

Further Studies of Hydrocarbon Flame Spectra

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Bowden and Grew⁵ over the range $3 \cdot 10^{-8}$ – 10^{-6} amp./cm² in which range the results of the latter authors are approximately 0.1 v lower than those of Levina and Sarinsky. Consequently it appears more probable that the measurements of Bowden and Grew are vitiated by the extremely small traces of impurity effective at such low c.d.s. than that they represent a true variation in the coefficient b .

The more important correction to the experimental basis of this suggestion concerns the behavior at high c.d.s. ($>10^{-2}$ amp./cm²) where Van Rysselberghe presumably, mainly on the basis of the work of Hickling and Salt,⁶ assumes that the coefficient b approaches zero. It has been shown by one of us⁷ that this behavior is not due to errors in the commutator method used by Hickling and Salt. Recently we have observed using a mercury cathode that this effect is removed by extensive electrolytic purification of the solution but reappears on the addition of substances such as H₂S to this purified solution. We conclude that the previously reported approach of overpotential to a constant value at high c.d.s. is due to the presence of those impurities which like H₂S are adsorbed at the electrode only at potentials far from the electrocapillary maximum. In agreement with this Azzam⁸ has found that for mercury and several other metals of high overpotential the Tafel equation is applicable to a c.d. of at least 150 amp./cm².

(iii) Van Rysselberghe's theory leads to the results that the overpotential is in the general case independent of hydrogen ion concentration, and in special cases dependent on it. Unpublished data obtained in the authors' laboratory⁹ together with the scanty published data^{3, 10, 11} obtained under satisfactory experimental conditions indicates that the reverse situation is observed. The overpotential is in fact independent of a pH only for high overpotential metals in solutions of pure acids at low and medium concentrations. For low overpotential metals in pure aqueous acids there is a variation of overpotential with pH even when the acid concentration is as low as $N/100$. In the presence of added salts, the overpotential appears to be a function of pH for both high and low overpotential metals.

¹ Van Rysselberghe, J. Chem. Phys. 17, 1226 (1949).

² Bockris, Chem. Rev. 43, 525 (1948).

³ Levina and Sarinsky, Acta Physicochimica 6, 491 (1937); *ibid.* 7, 485 (1937).

⁴ Agar and Llopis, Anal. fis. y quim. 43, 1087 (1947); Ruis and Llopis, *ibid.* 42, 897 (1946); Béthune, J. Am. Chem. Soc. 71, 1556 (1949).

⁵ Bowden and Grew, Trans. Faraday Soc. Discussion 1, 86 (1947).

⁶ Hickling and Salt, Trans. Faraday Soc. 36, 1226 (1940).

⁷ Bockris, Trans. Faraday Soc. 43, 417 (1947).

⁸ Azzam, Thesis, London (1949).

⁹ Conway, Thesis, London (1949); Potter (unpublished).

¹⁰ Bockris and Parsons, Trans. Faraday Soc. 45, 916 (1949).

¹¹ Lukovsev, Levina, and Frumkin, Acta Physicochimica 11, 23 (1939); Legin and Levina, *ibid.* 12, 251 (1940); Jofa, *ibid.* 10, 391, 617, 903 (1939); Frumkin, Trans. Faraday Soc. Discussion 43, 57 (1947).

Macroscopic Space Charge in Electrolytes during Electrolysis

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March 13, 1950

THIS is a reply to the Letter to the Editor, under the same title, by MacInnes, Shedlovsky, and Longworth¹ in which they claim to have shown that the work reported by Reed and Schrieffer² is faulty.

If significant changes in concentration near the current electrodes in our work had taken place, then the potential gradients should have increased as the cathode was approached. In five of the seven electrolytes investigated in the cathode half of the column, the gradients decreased; in the other two they first decreased to below average and then increased as the cathode was approached. Seven of the eight solutions exhibited a decrease in gradient as the anode was approached but one, Al₂(SO₄)₃, exhibited a large continuous increase through a distance of 5 cm. It is clear

that ordinary concentration changes cannot account for our data. A more detailed explanation appeared in our original paper.³

If, as they claim, "erratically changing concentration differences" had developed then our data should have been erratic. Our data were reproducible and not erratic. This is illustrated by Table I in our original paper. During the 15 minutes that the current passed, in our work, an ion moved only one millimeter. If all the ions in a one-mm layer next to the cathode were swept out, and a full extra set were swept into the one-mm layer next to the anode, the densities of these layers would have changed by only 2 parts in 10,000. Actually, of course, the concentration changes would be much less than this and, in addition, these changes built up from zero to less than 2 parts in 10,000 during the 15 minute interval. Does it not seem a little unreasonable to expect appreciable "erratic" convection to be produced by such small density differences in such a short time?

They also claim that our electrodes were at fault. Again the reproducibility of our data indicates that our electrodes must have been quite satisfactory. Even if the indicated potential differences were in error, as far as absolute magnitude is concerned, such an error would have been the same for all points along the column of electrolyte. This constant error would cause no change in either the calculated potential gradients or in the calculated space-charges. If erratic changes had occurred we could not have achieved reproducibility of data. Any gradual changes in our electrodes were taken into account by the application of our "standard curve" procedure.⁴

Their "admittedly relatively crude" experiment would have been convincing if they had used one of the solutions for which data were reported in our paper, instead of KCl, and if they could have obtained our type of results with their tube horizontal, and their type of results with the tube vertical. They do not describe how they took their "three series of measurements"; if they did not measure their potential differences at all points along the column, for a constant time of current-flow, then their data are not comparable to ours.

It so happens that one of my students has been working since last November with a 0.0024 normal solution of KCl between platinum electrodes, and using the tip of a platinum wire as the exploring electrode. The apparatus and methods are essentially the same as those used by Reed. Our data are not yet complete but they do show that the potential gradient is remarkably constant for most of the length of the 40-cm column. Near the cathode end of the column a small negative space charge is indicated. The data in the anode half of the column are yet too few to make certain that we shall be able to detect a space charge effect there.

Therefore, my guess is that MacInnes *et al.* would get essentially the same kind of results for KCl with their tube horizontal as they would with their tube vertical, if all measurements were carried out with care under exactly the same conditions. Their comments are very much appreciated.

¹ MacInnes, Shedlovsky, and Longworth, J. Chem. Phys. 18, 233 (1950).

² C. A. Reed and W. Schrieffer, J. Chem. Phys. 17, 935-944 (1949).

³ See reference 2, p. 943.

⁴ See reference 2, p. 939.

Further Studies of Hydrocarbon Flame Spectra*

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March 10, 1950

RECENTLY the authors reported some preliminary investigations of the spectra of stationary hydrocarbon flames, particularly those of ethylene and methane burning with oxygen at reduced pressures (~ 50 mm of Hg).^{1, 2} These investigations were carried out primarily to examine in greater detail the so-called hydrocarbon or ethylene flame bands. These bands, which

were first reported by Vaidya³ on the basis of low dispersion spectra, lie in the spectral range 2500–4100Å, appear degraded to the red, and have been assigned generally to the HCO radical.⁴ Our studies of hydrocarbon flames, burning under a variety of conditions, reveal in this region of the spectrum the band systems of OH and CH, the Schumann-Runge band system of O₂, the Deslandres-D'Azambuja band system of C₂, and the CN bands when the fuel is mixed with air rather than oxygen. Various of these band systems are more prominent according to the conditions of burning. For example, the Schumann-Runge system is relatively stronger the higher the oxygen concentration in the fuel-oxygen mixture, the bands of C₂ becoming weaker.

As a continuation of this investigation we have examined the spectrum of the acetylene-oxygen flame burning the premixed gases in an ordinary acetylene torch at atmospheric pressure with carefully regulated gas flow control. The results mentioned above are also obtained with this source. The purpose of the present note is to report the spectral changes that occur when the fuel/oxygen ratio is increased considerably beyond that for stoichiometric proportions. Spectra were taken of the inner cone with an acetylene/oxygen ratio of about unity in the second order of a 21'10" Jarrell-Ash grating spectrograph with a dispersion of about 2.4Å/mm. Under this condition the Fox-Herzberg⁵ system (³Π_g–³Π_u) of the C₂ molecule is found together with the bands of OH, CH, and all the other band systems of C₂.

Figure 1 is a densitometer tracing of the region ~3005–3064Å which shows the (0–4) band of the Fox-Herzberg system mixed with many lines of OH. A portion of this band is labeled so as to identify the *R* and *P* triplets. The Fox-Herzberg bands degrade to the red, do not have pronounced heads, and are known to extend from 2378Å (4–1) to 3283Å (0–6).^{5,6}

Our work would seem to indicate that hydrocarbon flames burning in different types of sources and under various conditions of pressure yield spectra which depend principally on the fuel/oxygen or fuel/air ratio. The spectra obtained appear to be the result of the overlapping of a large number of bands all of which

degrade to the red except those of CN and some of the Deslandres-D'Azambuja system. It is not surprising that hydrocarbon flame spectra under low dispersion are difficult to interpret. It should be pointed out that at higher dispersion there still remains residual structure to be identified which, however, is weak in comparison to that already described. In any event we have as yet found no prominent structure which cannot be attributed to the various diatomic radicals and molecules.

We wish to express our appreciation to Dr. G. Herzberg, National Research Council, Canada, and Dr. J. G. Phillips, Yerkes Observatory, University of Chicago, for their interest in our work.

* The work described herein was supported by the Bureau of Ordnance, U. S. Navy, under Contract NOrd-7386.

¹ G. A. Hornbeck and R. C. Herman, *J. Chem. Phys.* **17**, 842 (1949).

² R. C. Herman and G. A. Hornbeck, *J. Chem. Phys.* **17**, 1344 (1949).

³ W. M. Vaidya, *Proc. Roy. Soc. A* **147**, 513 (1934).

⁴ For example, see A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, Ltd., London, 1948).

⁵ J. G. Fox and G. Herzberg, *Phys. Rev.* **52**, 638 (1937).

⁶ J. G. Phillips, *Astrophys. J.* **110**, 73 (1949).

Exchange Reaction of Carbonate Ion with Carbonato-Tetrammine Cobaltic Ion

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March 9, 1950

SOME recent studies of the cobalt complexes utilizing radioactive cobalt have indicated the relative inactivity of these systems toward exchange reactions involving the central cobalt ion of the complex.^{1,2} It is desired to record here the results of a preliminary study of the system [Co(NH₃)₄CO₃]⁺–CO₃^{2–}. In this work, exchange between complexed and uncomplexed carbonate ion was studied by means of radioactive carbon-14.

Aqueous solutions of carbonato-tetrammine cobaltic nitrate and sodium carbonate, the latter containing a small proportion of Na₂C¹⁴O₃, were mixed in such proportions as to give a solution approximately 0.03*M* in the complex, and 0.01*M* in the carbonate. The reactant mixture was stored in the dark at 20°C, 1.5-ml samples being withdrawn for analysis at regular intervals. Free CO₃^{2–} ion was precipitated as BaCO₃, utilizing BaCl₂·NH₃ mixture 1*N* in each constituent. Separate tests showed that the complexed CO₃^{2–} ion remained unaffected by this reagent during several hours' standing at 20°C. The ~3-mg samples of BaCO₃ so obtained were counted in aluminium pans of 1 in. diameter according to standard radiochemical technique. The counts were of sufficient duration to give results with a standard deviation of within ±1 percent. Self-absorption corrections were unnecessary due to

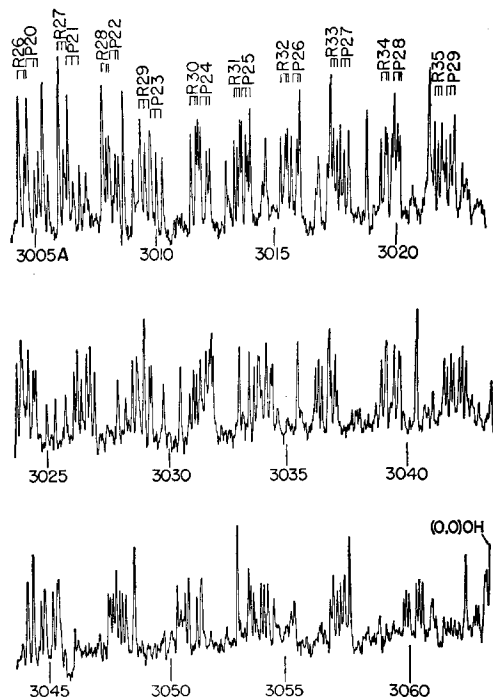


FIG. 1. Densitometer tracing of the spectrum of the acetylene-oxygen flame showing a portion of the (0–4) Fox-Herzberg band of C₂.

TABLE I.

Duration of exchange (min.)	Weight of BaCO ₃ sample (mg.)	Net activity (A _t) of BaCO ₃ sample (counts/mg./min.)	Fraction of exchange $f = \frac{A_0 - A_t}{A_0 - A_\infty}$	(1–f)
0	—	(109) ^a	0.00	1.00
10	2.87	107	0.03	0.97
62	2.97	100	0.11	0.89
120	2.89	94	0.19	0.81
246	2.82	84	0.32	0.68
425	2.86	71	0.48	0.52
660	2.88	56	0.67	0.33
1458	2.69	38	0.90	0.10
2892	3.08	30 ^b	1.00	0.00

^a Extrapolated value obtained from log A_t vs. t plot.

^b Sample taken at end of about 7 "half-lives" of the exchange, so within one percent of exchange equilibrium. This value thus assumed for A_∞ in calculation of "f".