$3.58 \pm 0.05$	1.16	4.1
Hg	423	13.23	1.82	6.6	$4.03 \pm 0.05$	1.19	4.8

From these data the adiabatic and isothermal compressibilities  $k_S$  and  $k_T$  at the same temperatures have been calculated and are given in Table II. Data for the densities,  $\rho$ , coefficients of thermal expansion,  $\alpha$ , and specific heats,  $C_p$ , have been taken from Landolt-Börnstein and International Critical Tables. In the absence of data for the density and coefficient of thermal expansion for liquid indium, these have been estimated to be 7.0 g/cm<sup>3</sup> and  $1.2 \times 10^{-4}$  deg.<sup>-1</sup>, respectively.

Mercury is the only metal for which previous data exist under similar temperature conditions. Carnazzi<sup>2</sup> gives for mercury  $k_T = 3.9 \times 10^{-6}$  atmos.<sup>-1</sup> at 52.8°C and  $4.4 \times 10^{-6}$  at 150.3°C. In view of the discrepancy between Carnazzi's values and the results of more recent investigations at room temperature (Carnazzi:  $k_T = 3.8 \times 10^{-6}$ , while the accepted value is  $4.0 \times 10^{-6}$  atmos.<sup>-1</sup>), the disagreement with the present investigation should not be disturbing. An interesting feature of the data above is the constant value of  $C_p/C_v$  at the melting points of the four metals, Na, K, In, Sn. Even if due allowance is made for the uncertainties associated with the accepted values for densities, expansion coefficients, and specific heats, this agreement is remarkable, and may have theoretical significance.

I am indebted to Dr. David Lazarus for invaluable technical help.

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<sup>1</sup> J. R. Peilam and J. K. Galt, *J. Chem. Phys.* **14**, 608 (1946).

### Extension of Fowler's Treatment of Surface Tension to Physical Adsorption

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May 5, 1949*

THE free volume model of a liquid can be applied to a liquid-like adsorbate<sup>1</sup> (of, say, three or more layers). We give here an analogous extension of Fowler's<sup>2</sup> treatment of surface tension. We are investigating both of these approximate approaches to this problem in more detail.

Consider a plane slab of liquid of area  $\mathcal{A}$ , thickness  $h$ , and density  $\rho$  ( $\rho = N/V$ ). In the present approximation we assume that  $\rho$  and the usual molecular distribution function  $g(r)$  are the same in the slab as in the bulk liquid. Let  $A$  be the Helmholtz free energy of the slab in its equilibrium position in the presence of adsorbent. Let  $A_0$  refer to the slab in the bulk liquid.  $A - A_0$  is then the reversible isothermal work  $W$  done on the system in (1) breaking a column of liquid of area  $\mathcal{A}$  at  $z=0$  and removing the part  $z < 0$  ( $W_1$ ), (2) breaking the remaining liquid at  $z=h$  and removing the part  $z > h$  ( $W_2$ ), (3) bringing the slab  $0 < z < h$  up to its equilibrium position next to the adsorbent ( $W_3$ ), and (4) rejoining the parts  $z < 0$  and  $z > h$  ( $W_4$ ). Since  $W_1 + W_4 = 0$ ,  $A - A_0 = W_2 + W_3$ . The adsorption isotherm is then

$$kT \ln p/p_0 = \partial(W_2 + W_3)/\partial N. \quad (1)$$

Let  $u(r)$  be the interaction energy between two liquid molecules, and  $F(r) = -du(r)dr$ . Then, on making straightforward modifica-

tions of Fowler's argument, one finds

$$-W_2 = \pi \rho^2 \bar{\alpha} \left( \frac{1}{2} \int_0^h r^4 g(r) F(r) dr + \frac{2h}{3} \int_h^\infty r^3 g(r) F(r) dr - \frac{h^2}{2} \int_h^\infty r^2 g(r) F(r) dr + \frac{h^4}{12} \int_h^\infty g(r) F(r) dr \right), \quad (2)$$

and

$$\partial(-W_2)/\partial h = \pi \rho^2 \bar{\alpha} \left( \frac{2}{3} \int_h^\infty r^3 g(r) F(r) dr - h \int_h^\infty r^2 g(r) F(r) dr + \frac{h^3}{3} \int_h^\infty g(r) F(r) dr \right). \quad (3)$$

The type of detailed computation of  $W_3$  used will depend on the nature of the adsorbent. For simplicity, we confine ourselves here to the following very approximate treatment: assume the adsorbent is structureless and that it does not perturb  $g(r)$ . Let the interaction energy between an adsorbent molecule and a liquid molecule be

$$u_1 = \epsilon_1(r_1/r)^{12} - 2\epsilon_1(r_1/r)^6. \quad (4)$$

Then the interaction energy between the entire adsorbent (density  $\rho_1$ ) and a liquid molecule at a distance  $z$  from the plane adsorbent surface is<sup>8</sup>

$$\begin{aligned} \phi &= (\alpha/z)^9 - (\beta/z^3) \\ \alpha &= \epsilon_1 r_1^{12} \pi \rho_1 / 45 \\ \beta &= \epsilon_1 r_1^6 \pi \rho_1 / 3, \end{aligned} \quad (5)$$

and the force is  $-d\phi/dz$ . On integration, one finds the total interaction energy  $\Phi$  between the liquid slab and the adsorbent (nearest edge of slab at distance  $z$  from adsorbent), and the corresponding total force  $f$ . Setting  $d\Phi/dz=0$  gives the equilibrium value of  $z$ ,  $z_0(h)$ :

$$\alpha[(z_0+h)^{-9} - z_0^{-9}] = \beta[(z_0+h)^{-3} - z_0^{-3}]. \quad (6)$$

Then

$$W_3 = \int_{z_0}^\infty f dz = \bar{\alpha} \rho \{ (\alpha/8)[z_0^{-8} - (z_0+h)^{-8}] - (\beta/2)[z_0^{-2} - (z_0+h)^{-2}] \}, \quad (7)$$

and

$$dW_3/dh = \bar{\alpha} \rho [\alpha(z_0+h)^{-9} - \beta(z_0+h)^{-3}]. \quad (8)$$

Substitution of Eqs. (3) and (8) into Eq. (1), using  $N = \bar{\alpha} \rho h$ , gives the adsorption isotherm. If we use

$$u(r) = \epsilon(r^*/r)^{12} - 2\epsilon(r^*/r)^6 \quad (9)$$

the isotherm reduces, for large  $\Gamma = N/\bar{\alpha}$ , to

$$\ln p/p_0 = (\delta - \delta_1)/\Gamma^3, \quad (10)$$

$$\delta = \pi \rho^4 \epsilon r^{*6} / 3kT, \quad (11)$$

$$\delta_1 = \pi \rho^3 \rho_1 \epsilon_1 r_1^6 / 3kT. \quad (12)$$

Equation (10) is identical with Eq. (9) of reference 1, so we shall not discuss it further here.

<sup>1</sup> T. L. Hill, J. Chem. Phys. **17**, 590 (1949).  
<sup>2</sup> R. H. Fowler, Proc. Roy. Soc. **A159**, 229 (1937). See also J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **17**, 338 (1949).  
<sup>3</sup> T. L. Hill, J. Chem. Phys. **16**, 181 (1948).

## Raman and Infra-Red Spectra of Oxalyl Chloride

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THE infra-red spectrum in the region 400-10000  $\text{cm}^{-1}$  and the displacements, semiquantitative relative intensities, and depolarization factors of the Raman lines have been obtained

TABLE I. Raman and infra-red spectral data for liquid oxalyl chloride (CIOC-COCl).\*

$\Delta\nu$	Raman		Infra-red	
	$I$	$\rho$	$\nu$	$I_s$
193	5	0.88		
261	33	(0.96)		
279				
354				
443	21	0.51		
465	28	0.48		
483	30	0.50	488	S
522	7	P		
533	12	P	532	S
			594	S
620	100	0.17		
709	1	—		
802	VW	—	752	VVS**
			942	S
			1058	VVS
1081	5	0.32	1310	VS
			1388	S
1416	VW	—	1754	VVS
1781	57	0.79	1826	VVS
			2510	S
			2830	VS
			3740	VS
			5140	W

\*  $\Delta\nu$  is the Raman displacement in  $\text{cm}^{-1}$ ,  $I$  is the relative intensity on the basis of 100 for the strongest Raman line,  $\rho$  is the depolarization factor,  $\nu$  is the wave number corresponding to the maximum absorption in the infra-red band,  $I_s$  is the estimated intensity of the infra-red bands (VVS = very, very strong; VS = very strong; S = strong; W = weak; VW = very weak); data in regard to which there is some uncertainty are enclosed in parentheses; and P indicates lines for which quantitative values of  $\rho$  could not be determined but which appear to be polarized.

\*\* Middle of a very broad band.

for liquid oxalyl chloride (CIOC-COCl) at room temperature. The depolarization factors were obtained by a previously described method<sup>1</sup> and the relative intensities were obtained with the aid of a Gaertner microdensitometer.<sup>2</sup> The infra-red absorption data were secured from records obtained with a Beckman IR-2 spectrophotometer with KBr optics. With a few exceptions, the present Raman data are in reasonably good agreement with the previous Raman data. So far as the authors have been able to determine, no previous infra-red data have been reported. The results are given in Table I.

An examination of the Raman and infra-red data indicates that there are only two coincident frequencies. Since in view of the large number of frequencies these two could well be chance coincidences, the rule of mutual exclusion may apply. If this is the case, the oxalyl chloride molecule has a center of symmetry and the structure would be that corresponding to the *trans*- or  $C_{2h}$  form. The values obtained for the depolarization factors and the absence of a second line near 1781  $\text{cm}^{-1}$  in the Raman spectrum represents additional evidence for the *trans*-form. This evidence is in partial agreement with the conclusion reached by Martin and Partington<sup>3</sup> on the basis of dipole moment and molar refractivity measurements, namely, that the small dipole moment of 0.92 Debye unit could be explained by either free rotation or oscillation about the stable *trans*-position.

A normal coordinate treatment (FG matrix method) is being carried out for the *trans*- model in order to determine whether a satisfactory assignment of the observed frequencies can be made on the basis of this model. Further experimental details and the results of the normal coordinate treatment will be reported later.

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<sup>1</sup> Forrest F. Cleveland, J. Chem. Phys. **13**, 101 (1945).

<sup>2</sup> Forrest F. Cleveland, J. Chem. Phys. **11**, 1, 227 (1943).

<sup>3</sup> G. T. O. Martin and J. K. Partington, J. Chem. Soc. 1178 (1936).