

The Lowest Energy of Symmetric Configurations

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The Lowest Energy of Symmetric Configurations

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June 5, 1950

FOR different cases it was shown by Seitz and Sherman¹ that the lowest state of a symmetric configuration is determined by the wave functions invariant under the group which expresses the symmetry of the atomic configuration; they expected that this will always be so.

In Steam *et al.*² a case is given where this expectation is not fulfilled.

I found another exception to this rule when calculating the activation energy for the addition of a diatomic molecule to a linear triatomic molecule. If we consider only plain configurations with a twofold rotation axis of symmetry A , approaching with the

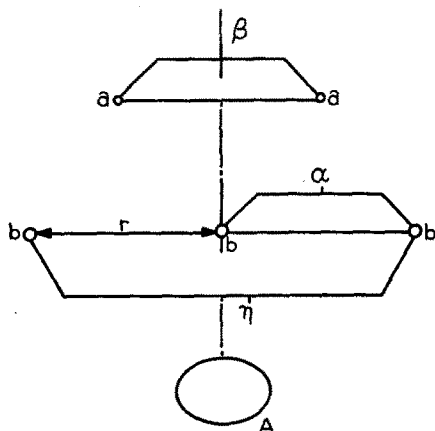


FIG. 1.

center of the diatomic molecule along the vertical through the middle of the triatomic molecule, the secular equation of the general 5-electron problem can be factorized in an equation of the third degree for the symmetric and in a quadratic for the antisymmetric wave functions. When the molecules are so far spaced that the Coulomb and the exchange integrals between a and b atoms may be neglected, the lowest root for the symmetric wave functions gives $E_2 = Q - \alpha + \beta + \eta$ if $(\beta + \eta) > \alpha$ or $E_3 = Q + \alpha - \beta - \eta$ if $(\beta + \eta) < \alpha$, where α stands for the exchange integral between the b atoms at a distance r and η for the exchange integral between b atoms at a distance $2r$. But the lowest root for the symmetric wave functions is higher than the lowest root for the antisymmetric wave functions $E = Q + \alpha + \beta - \eta$ because $(\alpha) > (\eta)$.

Numerical calculations on the adsorption of nitrogen on iron, where three iron atoms on a line were substituted for the actual surface, showed also for finite distances of the normal nitrogen that the lowest energy was given by the antisymmetric functions.

The conclusion of Seitz and Sherman that the calculation of binding and activation energies can be simplified by using only the reduced secular equation for the symmetric wave functions is, unfortunately, not always true.

¹ F. Seitz and A. Sherman, J. Chem. Phys. 2, 11 (1934).

² A. E. Stearn, C. H. Lindsley, and E. Eyring, *J. Chem. Phys.* **2**, 410 (1934).

Determination of Burning Velocities from Shadow and Direct Photographs of a Flame

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June 6, 1950

A METHOD of measuring the normal burning velocity of propane-air flames from shadow photographs has recently been reported by Andersen and Fein.¹ The observation that the area of the shadow cone varies with the distance from the flame to the film and the claim that the area to be used in the Gouy relationship is that obtained by extrapolation to the diametral plane of the flame, has led us to examine the method which we proposed for the determination of burning velocities.²

Our method possesses the advantage that the measurement of cone areas is not employed and consequently the effects of disturbances at the tip and base of the flame are avoided, since it is generally accepted that the cone area method gives only an average value of the burning velocity. The determination of burning velocity from measurements on a stationary flame involves the choice of a suitable part of the flame zone on which the measurements must be made, since combustion takes place in a zone of measurable thickness. Smith and Pickering³ and Garside, Forsyth, and Townend⁴ based their measurements upon the outer edge of the luminous cone, while Sherratt and Linnett⁵ and Andersen and Fein¹ have preferred to use the zone revealed by shadow photographs of the flame.

The present authors consider that both outer and inner edges of the flame zone must be taken into consideration and in an attempt to do this, use has been made of both shadow and direct photographs of the flame. This method is based upon an imaginary surface developed as shown in Fig. 1 from a consideration of the over-all effect of the flame zone so that all the assumptions upon which the relationship $V_B = U \sin \alpha$ are based, apply to this surface. Using this relationship, the apparent burning velocity at different points on the shadow and luminous cones is measured

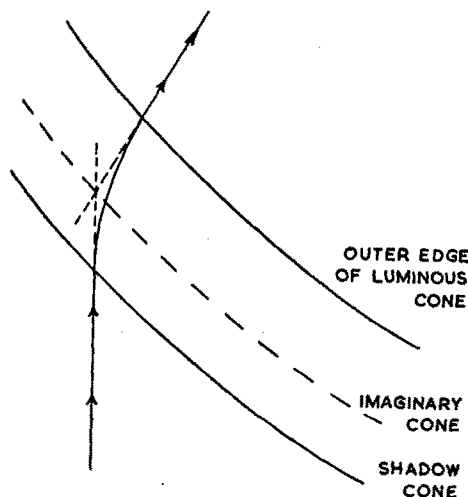


FIG. 1. Path of a gas flow line through the flame zone showing the development of the imaginary surface.

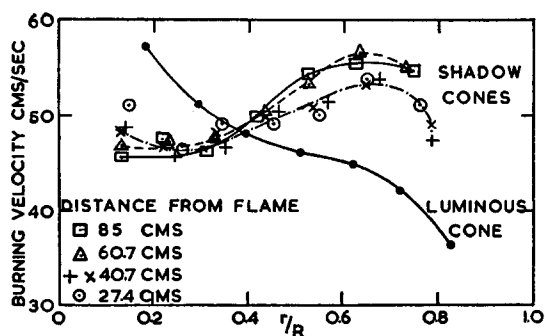


FIG. 2. Variation of the apparent burning velocity over the cone from measurements of the luminous and shadow cones.

and plotted against r/R where r is the radius of the flame cone at which the determination of α is made and R is the burner radius (Fig. 2). It has been shown² that the value at the point of intersection of the shadow and luminous curves is a true value of the burning velocity, this point corresponding to one value of r/R at which the shadow, luminous and imaginary cones are parallel and where the relationship $V_B = U \sin \alpha$ applies to all three surfaces.

Further experiments have been made in which the distance between the flame and film has been varied and the results are shown in Fig. 2. The apparent burning velocity over the shadow cone for a stoichiometric *n* heptane-air flame (with the mixture at 50°C and 740 mm Hg pressure) is plotted against r/R . While the curves are not independent of the distance between the flame and the screen, in the neighborhood of the point of intersection with the luminous curve, the agreement is such as to allow the above method to be applied. Normally the shadow cone is photographed with the flame midway between the light source and the screen for in this position the sensitivity of the shadow process is a maximum while the defocusing effects of diffraction and of the extension of the light source are not too great.

¹ J. W. Andersen and R. S. Fein, *J. Chem. Phys.* **18**, 441 (1950).

² Garner, Long, and Ashforth, *Fuel* **28**, 272 (1949).

³ F. A. Smith and S. F. Pickering, *J. Research Nat. Bur. Stand.* **17**, 7 (1936).

⁴ Garside, Forsyth, and Townend, *J. Inst. Fuel* **18**, 175 (1945).

⁵ S. Sherratt and J. W. Linnett, *Trans. Faraday Soc.* **44**, 596 (1948).

Nuclear Magnetic Resonance Absorption in Hygroscopic Materials

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May 29, 1950

EXPERIMENTS have been performed to measure the magnetic absorption¹ by the hydrogen nuclei in a number of hygroscopic substances. The materials studied are primarily of biological origin and include proteins, carbohydrates, and vegetable tissue. The main interest in these experiments was the form of the relationship between the peak intensity of the absorption (I_p) and water content of the material. The present note summarizes the results obtained on vegetable materials studied.

The absorption in such materials is due, of course, to hydrogen nuclei in the aqueous and in the non-aqueous (mostly solid) constituents of the tissue. The theory of nuclear magnetic phenomena leads to an expectation of a linear relation between I_p and the water content of the tissue providing the magnetic environment of the hydrogen nuclei is independent of the water content.² One source of variation from linearity might be the specific orientation of the initial water absorbed.³

The experimental arrangement used to measure the nuclear magnetic absorption is based upon designs described in the literature.⁴ A magnetic field of 3500 gauss was provided by a per-

manent magnet. Small coils on the pole pieces were energized with 60-cycle current in order to sweep the magnetic field through the resonance value and enable the absorption signal to be displayed on an oscilloscope. Means were provided to maintain the r-f magnetic field intensity at a fixed level during observations. I_p was determined by measurement of the maximum height of the absorption curve displayed on the oscilloscope. The r-f coil used to contain the sample under investigation was a solenoid of 0.5 cm internal diameter by 3.5 cm long. The specimens of tissue investigated were in the form of cylinders 0.3 cm in diameter by 5 cm long. Observations were made at room temperature (about 25°C).

The experimental results for apple and potato are summarized in Figs. 1 and 2. The graphs show I_p for the tissue at its original water content and for a number of water contents obtained by progressive dehydration. Early stages in the dehydration were performed in air under an infra-red lamp and the final dehydration was completed in a vacuum oven. The precision of the moisture determinations is about one percent. Both apple and potato shrank markedly during dehydration. Since shrinkage resulted in a significant change in the amount of material contributing to the magnetic absorption, the observed absorption signals were corrected to allow for shrinkage. The figures show the value of I_p as observed and after correction. Despite the rather large variations shown for different specimens of the same kind of tissue, the figures establish that I_p varies linearly with the amount of water in the tissue.

Since effects due to changes in the state of the water caused by interaction with the absorbent should be more pronounced when the water content is small,⁵ the nuclear absorption was measured for maple wood. Wood was chosen for preliminary work because it is typical of many interesting hygroscopic materials, provides a system that is mechanically self-supporting, and is thus easily handled in the nuclear resonance apparatus. The results of ex-

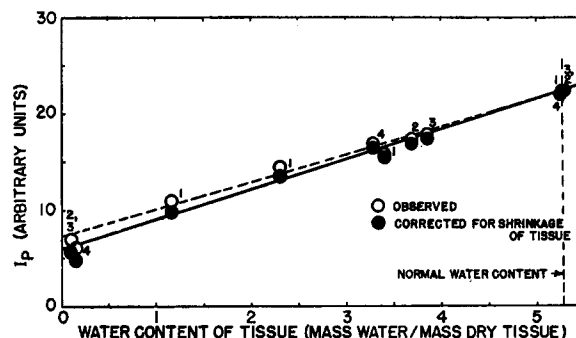


FIG. 1. Relation between peak intensity of nuclear absorption (I_p) and water content of apple tissue. The numbers near plotted points denote different samples of tissue. Zero absorption level uncertain because of noise.

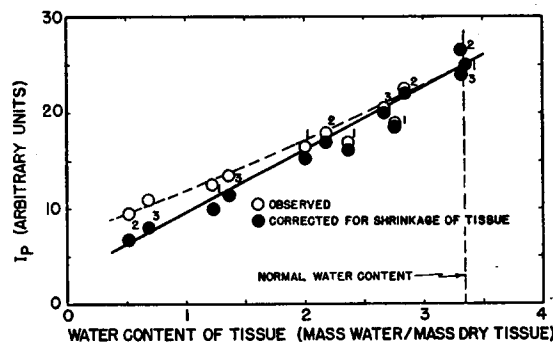


FIG. 2. Relation between peak intensity of nuclear absorption (I_p) and water content of potato tissue. The numbers near plotted points denote different samples of tissue. Zero absorption level uncertain because of noise.