

Decrease of an Electrical Discharge by External Radiation

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band was observed in the region from 1300 to 1000 cm^{-1} with pronounced Q branches at 1176, 1138, and 1099 cm^{-1} , the intensity alternation in this region being very marked. Another weak perpendicular type band was observed in the region from 800 to 650 cm^{-1} with a pronounced intensity alternation but a spacing of only 15 cm^{-1} . A very strong and complex absorption was observed in the region from 650 to 400 cm^{-1} with no apparent regular spacing. This absorption is presumably due to the two skeletal bending vibrations highly perturbed by Coriolis interaction.⁷ A more detailed interpretation of the spectrum will be published shortly but sufficient evidence has been presented above to establish conclusively the straight chain structure for the diazomethane molecule.

It is interesting to record that when the absorption spectrum was investigated in a metal cell with KBr windows a change in spectrum was observed on standing. The diazomethane bands disappeared completely during the course of 24 hours and new bands appeared which remained unchanged for several days. Some of these bands were identified as being caused by ethylene, but others could not be explained in this way. In particular two bands were observed at 1180 and 1102 cm^{-1} with well defined PQR structures and PR spacings of approximately 24 cm^{-1} . This spacing is altogether too small for bands of the cyclic monomer but is consistent with the spacing to be expected for the "parallel" bands of the hexacyclic dimer. No change in spectrum was observed, however, when diazomethane was investigated in a glass cell with KBr windows.

The author wishes to express his thanks to Mr. L. C. Leitch for assistance in the preparation of the diazomethane; to Dr. G. Herzberg for valuable discussion and to Dr. R. N. Jones for the use of the spectrometer.

* Published as Contribution No. 1936 from the National Research Laboratories, Ottawa, Canada.

¹ See N. V. Sidgwick, *The Organic Chemistry of Nitrogen* (Oxford University Press, New York, 1937), pp. 360-362.

² F. W. Kirkbride and R. G. W. Norrish, *J. Chem. Soc.* 119, (1933).

³ H. Boersch, *Monats. F. Chem.* 65, 331 (1935).

⁴ Sidgwick, Sutton, and Thomas, *J. Chem. Soc.* 406, (1933).

⁵ F. Halverson and V. Z. Williams, *J. Chem. Phys.* 15, 552 (1947); W. R. Harp, Jr., and R. S. Rasmussen, *J. Chem. Phys.* 15, 778 (1947).

⁶ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company Inc., New York, 1945), pp. 479-482.

⁷ Cf. formaldehyde, E. S. Ebers and H. H. Nielsen, *J. Chem. Phys.* 5, 822 (1937).

hydrogen, 0.955; oxygen, 1.02; carbon dioxide, 1.16; stoichiometric methane-air, 1.10. Hence, the energy flow by diffusion in a plane flame may equal or even exceed that caused by thermal conduction, thus yielding zero or negative excess energy; an elementary analysis reveals that the same considerations apply to a spherical flame.

Lewis and von Elbe compare experimental quenching distances with minimum flame radii calculated by their theory from minimum spark energies for ten gas mixtures, obtaining a correlation with 21 percent average deviation and 54 percent maximum deviation. However, this relationship can be treated without recourse to the concept of excess energy, simply by assuming the minimum ignition energy to be proportional to the surface area of the minimum flame sphere, independently of mixture composition and pressure. Minimum flame radii may be correlated with minimum ignition energies in this manner for the above ten mixtures, with 14 percent average deviation and 31 percent maximum deviation. The assumption of invariance with pressure is suggested by consideration of Fig. 3 in an earlier paper⁴ by the above authors, which shows minimum ignition energy to be very nearly proportional to the square of quenching distance, and hence to minimum flame surface, over a fivefold pressure range for stoichiometric methane-air mixtures. Lewis and von Elbe's theory does predict the correct order of magnitude for minimum flame radii, but this may be fortuitous.

It is interesting to note that a thermal theory of ignition, such as that suggested by Taylor-Jones, Morgan, and Wheeler⁵ and Coward and Meiter⁶ would yield the minimum energy to be proportional to the cube rather than the square of the minimum flame radius, as is actually observed. If the thermal theory were modified to include chemical energy liberated in the pre-ignition period, better correlation between theory and experiment might be obtained. However, such a treatment still would be open to the criticism that diffusion is not taken into consideration.

¹ B. Lewis and G. von Elbe, *J. Chem. Phys.* 15, 803-808 (1947).

² W. Jost and L. von Muffling, *Zeits. f. physik. Chemie* A181, 208 (1938).

³ N. N. Semenov, *Prog. Phys. Sci. (USSR)* 24, 433-486 (1940) (available as NACA T.M. 1026, September, 1942).

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⁵ E. Taylor-Jones, J. D. Morgan, and R. V. Wheeler, *Phil. Mag.* 43, 359 (1922).

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Spark Ignition of Gas Mixtures

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May 12, 1949

LEWIS and von Elbe¹ have presented a theory of spark ignition based upon the concept of excess energy in a flame front. The present writers wish to point out what appears to be a fundamental weakness in this theory, in that due consideration is not given to the process of diffusion. Lewis and von Elbe evaluate the excess energy integral by considering only thermal energy changes and chemical energy degradation by reaction, while ignoring energy transfer by diffusion.

It is apparent from work published by Jost and von Muffling² and by Semenov³ that energy transfer by interdiffusion of reactants and products is comparable in magnitude with heat conduction. Upon assuming that λ and the product $D\rho$ are independent of temperature, Semenov shows that, for a plane flame, the excess energy vanishes as the dimensionless ratio $D\rho C/\lambda$ approaches unity, where λ is thermal conductivity, D is the diffusion coefficient, ρ is density, and C is specific heat at constant pressure. The values of $D\rho C/\lambda$ at room temperature for some common gases are:

Decrease of an Electrical Discharge by External Radiation

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May 31, 1949

WE have observed the following curious effect.

An H-shaped discharge tube with aluminium electrodes and containing air was used and had side bulbs of P_2O_5 and crushed NaOH. It was run on a.c. and voltage adjusted so that discharge was in its initial stages and consisted of discontinuous bursts of excitation followed by quiescent periods. Light from an incandescent bulb was thrown as a spot of size 5-mm radius on the space just above one of the electrodes. The pressure of air in the discharge tube was 0.7 mm of mercury.

It was found that on external irradiation, the intensity of each burst of discharge as well as the frequency of bursts decreased.

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.

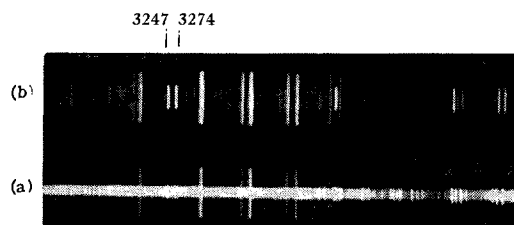


FIG. 1.

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.¹ 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 ± 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 ± 25	-0.3
K	64	1820 ± 20	-0.5
In	156	2215 ± 20	-0.5
Sn	232	2270 ± 20	-0.7
Hg	50	1440 ± 10	-0.7
Hg	150	1370 ± 10	

TABLE II.

Metal	$T^\circ\text{K}$	ρ (g/cm ³)	$\alpha \times 10^{-4}$	C_p	$k_S \times 10^6$ (bar ⁻¹)	C_p/C_v	$k_T \times 10^6$ (bar ⁻¹)
Na	371	0.930	2.8	7.5	18.7 ± 0.4	1.12	21.0
K	337	0.835	2.9	7.7	36.2 ± 0.8	1.11	40.3
In	429	7.0	1.2	7.0	2.9 ± 0.1	1.12	3.2
Sn	505	6.99	1.0	6.6	2.79 ± 0.05	1.11	3.1
Hg	323	13.47	1.82	6.6	3.58 ± 0.05	1.16	4.1
Hg	423	13.23	1.82	6.6	4.03 ± 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, ρ , coefficients of thermal expansion, α , 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/cm³ and 1.2×10^{-4} deg.⁻¹, respectively.

Mercury is the only metal for which previous data exist under similar temperature conditions. Carnazzi² gives for mercury $k_T = 3.9 \times 10^{-6}$ atmos.⁻¹ at 52.8°C and 4.4×10^{-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 4.0×10^{-6} atmos.⁻¹), 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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¹ 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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THE free volume model of a liquid can be applied to a liquid-like adsorbate¹ (of, say, three or more layers). We give here an analogous extension of Fowler's² 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 ρ ($\rho = N/V$). In the present approximation we assume that ρ 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-