

Exchange Reaction of Carbonate Ion with CarbonatoTetrammine Cobaltic Ion

Gordon M. Harris

Citation: *The Journal of Chemical Physics* **18**, 764 (1950); doi: 10.1063/1.1747759

View online: <http://dx.doi.org/10.1063/1.1747759>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Direct manipulation of the uncompensated antiferromagnetic spins in exchange coupled system by GeV ion irradiation](#)

Appl. Phys. Lett. **100**, 253102 (2012); 10.1063/1.4729472

[Ion irradiation effects on the exchange bias in IrMn/Co films](#)

J. Appl. Phys. **109**, 023905 (2011); 10.1063/1.3532044

[Exchange bias by implantation of O ions into Co thin films](#)

Appl. Phys. Lett. **96**, 132503 (2010); 10.1063/1.3377907

[Influence of ion bombardment induced patterning of exchange bias in pinned artificial ferrimagnets on the interlayer exchange coupling](#)

J. Appl. Phys. **103**, 123903 (2008); 10.1063/1.2939072

[Growth behavior and interfacial reaction between carbon nanotubes and Si substrate](#)

J. Vac. Sci. Technol. A **22**, 1461 (2004); 10.1116/1.1735908



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

GORDON M. HARRIS

Chemistry Department, University of Melbourne, Melbourne, Australia

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

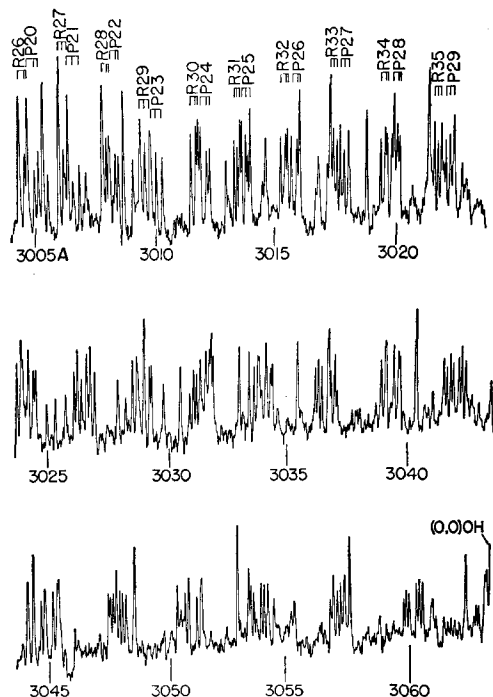


FIG. 1. Densitometer tracing of the spectrum of the acetylene-oxygen flame showing a portion of the (0–4) Fox-Herzberg band of C₂.

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".

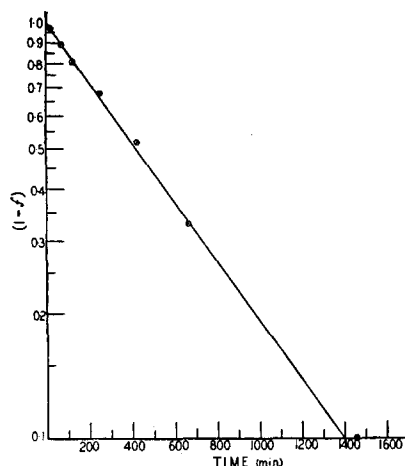


FIG. 1.

the thinness of the samples, and the fact that they were in any case closely comparable in weight. The data are summarized in Table I.

That the reaction appears to exhibit the conventional first-order characteristics of isotopic exchange³ is illustrated by the $\log(1-f)$ vs. t plot of Fig. 1. It is seen from the latter that the half-time of exchange of about 7 hr. is rather unexpectedly long in view of the known instability of the carbonato-type of complex.⁴ A detailed kinetic investigation of the reaction is now in progress in this laboratory, and a full report, including evidence as to the mechanism of the exchange, will be published at a later date.

¹ W. B. Lewis and C. D. Coryell, Brookhaven Conference Report BNL-C-8 (December, 1948).

² Hoshowsky, Holmes, and McCallum, Can. J. Research 27B, 258 (1949).

³ H. A. C. McKay, Nature 142, 997 (1938).

⁴ Abegg's *Handbuch der anorganischen Chemie* (Leipzig, 1935), Bd. IV, Abt. 3, Teil 3, Lief 2.

The Influence of the Shape of Molecules on the Thermodynamic Properties of Hydrocarbon Mixtures

I. PRIGOGINE AND V. MATHOT*

Faculté des Sciences de l'Université Libre de Bruxelles, Bruxelles, Belgium
March 7, 1950

IN recent experimental¹ and theoretical² work it has been shown to what extent the thermodynamic properties of solutions are affected by a difference in size of the molecules of the constituents.

The purpose of this investigation is to determine the influence of a difference in shape or symmetry of the molecules.

In order that the heat of mixing may be as small as possible, mixtures of saturated hydrocarbons have been chosen; the molecules of both constituents have practically the same size but they are either globular (more or less spherical) or chain-like as normal paraffins.

The total vapor pressure and the integral heat of mixing of the systems: cyclohexane-*n*-hexane at 20°C and tetraethylmethane (diethyl-3,3-pentane)-*n*-octane at 50°C have been measured.

The results have been calculated in terms of excess free energy g_e , excess entropy s_e , and excess enthalpy h_e related by the definitions

$$g_e = h_e - Ts_e$$

$$g_e = x_1 RT \lg f_1 + x_2 RT \lg f_2$$

(x_1, x_2 mole fractions; f_1, f_2 activity coefficients).

Figures 1 and 2 give these results, respectively, for cyclohexane-hexane and tetraethylmethane-octane, in calories per "mole" of solution against mole fraction. The accuracy is only about 10 per cent, as the observed effects are very small.

It must be emphasized that both systems are far from regular. In the system tetraethylmethane-octane, there even appears a negative excess entropy and a negative excess enthalpy (evolution of heat while mixing), the excess free energy remaining positive. As far as the authors are aware, this is the only example of a system of saturated hydrocarbons with a negative enthalpy of mixing.

The influence of symmetry of isomer constituents of a solution has also been investigated theoretically. According to Guggenheim's theory,² any mixture of unbranched and branched chains, both occupying the same number of lattice sites, must be ideal in the athermal case. Using the Bethe-Chang method³ we have calculated the combinatory factor for an assembly of linear rigid and right-angled triangular trimers on a two-dimensional lattice with square symmetry ($z=4$), assuming zero energy of mixing. This factor proved to be the same as for an ideal solution. Although there must be some effect with increasing size of the isomers, this seems to be zero or negligible for differences in shape met with in the more common hydrocarbon mixtures.

Therefore the origin of the entropy terms observed for both systems should be imputed to the enthalpies of mixing. Its effect would be to alter, not the combinatory factor—a contribution known to be very small and leading to negative excess entropy

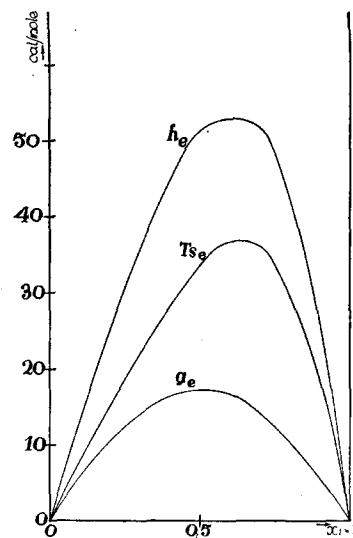


FIG. 1. Thermodynamic properties of cyclohexane-hexane solution (x_1 = mole fraction of cyclohexane).

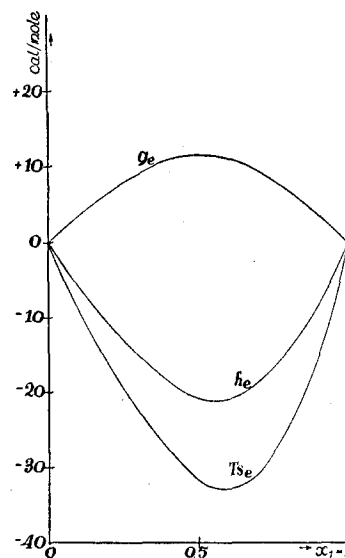


FIG. 2. Thermodynamic properties of tetraethylmethane-octane solution (x_1 = mole fraction of tetraethylmethane).