

The Energies of the Atomic Linkages in Methane, Ethane, Methanol and Ethanol

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Citation: [The Journal of Chemical Physics](#) **2**, 145 (1934); doi: 10.1063/1.1749440

View online: <http://dx.doi.org/10.1063/1.1749440>

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TABLE I.

Temperature	H ₂ k_1	H ₂ ² k_2	$\frac{k_1}{k_2}$
0°C	3.7	0.275	13.4
32°C	16.6	1.70	9.75

calculate $Q_1 - Q_2$ and s_1/s_2 . The values obtained are $Q_1 - Q_2 = -1630$ cal. and $s_1/s_2 = 0.66$. If the two types of hydrogen molecules are assumed to have the same collision diameters and the same steric factors, s_1/s_2 should be $2^{3/2}$. The difference between this value and that calculated from

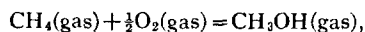
the data is not considered of any significance as an error of ten percent in one of the experimental ratios corresponds to a change in $Q_1 - Q_2$ of 540 calories and a change in s_1/s_2 of a factor of 2.7. We may conclude therefore that the molecules of heavy hydrogen are less reactive than those of ordinary hydrogen in the reaction to form hydrogen chloride due to the fact that the reaction involving the former has a slightly higher heat of activation.

G. K. ROLLEFSON

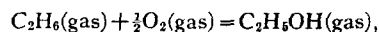
Department of Chemistry,
University of California,
Berkeley, California,
February 8, 1934.

The Energies of the Atomic Linkages in Methane, Ethane, Methanol and Ethanol¹

Data recently obtained in this laboratory on heats of combustion lead to the following values for the change in heat content associated with the addition of $\frac{1}{2}\text{O}_2$ to methane and ethane to form methanol and ethanol, respectively:



$$\Delta H^\circ_{298} = -30.24 \pm 0.09;$$

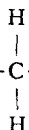


$$\Delta H^\circ_{298} = -36.09 \pm 0.15;$$

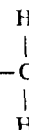
kcal. per mole.

These data show that the energy of the process of

breaking a C-H bond in the molecule $\text{R}-\text{C}-\text{H}$ and in-



serting an oxygen atom to form the molecule $\text{R}-\text{C}-\text{O}-\text{H}$



is appreciably affected by the nature of the substituent R; and that, contrary to what has been assumed by practically all investigators in this field, the energies of the atomic linkages in these and homologous compounds are quite significantly not additive.

In a subsequent paper which will appear in the *Bureau of Standards Journal of Research*, it will be shown that even in the normal paraffin hydrocarbons the energies of the atomic linkages are appreciably affected by the nature of the substituents, hydrogen atoms or alkyl groups.

FREDERICK D. ROSSINI

Bureau of Standards,
Washington, D. C.,
February 8, 1934.

¹ Publication approved by the Director of the Bureau of Standards, United States Department of Commerce.

Direct Experimental Measurement of Electron Affinities

The electron affinity of an electronegative gas, ΔE at 0°K of the reaction $X^- \rightarrow X + e^-$, may be readily calculated if the equilibrium constant of the above reaction can be measured. If the gas X_2 at low pressure is allowed to come in contact with a hot metallic surface (thermionic emitter), molecules X_2 , atoms X , electrons e^- , and ions will leave the surface. If it is assumed that the relative amounts of the various molecular species leaving the surface are independent of the temperature of the molecules X_2 hitting the surface, that is if complete equilibrium on the surface exists, then the equilibrium pressures and the electron affinity may be simply calculated from the numbers of X^- , X , and e^- leaving the surface. In the case of iodine, calculations predict, and observations show,¹ that at above 1500°K the molecules are completely dissociated into atoms, and since a very small fraction of the atoms are converted into ions on a tungsten surface, the

number of atoms leaving the surface will be twice the number of impinging molecules. The necessary data for the calculations are then, the temperature of the surface, the pressure of the gas X_2 in the vessel, and the ratio of the currents carried by the ions and electrons.

By using, in a cylindrical arrangement, a tungsten filament (0.2 mm diam. 0 volts) a wire net grid (10 mm diam. about +10 volts) and a cylindrical plate collector (40 mm diam. about +15 volts) inside a solenoid producing a magnetic field parallel to the axis of the cylinder, the electron current from the filament can be completely deflected from reaching the plate at fair solenoid currents even in the presence of considerable gas pressure. (Magnetron set-up.) The heavy ions I^- are unaffected by the magnetic field. The voltage necessary to obtain saturation

¹ Communication from Dr. Irving Langmuir.

TABLE I.

Filament temperature (°K)	Iodine pressure $\times 10^{-3}$ mm	Currents in arbitrary units		Electron affinity (kcal.)
		Ion	Electron	
1813	0.35	2.3	213	76.7
1886	0.92	14.4	930	76.1
1887	1.8	20.5	2450	71.6
1891	0.28	9.5	1320	78.3
1892	1.5	19.3	2430	72.4
1968	1.4	116.	15300	75.5
2031	1.8	560.	53000	78.6

currents can also be used as auxiliary measurement of the ion current.

A few preliminary measurements are reported in Table I. The results,* although capable of much greater refinement

indicate values in good agreement with other methods,² 74.2 kcal. being calculated from the theoretical lattice energies of the alkali iodides.

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The Johns Hopkins University,
Baltimore, Maryland,
February 9, 1934.

² J. E. Mayer and L. Helmholz, *Zeits. f. Physik* **75**, 19 (1932). J. E. Mayer, *Zeits. f. Physik* **61**, 798 (1930).

* The calculations assume no reflection of electrons, ions or atoms from the filament. The experimental electron emission of tungsten suggests a possible electron reflection coefficient 0.5; assuming this would decrease our electron affinities by about 2.5 kcal.

The Raman Spectrum of Lead Tetramethyl

We have been investigating the Raman spectra of a group of metallo-organic compounds. In this letter we will give some results we have obtained with lead tetramethyl.

The lead tetramethyl was distilled *in vacuo* into the Raman tube. The spectra were excited by the blue and violet mercury lines separately by using an apparatus described by one of us with D. H. Andrews.¹ The following lines were found: 135 (8br), 458(10), 472(8), 766(1/2), 930(0), 1155(3), 1169(2), 2921(8), 3000(3). The 2921 and 3000 lines are assigned to vibrations in which the C—H bond is stretched. The 930 line is probably an harmonic of 458. The remaining lines may be assigned to the bending and stretching motions of a pentatomic molecule whose structure is probably tetrahedral. The three lowest are probably due to bending and the others to stretching.

It is of interest to note that there are two pairs of close doublets of considerable intensity, and that the line at

135 cm^{-1} is broad and unsymmetrical, which suggests that it is also a doublet. The assignment of frequencies to types of vibrations is thus rather uncertain. The low intensity of 766 renders its association with the symmetrical motion improbable, but it is difficult to reconcile the doublet structure of the other frequencies with this kind of motion. The apparent absence of the line at 1450, which usually occurs in compounds containing the methyl group, is also of interest.

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JOHN W. MURRAY

Chemistry Laboratory,
The Johns Hopkins University,
February 14, 1934.

¹ D. H. Andrews, *J. Chem. Phys.* **1**, 406 (1933).