down to the assumed value of 7.40%, we have the figures of Col. 5 and the molar ratio of Col. 6, which agree with the calculated values as closely as may be expected. The formula of the salt is thereby established as $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$, an addition compound of $K_2CO_3 \cdot 3/2H_2O$ and $KHCO_3$ without change in hydration.

Summary

1. Isotherms have been constructed for the ternary system K_2CO_3–$KHCO_3$–H_2O at 5, 25, 35 and 50°.

2. The double salt first observed by Berthollet has been found to have a stable existence in contact with solution from −9.2°, its lower transition temperature, to something above 50°, but always within a very narrow range of concentrations.

3. A critique is offered of the methods for preparing incongruently soluble double salts for analysis.

4. The formula of the double salt is found to be $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2$-$H_2O$.

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THE QUENCHING OF MERCURY RESONANCE RADIATION. I. THE SATURATED HYDROCARBONS

BY JOHN R. BATES

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The reactions of the saturated hydrocarbons under the influence of excited mercury atoms have been studied by Taylor and Hill,[1] who found that, with the exception of methane, they are all decomposed to give hydrogen, methane and high-boiling mixtures such as are obtained in the thermal "cracking" of hydrocarbons. This behavior, which is analogous to that observed in the presence of hydrogen atoms,[2] seemed worthy of further study to determine whether the inactivity of methane arose from its inability to receive the energy of the mercury atom or whether it was similar to the case of hydrogen and excited cadmium atoms,[3] where the energy is transferred, but no reaction results.

Measurements have therefore been made of the quenching of mercury resonance radiation by the four hydrocarbons—methane, ethane, propane and butane—which make quite clear the reasons for the results obtained by Taylor and Hill and also furnish values for the collision radii for collisions of the second kind between excited mercury atoms and the hydro-

[1] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).

[2] Bonhoeffer and Harteck, *Z. physik. Chem.*, **139**, 64 (1928).

[3] Bates, *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

carbons, which are becoming of interest in the light of recent theoretical considerations of such collisions.

Experimental

The method used is that due to Zemansky.[4] A source of mercury resonance light (L in Fig. 1) is focused on one quartz window of a resonance lamp T, which consists of a tube containing mercury vapor at a definite pressure. The resonance light excited is then taken out of the quartz window perpendicular to the first and collimated by a lens. This parallel light is passed through a cell (B) of 8 mm. thickness and 40 mm. diameter. immediately behind which is an iris diaphragm. Behind this is a quartz platinum hydrogen filled photo-electric cell which can be moved so that it is either in contact with the diaphragm (position R) or at a distance of 15 cm. The photo-electric current is measured by a Compton quadrant electrometer.

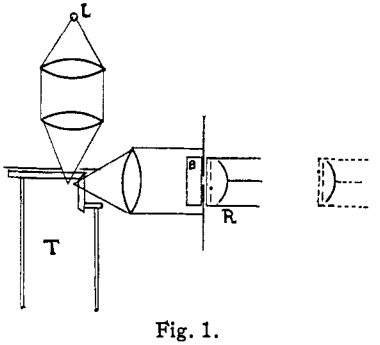

Fig. 1.

In measuring the quenching a reading is taken with B containing mercury vapor at 20°, and the photo-electric cell at R. The cell is then moved back to a position which records only the parallel light passing through the diaphragm. The difference between these two readings $I_R - I_\infty$ is the resonance light emitted by B. With the photo-cell at R, readings are then taken at various pressures of the foreign gas whose quenching is to be determined. The percentage of resonance light emitted. J. is then calculated from the equation

$$J = \frac{(I_{R_p} - I_{\infty_v})}{(I_{R_v} - I_{\infty_v})} \times 100$$

As a source of light a mercury arc rich in resonance light, which has already been described,[5] was used.

In order to have a standard by means of which fluctuations of the intensity of resonance light emitted by the resonance lamp could be corrected for, the cell B was made movable and could be replaced by a fused quartz window covered with a film of gelatin. Immediately before and after each reading of the resonance light a reading of the light transmitted by this "standard" was made.

To have as monochromatic resonance light as possible the precautions described by Kunze[6] were taken in constructing the resonance lamp.

Preparation of the Gases.—The hydrocarbons were obtained from cylinders containing these gases, whose source was natural gas. It was thought these would be considerably freer from hydrogen than any laboratory source. Since hydrogen is known to quench mercury resonance radiation at pressures of the order of 0.01 mm., it was important to insure its absence.

Methane, propane and butane were taken from the tank, dried over phosphorus pentoxide, frozen out and redistilled twice *in vacuo*, the middle fraction being taken both times.

Ethane, which contained 10–15% ethylene as it came from the tank, was twice bubbled through saturated bromine water and carried a distance of approximately

[4] Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[5] Taylor, THIS JOURNAL, **48**, 2840 (1926); Bates and Taylor. *ibid.*, **49**, 2483 (1927).

[6] Kunze, *Ann. Physik*, **85**, 1013 (1928).

three meters saturated with bromine vapor, then through sodium hydroxide solution, soda lime and phosphorus pentoxide. Higher-boiling substances such as bromine and bromides were removed by a solid carbon dioxide–ether mixture. It was then subjected to the distillations as in the other cases.

The intensity of the light falling upon the cell from the resonance lamp is very small and quite insufficient to bring about enough decomposition of the hydrocarbons into hydrogen to affect the values observed. Furthermore, this was experimentally shown by the following method. The gas was admitted in successive small quantities, a reading being taken after each addition. This process takes about six hours, allowing sufficient time to reëstablish the equilibrium vapor pressure of mercury, disturbed by the flow of gas into the cell. The gas was then pumped out in successive quantities, readings were again taken and found to agree within the experimental error with those observed previously.

Experimental Results

The quenching curves for the hydrocarbons are given in Figs. 2 and 3. They are represented by plotting J, the percentage of resonance light emitted, against the pressure of the various gases.

In determining the efficiencies of collisions between excited mercury atoms and foreign gas molecules, it has been the custom to take the value of the pressure where J equaled 50% and, assuming this to be the pressure at which the mercury atom has an equal chance of emitting or losing its energy on collision, calculate the number of fruitful collisions.[7] However, Zemansky[8] has derived a more exact relationship where $\tau k = f(J,p,\alpha,d)$; τ being the mean life of an excited mercury atom in the 2^3P_1 state (10^{-7} sec.), k the number of second kind collisions per atom per second, p the vapor pressure of mercury in the cell, α the absorption coefficient of mercury under the conditions employed, and d the thickness of the cell. From τk the value σ_E, or collision distance between excited mercury atoms and foreign gases, can be obtained from the gas kinetic equation

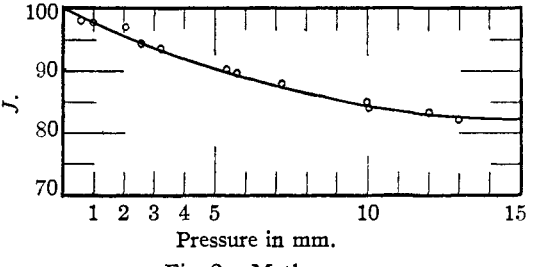

Fig. 2.—Methane.

$$K = 2\sigma_E^2 \times 9.81 \times 10^{18} \frac{p}{T}\sqrt{2\pi k T\left(\frac{1}{M}+\frac{1}{m}\right)} \qquad (1)$$

Substituting for $T = 293.0°$, and multiplying through by τ

$$\sigma_E^2 = \frac{\left(\frac{\tau K}{p}\right)}{3355\sqrt{\frac{1}{M}+\frac{1}{m}}} \qquad (2)$$

[7] Stuart, *Z. Physik*, **32**, 262 (1925).

[8] Zemansky, *Phys. Rev.*, **31**, 812 (1928).

Since the relationship between τk and J involves a laborious calculation involving the absorption coefficient of mercury, which could not be accurately determined by the system as set up, a curve representing this

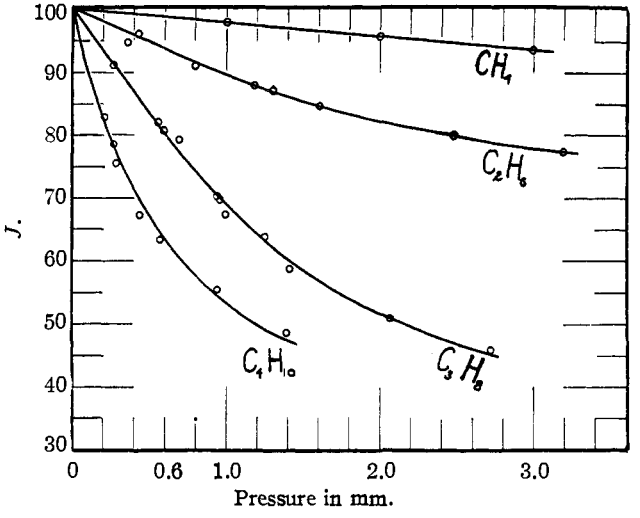

Fig. 3.

dependence was obtained from a curve of τk against p obtained through the kindness of Dr. Zemansky, who measured propane taken from the same sample as that used in the present measurements. From this and the propane curve in Fig. 3, the curve in Fig. 4 was obtained. Then from a knowledge of $J{:}p$ and $\tau k{:}J$ (Figs. 3 and 4) the final results in Fig. 5, which give the number of collisions of the second kind per excited mercury atom at any given foreign gas pressure, were obtained. The relationships for the various hydrocarbons are remarkably linear with respect to pressure, which is as expected. The slope of these curves gives $\tau K/p$ which, when placed in the numerator of Equation 2, gives values for σ_E.

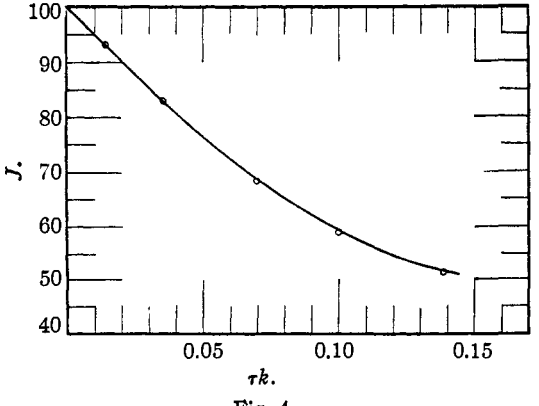

Fig. 4.

In Table I are shown the values of $\tau k/p$, and σ_E^2 thus obtained, together with σ_N^2 from kinetic theory. The values are accurate to within 5% and within themselves agree probably to a much better value.

TABLE I

RESULTS

Gas	$\tau K/p$	$\sigma_L^2 \times 10^{16}$	$\sigma_N^2 \times 10^{16}$[a]
CH_4	0.004	0.059	11.6
C_2H_6	.021	.421	16.4
C_3H_8	.0695	1.60	≥17?
C_4H_{10}	.158	4.06	≥18?
H_2[b]	1.13	6.01	8.89

[a] Herzfeld, "Handbuch der Physik," Vol. 22, p. 409.

[b] Taken from Zemansky for comparison.

From the $\tau k/p$ values it can be seen immediately that the relative probability of a transfer of the energy of the mercury atom does decrease as we go from butane down to methane, reaching a very small value for the latter. However, this does not indicate that methane should be entirely unaffected, especially at high pressure, if the energy is given over

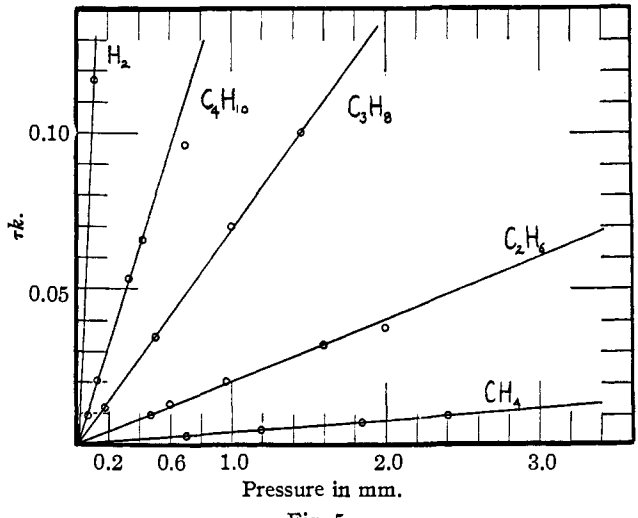

Fig. 5.

at all. There is always the possibility that the mercury atom only gives up the 0.2 volt which separates the 2^3P_1 state from the metastable 2^3P_0 level, which process is known to occur in many cases, *e. g.*, helium, carbon monoxide, nitrogen, water, etc. In this case the energy transferred, being too small to bring about any chemical reaction, would be accommodated in the translational and vibrational degrees of freedom of the methane molecule, and at low pressures the metastable mercury atom, having a long life, would diffuse to the walls and give up the remaining energy. At higher pressures, where the metastable atoms make a large number of collisions in diffusing to the walls, there is a probability that in some collision there will be sufficient kinetic energy available to bring the mer-

cury atom back to the 2^3P_1 level, where it may either radiate or be quenched once more.[9] The effect of this would obviously be to lower the apparent quenching at high pressures.

In order to see whether this occurred, the measurements on methane were extended to pressures of 200 mm. The results are plotted in Curve I of Fig. 6. The value of J at first decreases and then increases to impossibly high values, due to decreased absorption of mercury vapor in the presence of methane at higher pressures. The latter was determined by measurement and shown in Fig. 7, expressed as percentage transmission with transmission *in vacuo* 100%.[10] It will be seen that this change

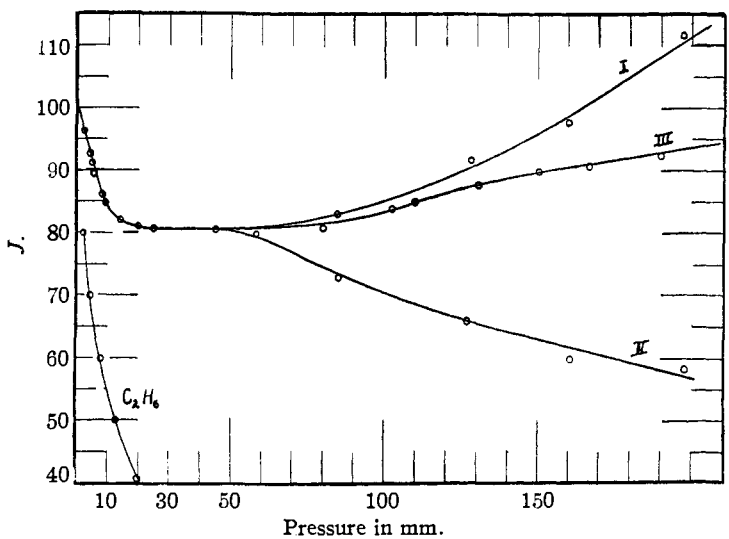

Fig. 6.

in absorption will not affect the results in Fig. 2, since at the pressures there considered, there is no measurable difference from vacuum conditions. However, at high pressures the equation $J = (I_{R_p} - I_{\infty_v})/(I_{R_v} - I_{\infty_v})$ must now have I_{∞_p}, instead of I_{∞_v} in the numerator. This correction, applied to Curve I in Fig. 6, gives Curve II. An additional correction to this, due to the fact that, with lower absorption, there is naturally proportionately lower emission of resonance light, gives as the final result III for the corrected quenching curve of methane at high pressures, obtained by multiplying the values of II by the corresponding values

[9] See Foote, *Phys. Rev.*, **30**, 288 (1927), and many other papers.

[10] The shape of the curve is very readily understood when it is realized that the line emitted even by a resonance lamp is somewhat broader than the Doppler breadth of mercury absorption *in vacuo*. Hence when the absorption line is at first broadened absorption increases, until the breadths coincide, after which there is a decrease. See Zemansky, Orthmann, and others for a quantitative treatment of this effect.

of transmission as obtained from Fig. 7. While this is perhaps not exact, due to the necessary assumptions, it is a very close approximation, and is what would be expected for a gas which quenched by lowering the mercury atoms to the metastable level. These atoms are able to diffuse to the walls and give up their energy to a pressure of about 10 mm., where an appreciable number begin to be returned to the 2^3P_1 level. This is also an indication that the methane used was surprisingly free from hydrogen, since metastable mercury atoms are efficiently quenched by this gas.[11] The values for ethane are shown up to 20 mm. (the curve continued for somewhat higher pressures) to show that there is no break similar to that in methane. This does not necessarily mean that ethane does not bring some atoms to the metastable level, but, that if it does

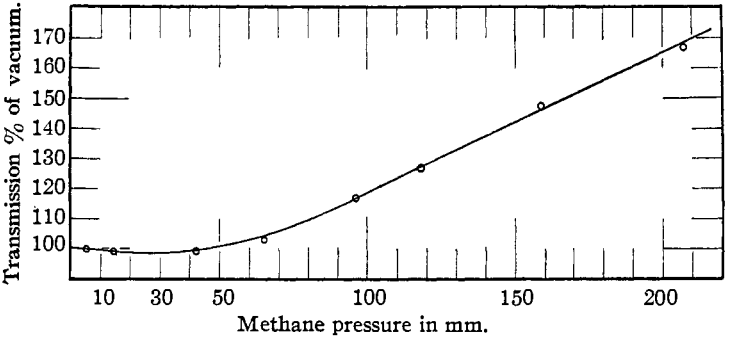

Fig. 7.

bring any considerable number, the transfer between these atoms and the ethane molecule is extremely efficient. Water, for instance, is known to bring about both types of transfer.[12]

Discussion of Results

The fact that methane quenches mercury resonance radiation in the same manner as the more inert type of gas molecules is quite in agreement with the other properties of the methane molecule.[13]

It is interesting to compare the pressure at which the methane quenching curve undergoes a break (about 10 mm.) with the value of the minimum in Zemansky's[8] determination of β, the exponential in the expression for the lifetime of an excited mercury atom in the presence of nitrogen, which is at 8 mm. These should roughly correspond, since the minimum in the β-curve is also due to the presence of a large number of metastable atoms, which are prevented from diffusing to the walls.

A calculation of the number of collisions made by a mercury atom in

[11] Meyer, *Z. Physik*, **37**, 639 (1926).

[12] Gaviola, *Phil. Mag.*, **6**, 1191 (1928).

[13] Glockler, THIS JOURNAL, **48**, 2021 (1926).

diffusing a distance of 1.5 mm. (the average distance traveled in a layer 3 mm. thick, where, in the side of the cell nearest the source of light, about 50% of the excited atoms are formed) using the Einstein displacement equation

$$\Delta X^2 = 2Dt$$

where t is the time in seconds and D the diffusion coefficient, obtained from the value for that of mercury into nitrogen (the values of diffusion coefficients into methane and nitrogen are, as a rule, very close in value) in the "International Critical Tables," and the value of K, the number of collisions per second per atom, gives a value of 7×10^4. The number of collisions made in which one has sufficient energy available to raise a metastable atom to the 2^3P_1 state is about 2.5×10^3, making every atom, in diffusing this distance, suffer about 28 collisions in which it might be raised to the higher level.

These results explain very satisfactorily why methane does not react as do the other hydrocarbons, since it cannot obtain sufficient energy from the excited mercury atoms.

The mechanism of the reactions of the higher hydrocarbons is in all probability quite complicated. In all cases, as soon as some hydrogen is formed, the reactions go in two ways—by the direct action of the excited mercury atoms on the hydrocarbons, and also by the reaction of hydrogen atoms produced by collisions with hydrogen molecules. From the ratios of the $\tau K/p$ values in Table I we can see that with ethane there is an equal probability of hydrogen atom or hydrocarbon decomposition, when hydrogen is present to the extent of 2%, with propane at 6%, and butane at 15%. Thus, in those reactions of Taylor and Hill where hydrogen predominated, the majority of the action came through the agency of hydrogen atoms.

Thanks are due Dr. M. Zemansky for much helpful advice and discussion during the course of this work.

Summary

The quenching of mercury resonance radiation by the gases methane, ethane, propane and butane has been measured, and values for the effective collision cross section have been calculated. Methane has been shown to quench to the metastable level. The results are in agreement with the mercury photosensitized decompositions of these hydrocarbons.

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