

## On the Theory of Burning Velocities in Gas Mixtures

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### On Grüneisen's Constant for Metals

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June 14, 1949

GRÜNEISEN'S constant  $\gamma = \alpha V / \kappa C_v$  can also be found—as Slater has pointed out—from the compressibility  $\kappa$  and change of compressibility with volume  $d\kappa/dV$  by the relation<sup>1</sup>

$$\gamma = -1/6 + 1/2 \cdot d(\ln \kappa) / d(\ln V) = -1/6 + 1/2 \cdot V / \kappa \cdot d\kappa / dV. \quad (1)$$

The theory of metals as developed by Gombás<sup>2</sup> makes it possible to determine this important metallic constant in a purely theoretical way. According to this theory the energy per atom in metals can be written as a polynomial of fourth degree in  $1/R$

$$U = A_0 + A_1/R + A_2/R^2 + A_3/R^3 + A_4/R^4,$$

where  $R$  is the radius of the unit sphere containing one atom. The  $A_i$ -s are constants characteristic for the metal and independent of  $R$ . The values of these constants are determined by the theory without the use of any empirical parameter.

It is well known that the pressure can be calculated as  $P = -dU/dV = -1/4\pi R^2 \cdot dU/dR$ , by means of which we get

$$\kappa = -1/V \cdot dV/dP = 1/V \cdot 1/(d^2U/dV^2) = 12\pi R / (d^2U/dR^2 - 2/R \cdot dU/dR)$$

and

$$d\kappa/dV = -3/R^2 \cdot (Rd^3U/dR^3 - 3 \cdot d^2U/dR^2 + 4/R \cdot dU/dR) / (d^2U/dR^2 - 2/R \cdot dU/dR)^2.$$

When we use for  $V$ ,  $\kappa$  and  $d\kappa/dV$  their values at the equilibrium configuration  $R=R_0$  obtained theoretically from the equation

$$(dU/dR)_{R=R_0} = -(A_1R_0^3 + 2A_2R_0^2 + 3A_3R_0 + 4A_4)/R_0^5 = 0, \quad (2)$$

$\gamma$  is given by the following formula

$$\gamma = 1/3 - R_0/6 \cdot (d^3U/dR^3)_{R=R_0} / (d^2U/dR^2)_{R=R_0} = 1/3 + 1/2 \cdot (A_1R_0^3 + 4A_2R_0^2 + 10A_3R_0 + 20A_4) / (A_1R_0^3 + 3A_2R_0^2 + 6A_3R_0 + 10A_4).$$

TABLE I.

	Calculated from (3)	Calc. with exp. data by Grüneisen	Calc. with exp. data of Bridgman from (1)	Obtained semi-empirically by Slater***
Na	1.552	1.25	1.83*	1.58
K	1.560	1.34	2.55*	1.53
Rb	1.567	1.48		1.48
Cs	1.570	1.29		1.48
Mg	1.521		1.62*	2.15
Ca	1.529		1.28**	1.98
Sr	1.536		0.83**	
Ba	1.539		0.58**	

\* J. C. Slater. See reference 1, p. 451.

\*\* F. Birch, Phys. Rev. 71, 809 (1947).

\*\*\* J. C. Slater. See reference 1, p. 454.

Taking into account (2), finally we get

$$\gamma = 4/3 + 1/2 \cdot (A_3R_0 + 4A_4) / (A_2R_0^2 + 3A_3R_0 + 6A_4).$$

The results obtained from (3) together with values for  $\gamma$  calculated otherwise are summarized in Table I.

As the table shows, the theoretical values are in a good accordance with the results obtained from experimental data or semi-empirically, especially for the alkaline metals. The agreement for the alkaline-earth-metals is not as good as for the alkalis. This is because the fundamental assumptions of the theory of Gombás are less adapted for these metals than for the alkalis.

<sup>1</sup> For a full discussion of this relation see for instance J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 217 and 238.

<sup>2</sup> P. Gombás, *Nature* 157, 668 (1946); *Hungarica Acta Physica* Vol. I. fasc. 2, (1947); *Die statistische Theorie des Atoms und ihre Anwendungen* (Verlag Julius Springer, Berlin, 1948).

### On the Theory of Burning Velocities in Gas Mixtures

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July 11, 1949

**I**N a recent paper, Badin, Stuart, and Pease<sup>1</sup> have compared the burning velocity ratios measured and calculated by them, for the stoichiometric mixtures of butadiene-1,3 with normal air and with "helium air" (He—79 percent, O<sub>2</sub>—21 percent).

Some of their conclusions are: (1) that in the calculations, the somewhat greater diffusibility of the H-atoms in the helium air than in the normal air must be taken into account; (2) higher burning velocities at pressures below 1 atmos. are due to the increase of the diffusion coefficient of the H-atoms with decreasing pressure.

A different interpretation may be obtained by the use of the theory in which the flame is treated as a shock and combustion wave with a small pressure drop (Jouguet<sup>2</sup>). This pressure drop  $\Delta p$  is determined, not by the diffusion of the hydrogen atoms into the unburned gases, but by a more dynamic phenomenon: the projection of the H-atoms into the unburned gases.<sup>3</sup> According to that theory, the burning velocity is given by:

$$V = [\mu \cdot \Delta p / \rho_u \cdot (1 - \mu)]^{1/2}, \quad (1)$$

where  $\mu = \rho_b / \rho_u$  is the ratio of the specific masses of the burned ( $\rho_b$ ) and the unburned ( $\rho_u$ ) gases. Since  $\Delta p = T_u \cdot p_H / 2T_b$  ( $T_b$  and  $T_u$  being the temperatures of these gases, and  $p_H$  the partial pressure of the H-atoms in the burned gases) the substitution of N<sub>2</sub> by He in the mixture not only increases  $T_b$  and  $p_H$  but also decreases  $\rho_u$  ( $\mu/(1-\mu)$  varying slightly). The same may be said for the influence of the pressure  $p$ ,  $\rho_u$  decreasing with  $p$ . These statements are more precisely expressed by the results of calculations summarized in Tables I and II.<sup>4</sup> They are also substantiated by a

TABLE I. Burning velocities of stoichiometric mixtures of butadiene-1.3 with normal air and helium air.

Mixture	Total pressure with p atmos.	Flame temp. (calc.) <sup>a</sup> T °K	Partial pressure of H-atoms <sup>a</sup> p <sub>H</sub> atmos.	Specific mass of fresh gases $\rho_u$ Kg/m <sup>3</sup>	$\frac{\mu}{1-\mu}$	Pressure drop $\Delta p$ mm H <sub>2</sub> O	Burning velocity V cm/sec.
							Calc. Obs. <sup>a</sup>
Normal air	1 0.5	2 380° 2 350°	8.8 10 <sup>-4</sup> 5.7 10 <sup>-4</sup>	1.21 0.60	0.137 0.139	0.57 0.37	79 92
Helium air	1 0.5	2 660° 2 600°	4.3 10 <sup>-3</sup> 2.64 10 <sup>-3</sup>	0.47 0.23	0.117 0.120	2.48 1.56	246 282

<sup>a</sup> See reference 1.

TABLE II. Burning velocity ratios of butadiene-1,3 with normal air and helium air mixtures.

Total pressure	ratio: $r = (V)_H / (V)_A$			ratio: $(V)p = 1 / (V)p = 0.5$			
	Obs. <sup>a</sup>	Calc. <sup>a</sup>	Calc.	Mixture	Obs. <sup>a</sup>	Calc. <sup>a</sup>	Calc.
1 atmos.	3.3	3.2	3.1	n air	0.81	0.88	0.86
0.5	3.4	3.1	3.1	He air	0.80	0.90	0.87

<sup>a</sup> See reference 1.TABLE III. Burning velocity ratios of flames in CO-O<sub>2</sub>-He and CO-O<sub>2</sub>-A mixture with H<sub>2</sub>O (mole fraction: 0.0269).

Mole fraction of inert gas	[CO]/[O <sub>2</sub> ] = 0.503		Ratio: $r = (V)_H / (V)_A$							
	Obs. <sup>a</sup>	Calc. <sup>b</sup>	= 1.083		= 1.234		= 2.698			
	Obs. <sup>a</sup>	Calc. <sup>b</sup>	Obs. <sup>a</sup>	Calc. <sup>b</sup>	Obs. <sup>a</sup>	Calc. <sup>b</sup>	Obs. <sup>a</sup>	Calc. <sup>b</sup>	Obs. <sup>a</sup>	Calc. <sup>b</sup>
0.10	1.05	1.07	1.09	1.07	1.05	1.07	1.03	1.07		
0.15	1.09	1.12	1.12	1.10	1.09	1.10	1.06	1.10		
0.20	1.13	1.15	1.19	1.14	1.13	1.14	1.08	1.14		
0.25	—	—	1.25	1.18	1.16	1.18	—	—		

<sup>a</sup> See reference 4.<sup>b</sup> Formula (2).

study of the ratios of burning velocities in mixtures of CO-O<sub>2</sub>-H<sub>2</sub>O with helium or argon as investigated by Fiok and Roeder<sup>6</sup> by means of the soap bubble method. It is then found that (Table III)

$$r = \frac{V \text{ in mixture with He}}{V \text{ in mixture with A}} = \left[ \frac{\rho_u \text{ of the mixture with A}}{\rho_u \text{ of the mixture with He}} \right]^{\frac{1}{2}} \quad (2)$$

These remarks as well as others show that at present the theory of shock and combustion waves supplemented by the hypothesis of the projection of the hydrogen atoms (which explains the pressure drop in the combustion zone) yields a rather complete interpretation of the influence of various factors on the burning velocities in gas mixtures.

<sup>1</sup> Badin, Stuart, and Pease, *J. Chem. Phys.* **17**, 324 (1949).<sup>2</sup> E. Jouguet, *La Mécanique des Explosifs* (Ed. Doin, Paris, 1947).<sup>3</sup> N. Manson, *Comptes Rendus* **226**, 230 (1948); *Revue de l'Institut Français du Pétrole* **4**, No. 7, 9 (1949).<sup>4</sup> In the comparison of values of  $V$  calculated by means of Eq. (1) and measured by the burner method, one must not forget that the latter method yields (as B. Lewis and G. von Elbe, *J. Chem. Phys.* **11**, 75 (1943) and others have shown) a certain average velocity along the flame cone and not the velocity actually defined in theory.<sup>5</sup> E. F. Fiok and Ch. Roeder, N.A.C.A. Report No. 553.

## Infra-Red Absorption Spectra at Low Temperatures

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July 18, 1949

THE temperature dependence of infra-red absorption bands has been studied by Avery and Ellis,<sup>1</sup> who state that for several aliphatic hydrocarbons there is a distinct sharpening of the bands in going from room temperature to -195°C. They interpret their results on the basis of Bjerrum's formula, according to which the separation of the maxima of the  $P$  and  $R$  branches of an absorption band is proportional to  $T_{ab}$ .<sup>2</sup> This formula obviously only applies to gases, and would not be expected to hold for liquids and solids, whose spectra do not normally exhibit rotational structure. All the compounds studied by Avery and Ellis were either liquid or solid at -195°C, and it is surprising to find that Bjerrum's formula is even approximately true. For low boiling gases, such as ethane, appreciable narrowing of the bands will occur before the gas liquefies, and thus we might expect the low temperature spectrum of the liquid to have narrower bands than the gas at room temperature, quite apart from any changes accom-

panying liquefaction. In the case of 2,2-dimethylbutane, which boils at 50°C, it is difficult on this basis to see why the bands of the liquid spectrum at -195°C should be much narrower than those in the vapor at room temperature. It is even more surprising that the narrowing actually observed by Avery and Ellis is in good agreement with the Bjerrum formula. In our opinion this agreement is entirely fortuitous, since comparison with spectrogram No. 245 issued by the American Petroleum Institute shows that the absorption bands in the spectrum of liquid 2,2-dimethylbutane at room temperature have the same width as those in the low temperature spectrum given by Avery and Ellis. The band-narrowing attributed by these authors to the temperature effect is thus seen to be entirely due to the change of state.

We have recently obtained the infra-red spectra of several solids at room temperature and at -180°C, and find no systematic change of band-width with temperature. In general there is little or no narrowing of the bands with decreasing temperature, though minor changes in the spectrum do sometimes occur, due perhaps to changes in crystal structure or to  $\lambda$ -point transitions. In the case of a mixture of higher paraffins (Nujol), there is practically no change in going from the liquid at room temperature to the solid at -180°C.

In a later paper<sup>2</sup> Avery and Morrison imply that the Bjerrum formula holds quite generally, irrespective of the state of the sample, and suggest that further narrowing of absorption bands may be obtained by using liquid hydrogen or helium as cooling agents. In view of our results we consider this to be unlikely, since most compounds are solid at -195°C, and we do not consider that any further decrease in temperature will result in appreciable narrowing of the absorption bands.

A full report of our investigations will be published subsequently.

<sup>1</sup> W. H. Avery and C. F. Ellis, *J. Chem. Phys.* **10**, 10 (1942).<sup>2</sup> W. H. Avery and J. R. Morrison, *J. App. Phys.* **18**, 960 (1947).

## Infra-Red and Raman Spectra of Hexachloroethane

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July 7, 1949

AS a part of a series of researches on intra-molecular rotation we studied the Raman spectrum of hexachloroethane.<sup>1</sup> This was also studied by Hamilton and Cleveland in various solutions.<sup>2</sup> Recently, one of us has calculated the normal vibrations of ethane-like molecules in the staggered form  $D_{3d}$  by use of the Urey-Bradley field.<sup>3</sup> However, it is evident from the symmetry of the molecule that the normal frequencies of this form are coincident with those of the eclipsed form  $D_{3h}$ , so far as the interaction between the chlorine atoms attached to different movable parts of the molecule is neglected. Therefore, for the discrimination between these two molecular forms we have to refer to the selection rule: in other words, we must observe not only the Raman effect but also the infra-red absorption.

TABLE I. Infra-red and Raman spectra of hexachloroethane.

Infra-red spectrum*		Raman spectrum	
Wave number (cm <sup>-1</sup> )	Intensity	Wave number (cm <sup>-1</sup> )	Intensity
675	Medium	140	1 broad
		169	2 broad
		224	6
769	Strong	341	5
		432	10
1008	Weak	853	2
		974	1

\* The spectrum observed in CCl<sub>4</sub> solution was essentially the same as that in the solid state.