

I

THE DECOMPOSITION OF DI-ORTHO-TOLYLIODONIUM IODIDE

II

JOULE-THOMSON COEFFICIENTS OF SOME HYDROCARBON GASES

III

THE HYDRATION OF ACETYLENE

Thesis by

Edwin Russell Kennedy

In Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

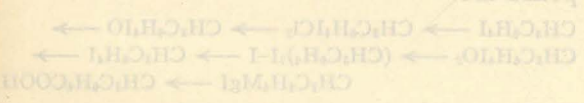
1936

I

THE DECOMPOSITION OF DI-ORTHO-TOLYLIODONIUM IODIDE

found to be almost pure *o*-iodotoluene unaccompanied by any isomeric product the evidence indicates that the decomposition proceeds through an intermediate positively charged σ -tolyl ion in which the positive charge is carried by a carbon atom. The conclusion that a C-I bond rather than a C-H bond breaks first is in agreement with bond energy values.³

Although Heilbronner⁴ concluded that *o*-iodotoluene was the product of this rearrangement, his method of identification did not exclude the presence of the meta isomer. In the present work the reaction product was converted into the acyl magnesium iodide and this by reaction with carbon dioxide was converted into the corresponding toluic acid. This proved to be the pure *ortho* acid, mixed with any *meta* toluic acid or with any methylphthalic acid. The steps involved in the preparation and decomposition of the iodonium compound are



Experimental

Materials.—*o*-Iodotoluene was prepared through the diazo reaction from *o*-toluidine purified by distillation in vacuo after having been crystallized three times. *m*-Iodotoluene was prepared from *m*-nitrotoluene through *o*-toluidine. The

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 489]

The Decomposition of Di-*ortho*-tolylidonium Iodide

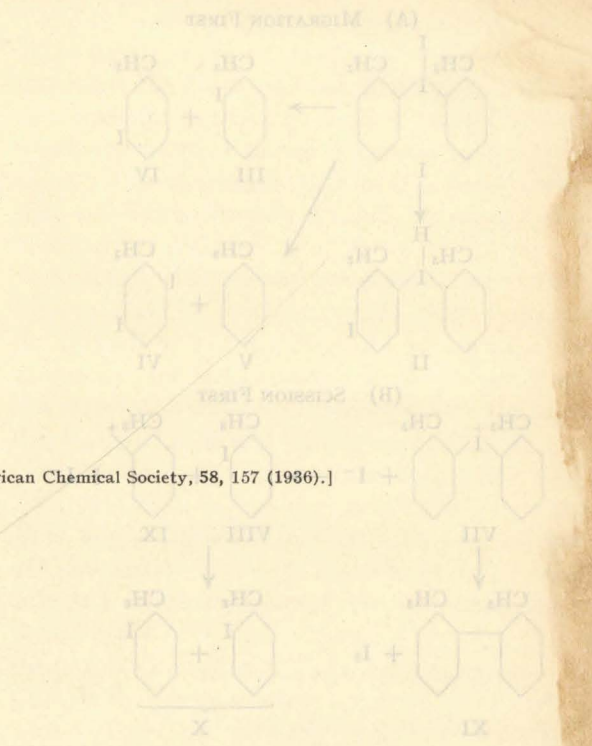
BY H. J. LUCAS, E. R. KENNEDY AND C. A. WILMOT

Introduction

The belief that organic reactions may take place via the mechanism of a positive organic ion in which the carbon atom carries the positive charge is not new.¹ The important role which the positive ion plays in certain molecular rearrangements has been pointed out by others.² Recently, Whitmore³ has interpreted molecular rearrangements on the basis of electron structures.

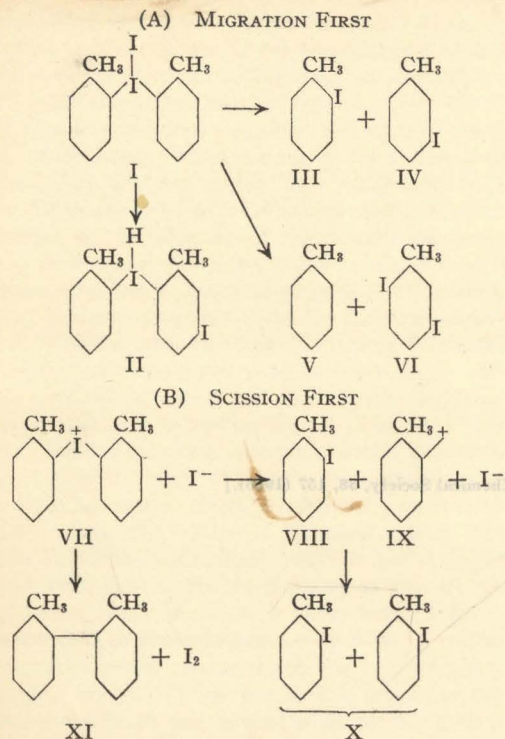
A reaction which may proceed via the mechanism of an intermediate, positively charged positive ion is the decomposition of di-*o*-tolylidonium iodide. From the nature of the reaction product

(1) Euler, *Ber.*, **39**, 2726 (1906); Biilmann, *Ann.*, **388**, 330 (1912); Holmberg, *Ber.*, **59**, 1569 (1926).
 (2) McKenzie, Rogers and Mills, *J. Chem. Soc.*, 778 (1926); Meerwein and Wortmann, *Ann.*, **435**, 190 (1924); Meerwein and Montfort, *ibid.*, **435**, 214 (1924); Meerwein, *ibid.*, **453**, 16 (1927).
 (3) Whitmore, *THIS JOURNAL*, **54**, 3274 (1932).



one may draw conclusions in regard to the mechanism. There are two possible mechanisms by which this decomposition might take place: (a) migration of the iodine to one of the benzene rings in a position *ortho* or *para* to the C-I bond, followed by the scission of a C-I bond; (b) the scission of a C-I bond, followed by the attachment of the resulting positive organic ion to the negative iodide ion. These two mechanisms are pictured below.

On the assumption that the two iodine atoms are held together by a covalent bond (I), the migration of iodine to an *ortho* or *para* position on the benzene ring is quite plausible since atoms or radicals attached to other electronegative atoms (oxygen and nitrogen especially) readily migrate. If migration is the first step, then scission of a



C-I bond in the hypothetical intermediate (II) should lead to the formation of a mixture of equal parts of *o*-iodotoluene (III) and *m*-iodotoluene (IV) or a mixture of equal parts of toluene (V) and 2,5-diiodotoluene (VI) or a mixture of all four compounds.

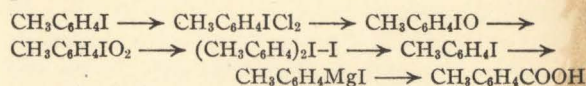
On the other hand, if the original compound is ionized, the iodide ion would not migrate to the ring. A plausible mechanism of the rearrangement might involve first the formation, from di-*o*-tolyliodonium ion (VII), of equal amounts of *o*-iodotoluene (VIII) and positive *o*-tolyl ion (IX) by the scission of a C-I bond, and second the combination of this ion with the negative iodide ion, to form a second molecule of *o*-iodotoluene (X). The reaction product would then be pure *o*-iodotoluene. In case both C-I bonds should break simultaneously, the reaction products would be *o,o'*-bitolyl (XI) and iodine. If the reaction product should prove to be pure *o*-iodotoluene unmixed with the meta isomer or with diiodotoluene, then mechanism B would appear to be established.

The ionic character of iodonium compounds has been generally recognized for years. However, it is now known definitely that the I-I bond in diphenyliodonium iodide is an ionic, not a covalent, bond.⁴ Since the reaction product was

(4) Medlin, *THIS JOURNAL*, **57**, 1026 (1935).

found to be almost pure *o*-iodotoluene uncontaminated by any isomeric product the evidence indicates that the decomposition proceeds through an intermediate, positively charged *o*-tolyl ion in which the positive charge is carried by a carbon atom. The conclusion that a C-I bond rather than a C-H bond breaks first is in agreement with bond energy values.⁵

Although Heilbronner⁶ concluded that *o*-iodotoluene was the product of this rearrangement, his method of identification did not exclude the presence of the meta isomer. In the present work the reaction product was converted into the arylmagnesium iodide and this by reaction with carbon dioxide, into the corresponding toluic acid. This proved to be the pure ortho acid, unmixed with any metatoluic acid or with any methylphthalic acid. The steps involved in the preparation and decomposition of the iodonium compound are



Experimental

Materials.—*o*-Iodotoluene was prepared, through the diazo reaction, from colorless *o*-toluidine purified by distillation *in vacuo* after having been crystallized three times, in the form of the nitrate, from water. *m*-Iodotoluene was prepared from *m*-nitrotoluene through *m*-toluidine. The *m*-nitrotoluene was purified by freezing three times, with removal of unfrozen material, to give a product melting at 16°. The *p*-iodotoluene was prepared from *p*-toluidine (Eastman pract.). The yields of final purified iodotoluenes from the toluidines were, ortho 80%, meta 76% and para 74%.

Properties of the Iodotoluenes.—The ortho isomer was purified by distillation at 745 and 24 mm., the meta and para by distillation at 745 mm. The latter was crystallized from alcohol-water mixture. The ortho and meta were obtained as colorless liquids which slowly darkened in the light, and the para as a cream-colored solid. They remained unchanged for months when kept in the dark and in an atmosphere of carbon dioxide. The properties of the iodotoluenes differ somewhat from previous values. They are shown in Table I.

TABLE I
PHYSICAL CONSTANTS OF IODOTOLUENES

Isomer	Ortho	Meta	Para
B. p., °C., corr.	745 mm. 205.5 24 mm. 95.5	210.0
Sp. gr. 20/20		1.7090	1.6981
Ref. index, n_D^{20}	1.6030	1.6012
M. p., °C., corr.	34.5-35.0

(5) These values are: C-I, 56.5 kg. cal. per mole; C-H, 97.7 kg. cal.

(6) Heilbronner, *Ber.*, **23**, 1815 (1895).

Conversion of Iodotoluenes to the Toluic Acids.—This was done in order to obtain the pure toluic acids and to investigate the yields to be expected when working with small quantities (about 15 g.) of iodotoluenes. The Grignard reagents were first prepared from each of the three pure iodotoluenes. After passing in dry carbon dioxide, dilute sulfuric acid was added. The toluic acids were extracted from the ether with sodium carbonate solution and recovered by acidification of the latter. No essential difference was observed in the behavior of the three iodotoluenes, all giving a yield of about 50%. The addition of a small amount of methyl iodide to the magnesium and ether (1% of the ether by volume) two hours before adding the iodotoluene raised the yield to about 75%. Bitolyl was a by-product, resulting from a Wurtz coupling. Its formation accounts in part for the low yields.

The crude acids melted as follows: ortho, 102.5–103.6°; meta, 108–109°; para, 175–177°; and after crystallization from hot water, ortho, 103.5–103.7°; meta, 110.6–111.2°; para, 178.5–178.8°. Titration against 0.05 *N* sodium hydroxide, standardized against Merck analytical benzoic acid, gave equivalent weights as follows: ortho, 136.1; meta, 136.8; para, 136.5; theoretical is 136.1.

Preparation of Iodosotoluenes.—In order to obtain the intermediate iodosochlorides pure, and in good yield, the method of Willgerodt⁷ was modified by concentrating the chloroform solution and then filtering off the solid iodosochlorides; yield of iodosotoluene, 70%.

The purity of the iodosotoluene was established by iodimetry. In the analysis, the liberation of iodine in a solution containing hydrogen and iodide ions is markedly accelerated by the addition of a few ml. of chloroform. The analytical results indicate that the iodosotoluenes form monohydrates which are stable at room temperature. Thus, three samples of *o*-iodosotoluene dried in the air for three days averaged 92.0% pure on the basis of their oxidizing power, but when dried over sulfuric acid *in vacuo* they averaged 100.4%. The theoretical oxidizing power of the monohydrate is 92.9% that of the anhydrous.

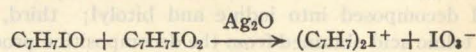
Preparation of *o*-Iodoxytoluene.—The use of hypochlorous acid as the oxidizing agent⁸ for converting the iodoso to the iodoxy compound proved to be unsatisfactory, for an excess of hypochlorite destroys the compound. Steam distillation of the iodosotoluene, according to the procedure of Willgerodt, was found to be satisfactory, since the recovered iodotoluene could be utilized. Two preparations from 50 g. of *o*-iodosotoluene gave *o*-iodoxytoluene in yields of 38 and 34% and iodotoluene in yields of 36 and 49%.

The first sample of iodoxytoluene was dried for two days in air, the second for one day *in vacuo* over concentrated sulfuric acid. Iodometric titration showed the first to have an oxidizing strength of 97.5% on the basis of iodoxytoluene and the second, 98.3%.

Preparation of Di-*o*-tolylidonium Iodide.—Following the method which Meyer and Hartman⁹ used when they obtained a 93% yield of diphenyliodonium iodide, that is, agitation for two days of an equimolar mixture of iodoso and iodoxy compound with an excess of silver oxide sus-

pending in water, only an 18% yield of the *o*-tolyl compound resulted. It was found preferable to grind in a mortar equimolar amounts of the iodosotoluene, iodoxytoluene and freshly precipitated moist silver oxide (9.0, 9.3 and 10.0 g., respectively) with 10 ml. of chloroform and a few ml. of water. At intervals the water was poured off into a flask, more water was added to the mixture in the mortar and the grinding continued. Finally the mixture was allowed to stand overnight. The combined aqueous extracts were reduced by sulfur dioxide, resulting in the precipitation of di-*o*-tolylidonium iodide. A much whiter product is obtained by adding a solution of potassium iodide instead of reducing with sulfur dioxide. The yield of washed and dried product was 44%. A duplicate experiment, using however only 0.5 g. of silver oxide (1/20 molal ratio), gave practically the same yield (43.5%). A third preparation, using 16.5 g. of the iodoso (a slight excess), 16.3 g. of the iodoxy compound and 1.0 g. of silver oxide gave 20.7 g. of the iodide, a yield of 73%. In this case the mixture was allowed to react for two days and the silver oxide was added in two portions.

These results indicate that the rate with which the tolyliodonium ion is formed is much slower than the rate of formation of the corresponding phenyl compound. This may be due in part to lower solubilities of the tolyl compounds and in part to steric hindrance. The results also indicate that silver oxide catalyzes the reaction by which the iodonium compound is formed. The reaction presumably is as follows.



Decomposition of Di-*o*-tolylidonium Iodide.—Preliminary experiments showed that the reaction did not take place until the solid was heated to 150°. The decomposition was effected by immersing in a glycerol bath at 155° a 100-ml. spherical flask containing approximately 16 g. of the iodide. The flask was provided with a 7-mm. diameter reflux tube. About two minutes after immersion the reaction started and was apparently complete within five seconds. A small amount of liquid condensed on the reflux tube but there was not enough to run back into the flask. A small amount of iodine vapor was visible. A small portion of the liquid was analyzed for free iodine and the refractive index determined (Table II).

TABLE II
DATA ON REACTION AND PRODUCT

Experiment.....	1	2
(C ₇ H ₇) ₂ I ₂ taken, g.....	16.35	15.91
Bath temp., °C.....	155	155
Loss during reaction {		
g.....	0.11	0.34
%.....	.07	.22
Iodine present {		
g.....	.0045	.0055
%.....	.38	.46
Refractive index, n _D ²⁰	1.607	1.607

Identification of the Reaction Product.—The bulk of the reaction product was converted into the corresponding toluic acid by the method previously mentioned, with results shown in Table III.

The rearranged tolyl iodide is believed to be nearly pure *o*-iodotoluene for the following reasons: first, the refrac-

(7) Willgerodt, *Ber.*, **26**, 357 (1893).

(8) Willgerodt, *ibid.*, **29**, 1568 (1896).

(9) Meyer and Hartman, *ibid.*, **27**, 426, 502 (1894).

TABLE III

CONVERSION OF REARRANGED TOLYL IODIDE TO TOLUIC ACID

CH ₃ C ₆ H ₄ I	g.....	14.38 ^a	15.32 ^b
	mole.....	0.066	0.070
Magnesium	g.....	1.8	2.2
	mole.....	0.074	0.090
Ether, ml.....		70 ^c	110 ^c
Time, hours	Addition...	3	6
	Stirring....	3	12
Toluic acid	g.....	5.75	6.05
	m. p.....	64.0	63.4
Residue	g.....	102.4-103.0	103.3-103.7
	%.....	1.55	1.50
		25	22.5

^a Plus 15 ml. of anhydrous ether. ^b Plus 60 ml. of anhydrous ether. ^c Plus 0.90 ml. of methyl iodide.

refractive index 1.607 is higher than the value of 1.603 for *o*-iodotoluene, and for that reason the main impurity is not likely to be *m*-iodotoluene, the refractive index of which is 1.601; likewise, it is not likely to be bitolyl, for the refractive index of a 10% solution of crude bitolyl (from the Grignard reaction) in *o*-iodotoluene is 1.592; the presence of the dissolved iodine does not compensate for the influence of any dissolved material because 0.5% of dissolved iodine does not change the refractive index; second, the small percentage of free iodine in the decomposition product (0.46%) shows that less than 1% of the iodonium compound decomposed into iodine and bitolyl; third, the crude toluic acid obtained from the decomposition product is pure *o*-toluic acid, uncontaminated by methylphthalic acid or by any *m*- or *p*-toluic acid, as shown by (a) the equivalent weight (136.7 against theoretical of 136.1), (b) the high melting point of the crude acid, 103.3-103.7°, a value

practically identical with the best value of recrystallized *o*-toluic acid obtained in this work, viz., 103.5-103.7°; (c) the mixed melting point of the crude with the purest *o*-toluic acid, viz., 103.4-103.7°; and (d) the lowering of the melting point of the crude acid by its admixture with the isomeric acids, 5% of which gave these values, meta, 99.5-101.6°; para, 98.5-100°.

Although the yield of *o*-toluic acid was 64%, a part of the reaction product, namely, 22-25%, was accounted for as bitolyl. The molecular weight of the crude bitolyl, as determined by the camphor method,¹⁰ was found to be 204, whereas that of bitolyl is 182.

Since the yield of toluic acid was 64% and that of bitolyl 22-25%, 86-89% of the original material is accounted for. The presence of water in traces, during the preparation of the Grignard reagent, would lead to the formation of some toluene, which would be lost.

Summary

Di-*o*-tolylidonium iodide decomposes at 155° into *o*-iodotoluene and not into a mixture of iodotoluenes. The nature of the reaction product indicates that the ditolylidonium ion splits into *o*-iodotoluene and positively charged *o*-tolyl ion by a scission of the C-I bond. The combining of this ion with the negative iodide ion produces *o*-iodotoluene.

In the formation of di-*o*-tolylidonium iodate from *o*-iodosotoluene and *o*-iodoxytoluene, silver oxide acts catalytically.

(10) Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

PASADENA, CALIFORNIA RECEIVED JULY 30, 1935

TABLE II

DATA ON REACTION AND PRODUCT

Refractive index, n _D ²⁰	1.607	
Iodine present	%.....	0.46
Loss during reaction	%.....	0.7
Bath temp., °C.....	185	
(C ₆ H ₄) ₂ I ⁺ taken, g.....	10.36	
Experiment.....	I	

Identification of the Reaction Product.—The bulk of the reaction product was converted into the corresponding toluic acid by the method previously mentioned, with the results shown in Table I.

The refractive index of the toluic acid obtained in this work is 1.607, which is higher than the value of 1.603 for *o*-toluic acid.

The first sample of iodoxytoluene was dried for two days at 100°C. The second for one day in vacuum over concentrated sulfuric acid. Iodometric titration showed the first to have an oxidizing strength of 97.5% on the basis of iodoxy-

toluene and the second, 98.3%. Preparation of Di-*o*-tolylidonium Iodide.—Following the method of Meyer and Hartman,⁸ used when they obtained a 93% yield of diphenylidonium iodide, that is, reaction for two days of an equimolar mixture of iodoso-

toluene with an excess of silver oxide sus-

preparation of *o*-iodoxytoluene.—The use of hypochlorous acid as the oxidizing agent for converting the toluic acid into the iodoxy compound proved to be unsatisfactory for an excess of hypochlorous destroys the compound.

From the distillation of the iodotoluene, according to the procedure of Willgerodt,⁹ was found to be satisfactory. Two runs of the recovered iodotoluene could be utilized. Two preparations from 50 g. of *o*-iodosotoluene gave *o*-iodoxy-

toluene in yields of 38 and 34% and iodotoluene in yields of 58 and 49%.

The first sample of iodoxytoluene was dried for two days at 100°C. The second for one day in vacuum over concentrated sulfuric acid. Iodometric titration showed the first to have an oxidizing strength of 97.5% on the basis of iodoxy-

II

JOULE-THOMSON COEFFICIENTS OF SOME HYDROCARBON GASES

PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS
 XIII. JOULE-THOMSON COEFFICIENTS OF PROPANE *

B.H.Sage, E.R.Kennedy and W.N.Lacey

Abstract

In determining the thermal properties of hydrocarbons in the gaseous region the Joule-Thomson coefficient is a powerful tool when known as a function of the state. The purpose of the present paper is to describe an apparatus developed to measure this property, to report upon the data obtained for propane, and to outline the usefulness of this measurement in thermal calculations.

The Joule-Thomson coefficient is defined as $(\partial T/\partial P)_H$, which may be considered to be the change in temperature resulting from a very small change in pressure occurring at constant heat content:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{-(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = \frac{-(\partial H/\partial P)_T}{C_p} \quad (1)$$

It may be used to advantage in (a) calculating changes in specific heat at constant pressure of the superheated gas at low pressures; (b) obtaining the partial differential of H with respect to P at constant T at low pressures; (c) calculating the specific heat in the region of the critical state; and (d) constructing throttling curves.

* This article appeared in the May (1936) issue of Industrial and Engineering Chemistry.

Apparatus

Previous experimenters (1) have used throttling experiments to determine the Joule-Thomson coefficient, since the slope of a throttling curve is directly $(\partial T / \partial P)_H$. This method used very large pressure and temperature changes, which, when the derivative μ changes rapidly with the pressure or temperature, leads to inaccurate results. It is thus unsuited for use with most hydrocarbons in the limits of pressure and temperature which are encountered in petroleum formations and for which the present apparatus was designed. The apparatus developed utilized a small automatically maintained constant pressure drop across a radial flow porous plug at a given temperature and pressure; the measurement being that of the fall in temperature of the gas in passing the porous plug. A flow sheet diagram of the apparatus is shown in Figure 1.

A cam pump delivered gas to a header, one valve of which, A, allowed a given amount of gas to by-pass to the pump intake, thus aiding in adjusting the pressure drop across the porous plug. Almost all of the gas not so by-passed passed through the throttle valve, B, and into the outlet chamber of the magnetic valve. The remainder was automatically controlled by the magnetic valve. The gas coming out of the magnetic valve chamber passed through a conditioning coil to insure temperature equilibrium with the thermostated oil bath which surrounded the apparatus. It then passed through the porous plug and returned to the pump. Since the apparatus used an entirely closed circuit it was suited for use with mixtures of known composition over the desired ranges of pressure and

temperature.

The pressure existing in the system was measured by means of fluid pressure scales. The oil-filled tubing from the pressure scale was connected to the system through a mercury trap (3). The pressure reported, however, was the average of the entrance and exit pressures at the plug, having an absolute accuracy of at least 0.5 percent of the pressure reading. Mercury at pressures up to 3000 pounds per square inch could be added to the space below the pump to increase the pressure on the confined gas. The automatically maintained temperature of the oil bath was determined by a calibrated thermometer. It is believed that the maximum temperature variation throughout the bath was 0.02°F , with a localized variation with time at the control heater of 0.005°F .

The cam pump, A, Figure 1, was constructed of cold rolled steel. The stationary contact surfaces were inserts of a special alloyed cast iron. The sliding vanes in the rotor were of hardened tool steel. The rotor was of cold rolled steel, chromium plated. Ball bearings at the base of the rotor took up side thrust. Bearing surfaces were lubricated with a very thin film of petroleum jelly. The pump was driven by a vertical shaft which passed through a packing gland below the oil bath. The pump was driven at nearly constant speed by a belt-connected induction motor. Variable demands upon the pump due to changes in pressure and temperature were adjusted by means of the by-pass valve, A. In operation, this valve was adjusted until just slightly less gas than was necessary to maintain the pressure drop across the porous plug was flowing through the throttle valve, whereupon the

operation of the magnetic valve maintained the desired pressure drop.

The magnetic valve consisted of an iron core sliding vertically in a monel metal tube under the influence of a solenoid coil which surrounded it. A spring served to return the iron core to its original position when the current was broken. The magnetic valve was controlled through a relay by the high pressure manometer which was constructed of 1 inch Shelby tubing surrounded by a steam jacket to maintain constant temperature. An insulated iron rod in one leg of the manometer made contact with the mercury surface and completed the relay circuit when the pressure was at the desired value. The pressure drop at which the manometer operated could be changed by adding or withdrawing mercury. The pressure drop was calibrated at atmospheric pressure by using an auxiliary mercury-in-glass manometer and measuring the difference in levels with a vertical interval cathetometer. For calibration the manometers were connected together and air was very slowly withdrawn from the contact side of the manometers until the signal lamp on the relay flashed on. Another reading was secured by then adding air until the lamp flashed off. The reproducible accuracy of this pressure drop measurement was 0.3 percent. The pressure drop used varied from 0.9 to 1.3 pounds per square inch, as compared to values of 15 to 100 pounds previously used in similar work.

The porous plug was constructed of a fine-grained alundum extraction thimble. The gas entered the bottom of the of the porous plug chamber, flowed up around a radiation

shield and past three thermocouple junctions and then downward to pass into the porous plug. After passing through the lower part of the plug (the upper third being covered with an impervious coating), the gas passed three more thermocouple junctions before leaving the thimble. Pressure lines leading to the high pressure manometer were connected to the high and low pressure sides of the porous plug. The three-junction copper-constantin thermocouples, made of number 36 wire, were strung on a drilled bakelite mounting. This arrangement served also to integrate minute fluctuations in temperature. The thermocouple wire was separately calibrated at the various temperatures used. A high-sensitivity, low resistance galvanometer in connection with a calibrated potentiometer (4) was used to measure the electromotive force and this value, combined with the calibration of the thermocouple wire at the average temperatures encountered, gave the temperature changes. The temperature change could be measured to the same accuracy as the pressure drop (0.3 percent). It was essential that the gas entering the plug be at a uniform temperature and for this reason the gas traversed a conditioning coil of medium sized tubing to bring it to the average temperature of the oil bath. The heaters in the oil bath were necessarily adjusted so that fluctuations in the bath temperature were at a minimum. A signal lamp connected to the relay operating the control heater showed, by the frequency of its operation (5 - 10 seconds), that sensitive temperature control was being maintained. A thermocouple, mounted near the conditioning coil showed that under this condition of operation temperature fluctuations

over short intervals of time were about 0.001°F .

Tests of the Apparatus

The Joule-Thomson coefficients of carbon dioxide, which have been investigated by Burnett (1a), were determined on this apparatus to check up on the reliability of the instrument. The agreement obtained was reasonable, especially at higher pressures. It is worthy of note that several different settings of the differential manometer gave the same Joule-Thomson coefficient. A maximum was obtained in isothermal curves of μ versus pressure at 200 to 300 pounds per square inch, the value then decreasing as the pressure decreased. This trend extends into a region where experimental inaccuracies leave uncertainty as to what values the Joule-Thomson coefficient and $(\partial H/\partial P)_T$ approach as the pressure approaches zero. Values of μ given by Burnett continue to increase as the pressure decreases.

The Joule-Thomson coefficients obtained with the present apparatus would be too low if heat were transferred from one surface of the porous plug to the other faster than the gas flowing could maintain the temperature difference. This effect would be more noticeable at low pressures where the volumetric thermal capacity was smaller. A test was made to indicate the amount of this thermal leakage. With the pump running and the plug at equilibrium at about 30 pounds per square inch pressure of propane, the pump was stopped and readings made of the temperature difference existing in the stationary gas on each side of the plug. Less than ten sec-

onds after the pump was stopped the temperature difference dropped off to less than one half of its equilibrium value, due to the adiabatic expansion of the gas on the high pressure side. Inside of two minutes the temperature difference had risen to its previous value; and then it very slowly decreased. The decrease was so slow that at the end of forty-five minutes the temperature difference was still more than half the value before stopping the pump.

On starting up the pump some time was required for the apparatus to reach equilibrium. Over the period of about one-half hour a gradual shift could be observed in the temperature difference obtained. At lower pressures, due to lower volumetric thermal capacity, this period of reaching equilibrium became longer.

Some fluctuations were noticed in the readings obtained. The galvanometer needle, when connected to the thermocouple, at times oscillated slowly back and forth, especially if the magnetic valve was controlling any considerable proportion of the gas flowing. This oscillation is to be explained in the slight pulsations of the pump and the magnetic valve, causing adiabatic compressions and expansions. The oscillations are regular and have a reproducible center. By proper adjustment of the valves it was possible to decrease the oscillation to a barely noticeable amount, which was about 2 percent of the temperature difference being measured. Violent fluctuations of the temperature difference were noticed when the pressure was brought very close to saturation; showing the presence of a small amount of liquid spray.

Materials

The propane used in this study was obtained from the Philgas Company, Bartleville, Oklahoma. Their analysis showed it to be pure propane, containing neither ethane nor iso-butane in appreciable amounts. The same material was used in previous studies (5) of thermodynamic properties. Carbon dioxide used for testing was the commercial product.

Experimental Results

The Joule-Thomson coefficients of propane gas were measured at six temperatures and at pressures up to 550 pounds per square inch. Several samples were used for each temperature except 220°F. Overlapping measurements were made ascending and descending the pressure scale. The experimental data are shown in Figure 2. However, the isotherms of μ against pressure were drawn from smoothed curves obtained by plotting isobaric curves of μ against temperature. Such a plot is shown in Figure 3. Saturation curves were drawn upon the basis of a knowledge of the vapor pressure of propane (5). Smoothed values read from these plots are listed in Table I. It is felt that the probable accuracy of the listed data is one percent.

Calculated Data

For completeness the Joule-Thomson coefficients of propane for saturated liquid have been included in Figure 2, and those for the condensed region are shown in Figure 4. They can be calculated more accurately than they can be measured directly. The calculation was made by substituting in

equation 1 values of $(\partial H/\partial P)_T$ for the condensed region obtained from P-V-T data (5) and values of C_p . The values of C_p for saturated liquid were measured experimentally (4) and from these were calculated values for the condensed region by evaluating the isothermal change in C_p with increase of pressure. This step was accomplished by graphical integration of the equation:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (2)$$

The latter term is obtainable from the P-V-T measurements.

To illustrate an application of the above data, the specific heat at constant pressure of gaseous propane was calculated and is shown in Figure 5, together with values for liquid propane. The values for the liquid region were obtained in the calculation of μ outlined above. These values are in satisfactory agreement with previously reported results (5) obtained by a different method. The values in the superheated gas region were calculated from C_p of the gas at atmospheric pressure (4) and the integration of $(\partial C_p/\partial P)_T$, which was obtained by differentiating equation 1 with respect to temperature:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial(\partial H/\partial P)_T}{\partial T}\right)_P = -\mu \left(\frac{\partial C_p}{\partial T}\right)_P - C_p \left(\frac{\partial \mu}{\partial T}\right)_P \quad (3)$$

In evaluating equation 3, μ and $(\partial \mu/\partial T)_P$ were known throughout the pressure and temperature ranges, while C_p and $(\partial C_p/\partial T)_P$ were known only at atmospheric pressure but throughout the temperature range. Values of C_p for higher pressures were obtained by progressive approximative integration of the equa-

tion. The agreement of these values of specific heat when compared with previous tentative values (2) was unsatisfactory near saturation, indicating the possible presence of traces of oil in the apparatus during the P-V-T work, which would affect the results strongly in this region. The agreement obtained by calculation of $-T(\partial^2 V / \partial T^2)_P$ for the gas from P-V-T data and comparison with the values of $(\partial C_p / \partial P)_T$ obtained above was considered satisfactory.

A further application of the Joule-Thomson data lies in the calculation of $(\partial H / \partial P)_T$ for the superheated gas region. Rearranging equation 1:

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_p \quad (4)$$

Values calculated by equation 4, which are substantially independent of P-V-T data and depend only upon Joule-Thomson and specific heat measurements, are shown in Figure 6. Changes in heat content calculated by integration of values shown in the curves of Figure 6 are in good agreement with those calculated from P-V-T data, except near saturation. However, high accuracy is required in P-V-T data in the calculation of $(\partial H / \partial P)_T$ and is markedly affected near saturation by traces of oil in the apparatus.

Throttling curves may also be constructed by the use of Joule-Thomson data, but this calculation has not been made here since such curves have already been published (2).

TABLE I
Joule-Thomson Coefficients of Gaseous Propane

Abs. Pressure Lb./Sq. In.	μ , °F per pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. gas	0.3040	0.2677	0.2589	0.2518	0.217	--
25	0.2150	0.1824	0.1542	0.1339	0.116	0.100
50	0.2409	0.1995	0.1658	0.1433	0.1232	0.1040
100	0.2831	0.2242	0.1862	0.1589	0.1340	0.1100
150	--	0.2475	0.2052	0.1732	0.1436	0.1158
200	--	--	0.2252	0.1853	0.1506	0.1225
250	--	--	0.2468	0.1986	0.1575	0.1288
300	--	--	--	0.2152	0.1653	0.1342
350	--	--	--	0.2353	0.1735	0.1410
400	--	--	--	--	0.1818	0.1458
450	--	--	--	--	0.1925	0.1500
500	--	--	--	--	0.2080	0.1540
550	--	--	--	--	--	0.1557

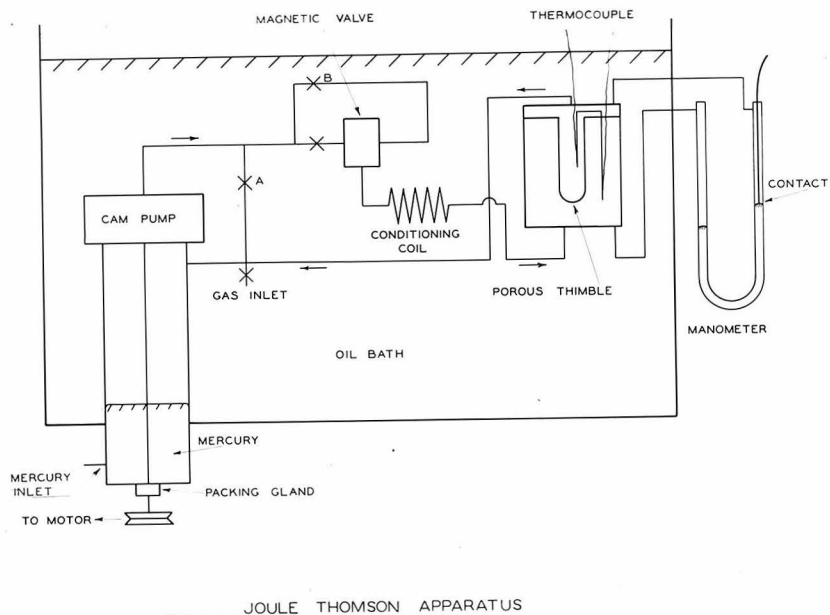


Figure 1.
Diagram of Apparatus

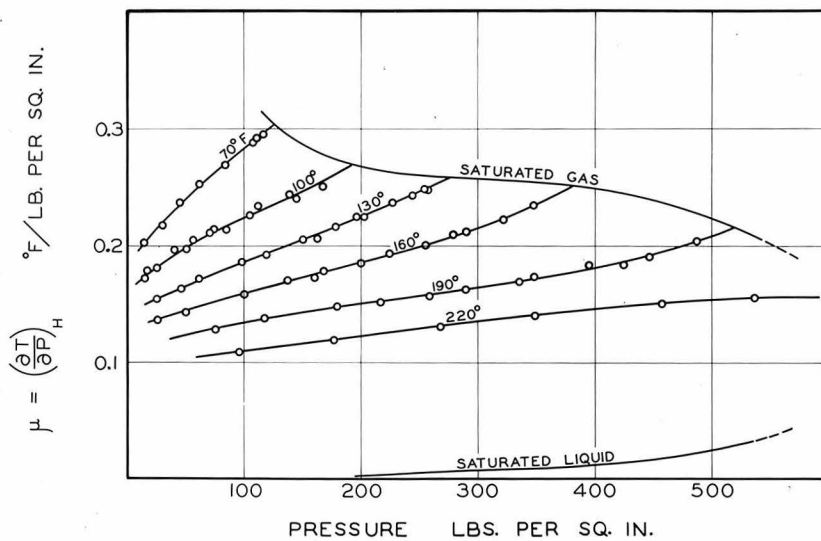


Figure 2.
Experimental Values of Joule-Thomson Coefficients
of Propane Gas

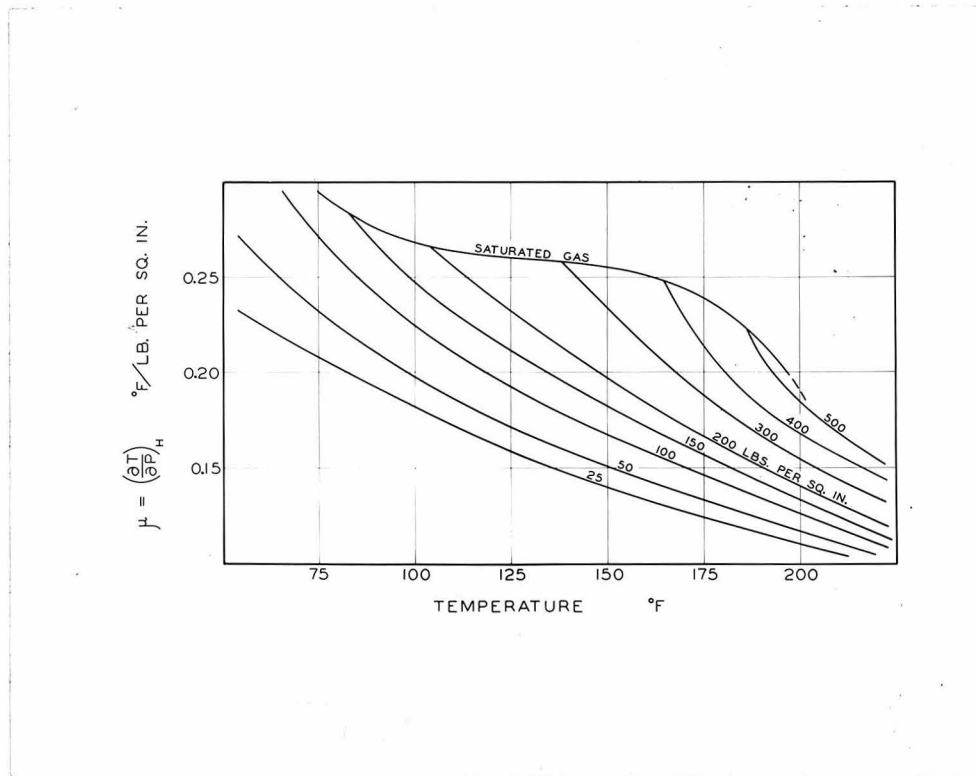


Figure 3.
Joule-Thomson Coefficient of Propane Gas as
Function of Temperature

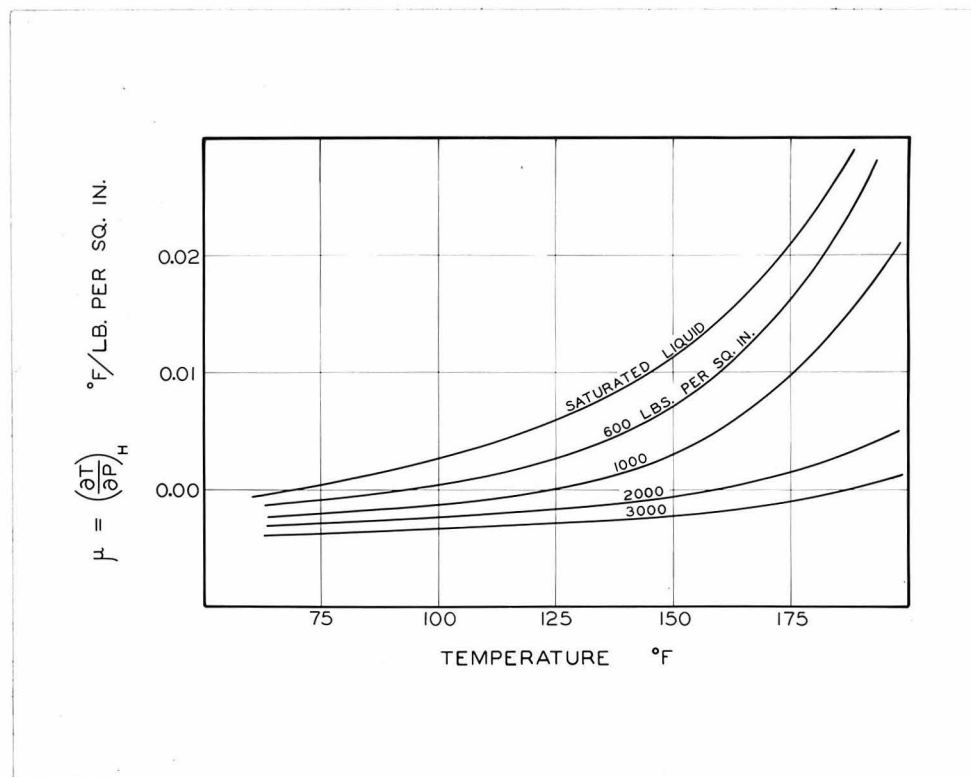


Figure 4.
Joule-Thomson Coefficient of Liquid Propane
as Function of Temperature

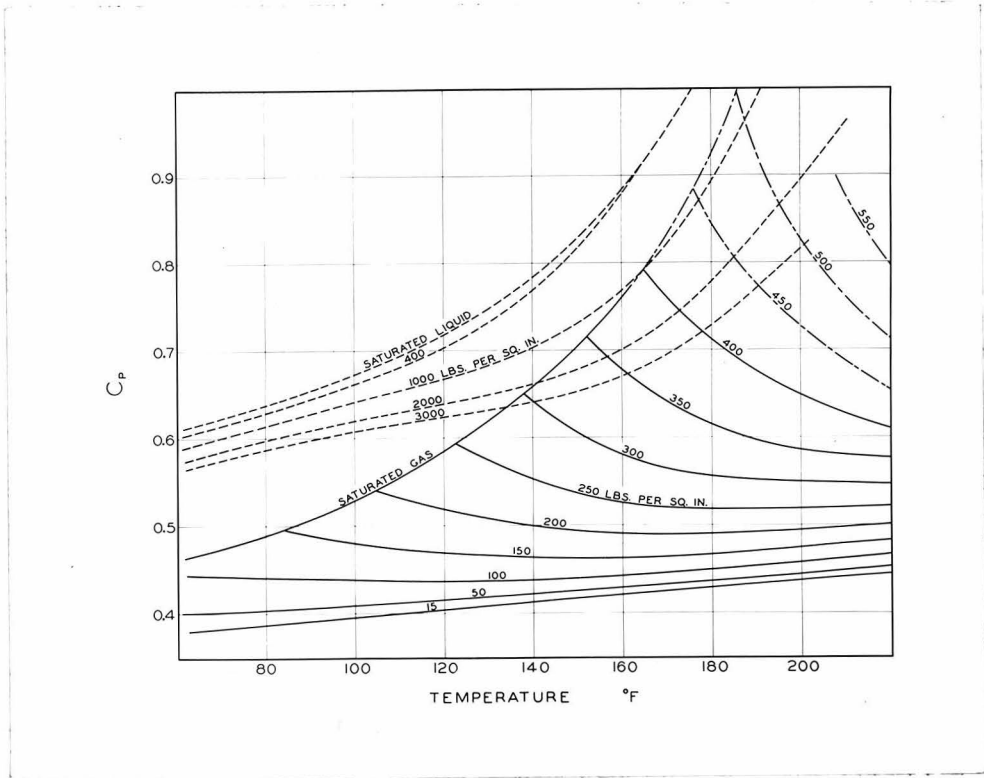


Figure 5.
Specific Heat at Constant Pressure of Gaseous and Liquid Propane

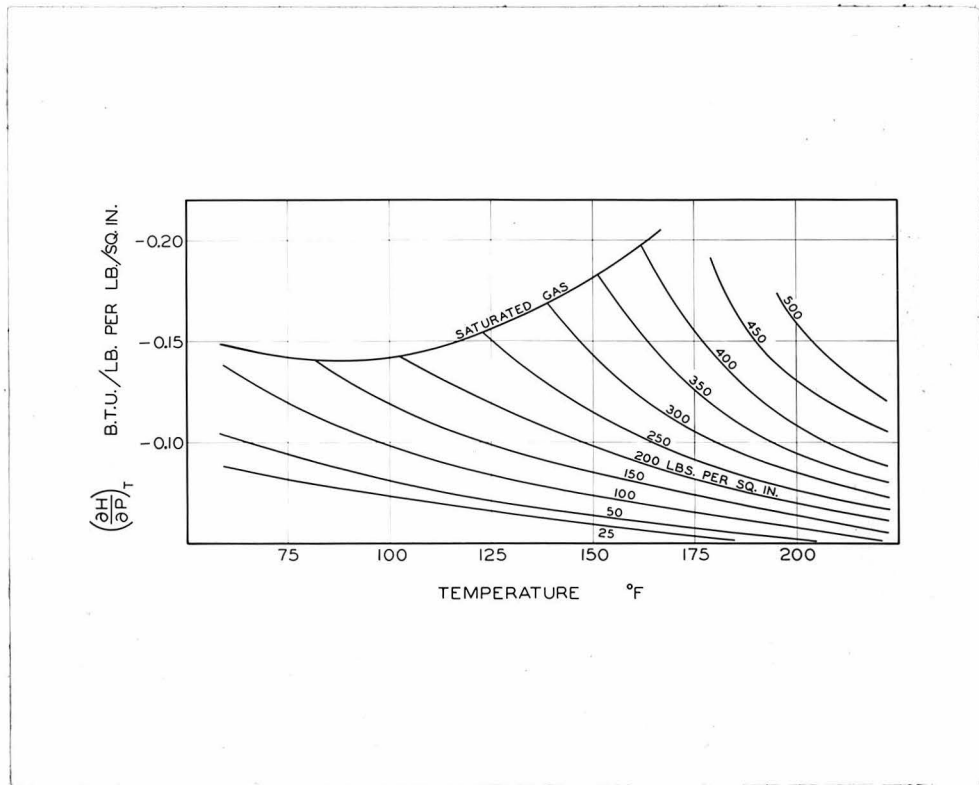


Figure 6.
Values of $(\frac{\partial H}{\partial P})_T$ for Gaseous Propane

Acknowledgment

The financial assistance of the American Petroleum Institute in this work, carried out as a part of the work of its Research Project 37, is gratefully acknowledged. Thanks are due D.S.Clark for suggestions regarding the design of the cam pump and for the special cast iron used therein.

Literature Cited

1. a) Burnett, E.S., Phys.Rev., 22, 590 (1923).
b) Hoxton, L.G., *ibid.*, 13, 438 (1919).
c) Pattee, E.C., and Brown, G.G., Ind.Eng.Chem. 26, 511 (1934).
d) Roebuck, J.R., Proc.Am.Acad., 60, 537 (1925).
e) Roebuck, J.R., *ibid.*, 64, 287 (1930).
f) Roebuck, J.R., and Osterberg, H., Phys.Rev., 43, 60 (1933).
2. Lacey, W.N., and Sage, B.H., Petroleum World, Dec. 1934.
3. Sage, B.H., and Lacey, W.N., Ind.Eng.Chem., 26, 103 (1934).
4. Sage, B.H., and Lacey, W.N., *ibid.*, 27, 1484 (1935).
5. Sage, B.H., Schaafsma, J.G. and Lacey, W.N., *ibid.*, 26, 1218 (1934).

PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

XIV. JOULE-THOMSON COEFFICIENTS OF n-BUTANE AND n-PENTANE *

E.R.Kennedy, B.H.Sage and W.N.Lacey

Abstract

Joule-Thomson coefficients were experimentally determined for n-butane gas at a series of temperatures from 70°F to 220°F and at pressures from atmospheric to those approaching saturation pressures. Similar measurements for n-pentane were made, the lowest temperature used being 130°F in this case. The results are compared with those for propane at equal reduced temperatures and pressures. From the experimental data were calculated values of specific heat at constant pressure and of isothermal change of heat content with change of pressure.

The Joule-Thomson coefficient is defined as $(\partial T/\partial P)_H$, which may be considered to be the change in temperature resulting from a very small change in pressure occurring at constant heat content. Some of its uses in thermodynamic calculations have been indicated in a previous paper of this series (3).

Direct experimental information relating to the Joule-Thomson coefficients of hydrocarbon gases has been sel-

*This article has been accepted for publication by the editors of Industrial and Engineering Chemistry and will appear in the June (1936) issue.

dom reported in the literature. Pattee and Brown (1) report values for n-pentane and painter's naphtha for temperatures above 200°F obtained by evaluation of changes of heat content (enthalpy) resulting from throttling the gases, using pressure drops ranging from 35 to 991 pounds per square inch.

The methods and apparatus used in the present investigation have been previously reported (3). The determination consisted essentially in circulating a sample of gas continuously through a porous plug, a constant small pressure drop being automatically maintained through the plug and the corresponding change in temperature being measured. The only modification of the apparatus found necessary was variation of the permeability of the porous plug to give suitable pressure drops at optimum gas velocities. No variation in the value of the coefficient was observed until the rate of flow had been decreased to such an extent that heat conduction through the plug wall began to have an appreciable effect upon the temperature of the slowly moving gas on the downstream side.

Materials

The sample of n-butane used in this work was obtained from the Phillips Petroleum Company, who submitted the following special analysis with it: 99.7% n-butane and 0.3% iso-butane. Results obtained with this sample showed no appreciable difference from corresponding values using a less pure sample, indicating that small amounts of impurities of similar character do not cause serious impairment of accuracy.

This less pure material was used in earlier studies (4, 5) and consisted of 99.21% n-butane, 0.18% iso-butane and 0.61% iso-pentane.

The n-pentane was obtained from the same company. Its analysis showed it to consist of 99.3% of n-pentane and 0.7% of iso-pentane. The same material was used in earlier work (6).

Experimental Results

Measurements were made upon n-butane gas at six temperatures from 70°F to 220°F and at pressures as close to saturation as feasible, the highest being approximately 200 pounds per square inch absolute at 220°F. The experimental results were obtained by two investigators independantly, upon several different samples at each temperature. Readings were taken subsequent to increase and to decrease of total pressure. The pressure drop across the porous plug was in all cases approximately 1 pound per square inch. These results are shown by the points in Figure 7. The precision of the various measurements was the same as was the case in the similar study of propane (3). Figure 8 shows values taken from the curves of Figure 7 replotted on a μ versus temperature diagram. The saturation curves of these two figures were constructed from vapor pressure data as yet unpublished, by an extrapolation of the isothermal curves of Figure 7 to the corresponding vapor pressures and then connecting these points by a smooth curve. Values read from large-scale curves corresponding to Figure 7 are presented in Table II. It is believed

that the accuracy of these values is approximately 1 percent.

The measurements on n-pentane were made in a manner entirely analogous to those on n-butane. In this case, however, the liquid pentane was boiled for a short time under reduced pressure to eliminate dissolved air before being transferred to the apparatus. The low vapor pressure of n-pentane at 70°F and 100°F precluded satisfactory measurements at those temperatures because of the small mass-velocities obtainable in the circulation system. The maximum pressure studied at 220°F was approximately 70 pounds per square inch. The results are shown in Figures 9 and 10 and the values taken from the smooth curves are listed in Table III. The values are believed to be accurate to 1 percent. The dashed-line curves in Figures 9 and 10 represent estimated values resulting from short extrapolations. Vapor pressure values used in locating the line for saturated gas were taken from a previous publication (6). In Figures 7 to 14 inclusive, the results for each of the materials were plotted with the same scale and coordinate range (except the pressure scales of Figures 7 and 9) in order that the differences could be visualized readily.

Values of the specific heat at constant pressure for each substance in the gaseous state were calculated from the experimental data presented above. These calculations involved the solution of the following equation from atmospheric pressure to each pressure concerned, as described previously for propane (3):

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\mu\left(\frac{\partial C_p}{\partial T}\right)_P - C_p\left(\frac{\partial \mu}{\partial T}\right)_P .$$

In the case of n-butane, the values of C_p at atmospheric pressure were obtained from a previous investigation (4). Those for n-pentane were not available and so were estimated from the corresponding values for propane and n-butane (4). The variation from one member of the series to the next is small enough that an uncertainty of only about 1 percent is involved in this estimation. Furthermore, such uncertainty would cause only a small vertical displacement of the specific heat curves without affecting their slopes. The values obtained from such calculations are shown in Figures 11 and 12. The curves for saturated liquid were shown for comparison, being constructed from information taken from earlier papers of this series (2, 3).

A further use may be made of the Joule-Thomson coefficients in calculating isothermal changes of heat content with change of pressure by a method which is independent of P-V-T measurements and which therefore offers a valuable check upon values obtained through these measurements. Since

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_p$$

the values of μ and of C_p previously discussed can be combined to obtain the desired result. Such calculations were the basis for the curves shown in Figures 13 and 14. Values of $(\partial H/\partial P)_T$ are useful because, by suitable integration, isothermal changes in heat content can be calculated for various changes in pressure.

The Joule-Thomson coefficients of the three gases, propane, n-butane, and n-pentane furnish a sufficient basis

for a comparison. Such a comparison can be made advantageously by reference to Figure 15. The values of μ are there plotted against reduced pressure (ratio of actual pressure to critical pressure) for a series of reduced temperatures. The solid lines show the curves for n-butane while the marked points indicate values obtained from the n-pentane curves presented above. The agreement for these two hydrocarbons is good. However, values for propane (3), as illustrated by the dashed line curves for reduced temperature of 0.80 and 0.85, show marked deviation from the other curves. This is not surprising, it being expected that the first few members of a homologous series of compounds differ from the rest when compared on a reduced basis. It is seen that the curves for propane and n-pentane at the lower pressures lie upon opposite sides of those for n-butane, as would be expected. Since the curves for n-butane and n-pentane so nearly coincide, it follows that the values of μ for these two substances must be nearly equal at their critical states.

TABLE II
Joule-Thomson Coefficients of Gaseous n-Butane

Abs. Pressure Lb./Sq. In.	μ , °F per pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. gas	(0.3750)	(0.3336)	(0.2984)	(0.2712)	(0.2501)	(0.2295)
Atmos.	0.2885	0.2343	0.1996	0.1708	0.1430	0.1173
20	0.3164	0.2486	0.2086	0.1772	0.1472	0.1200
40	--	0.3012	0.2410	0.1988	0.1634	0.1310
60	--	--	0.2706	0.2184	0.1778	0.1412
80	--	--	0.2954	0.2362	0.1910	0.1512
100	--	--	--	0.2526	0.2032	0.1608
125	--	--	--	--	0.2176	0.1720
150	--	--	--	--	0.2330	0.1830
175	--	--	--	--	0.2476	0.1947
200	--	--	--	--	--	0.2069
225	--	--	--	--	--	0.2188

TABLE III
Joule-Thomson Coefficients of Gaseous n-Pentane

Abs. Pressure Lb./ Sq. In.	μ , °F per pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. gas	--	--	(0.3570)	(0.3202)	(0.2926)	(0.2660)
Atmos.	--	--	0.2838	0.2288	0.1952	0.1720
20	--	--	0.3168	0.2470	0.2068	0.1802
30	--	--	--	0.2810	0.2284	0.1950
40	--	--	--	0.3134	0.2496	0.2090
50	--	--	--	--	0.2684	0.2214
60	--	--	--	--	0.2856	0.2328
70	--	--	--	--	--	0.2432
80	--	--	--	--	--	0.2528
90	--	--	--	--	--	(0.2620)

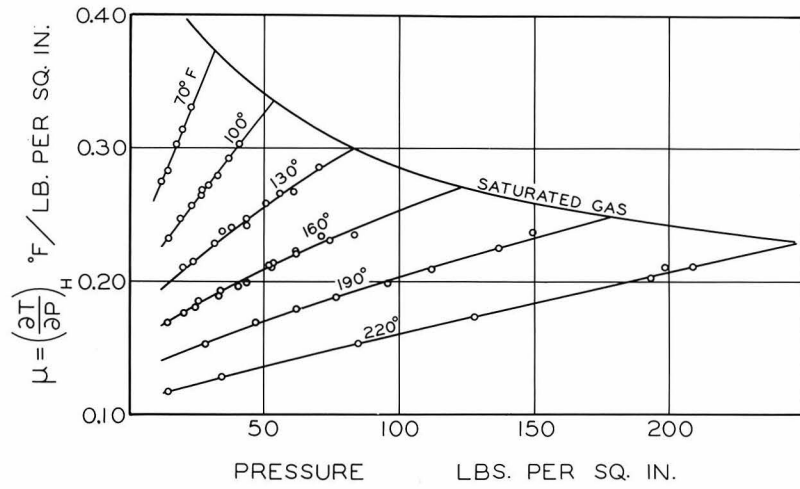


Figure 7.
Experimental Results for n-Butane Gas

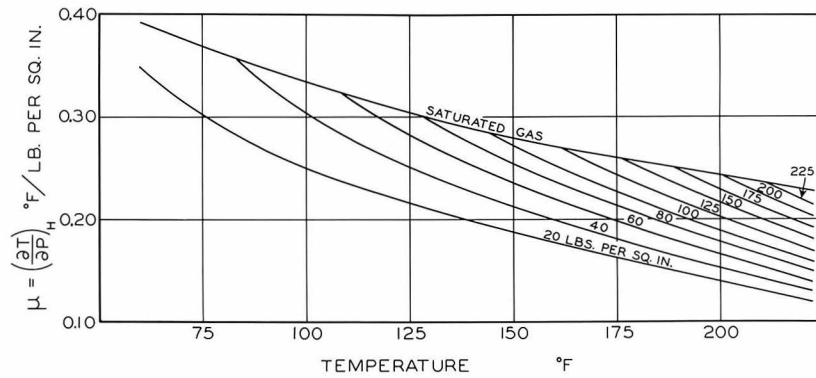


Figure 8.
Effect of Temperature on the Coefficients of n-Butane

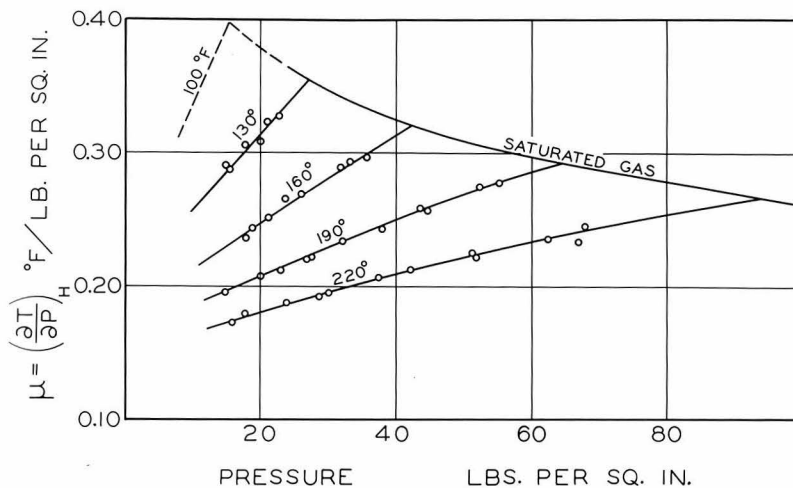


Figure 9.
Experimental Results for n-Pentane Gas

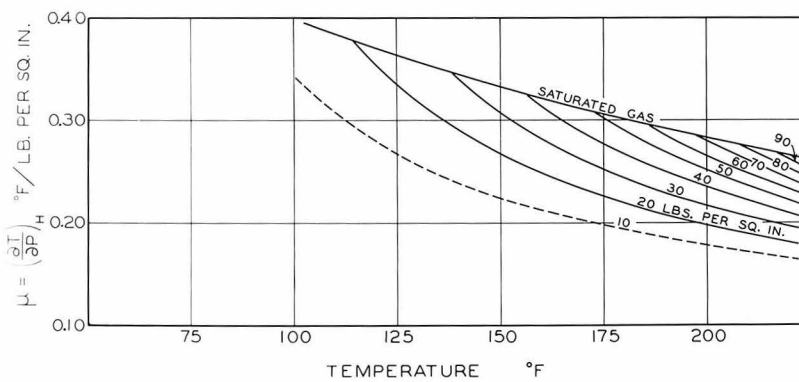


Figure 10.
Effect of Temperature on the Coefficients for n-Pentane

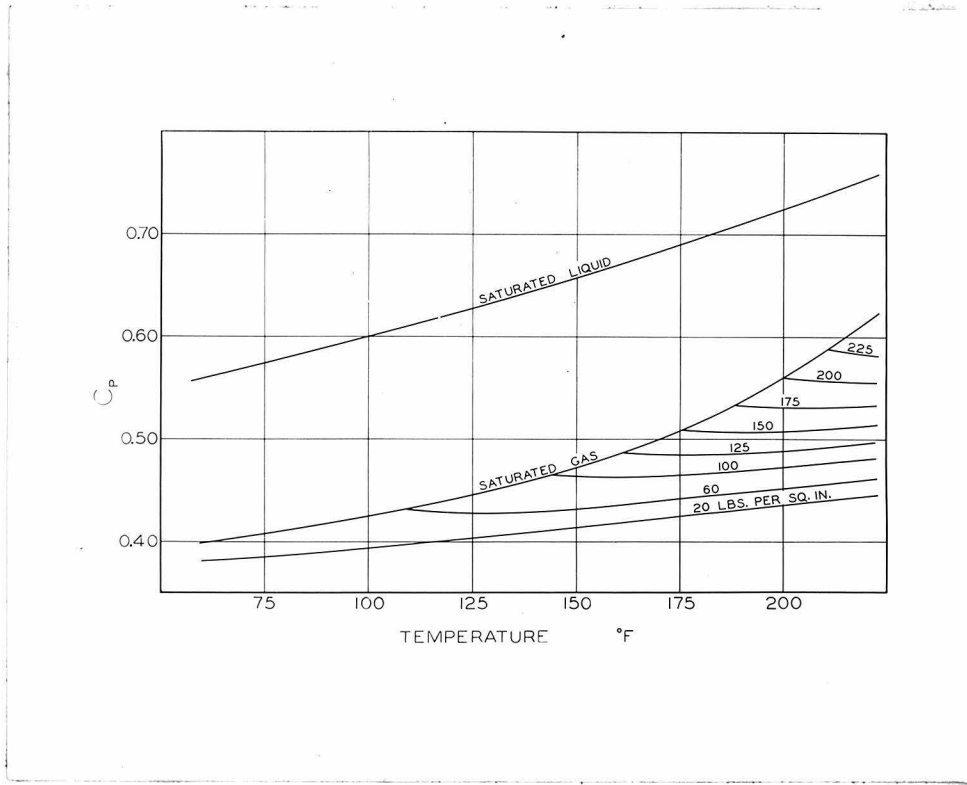


Figure 11.
Specific Heat at Constant Pressure for n-Butane Gas

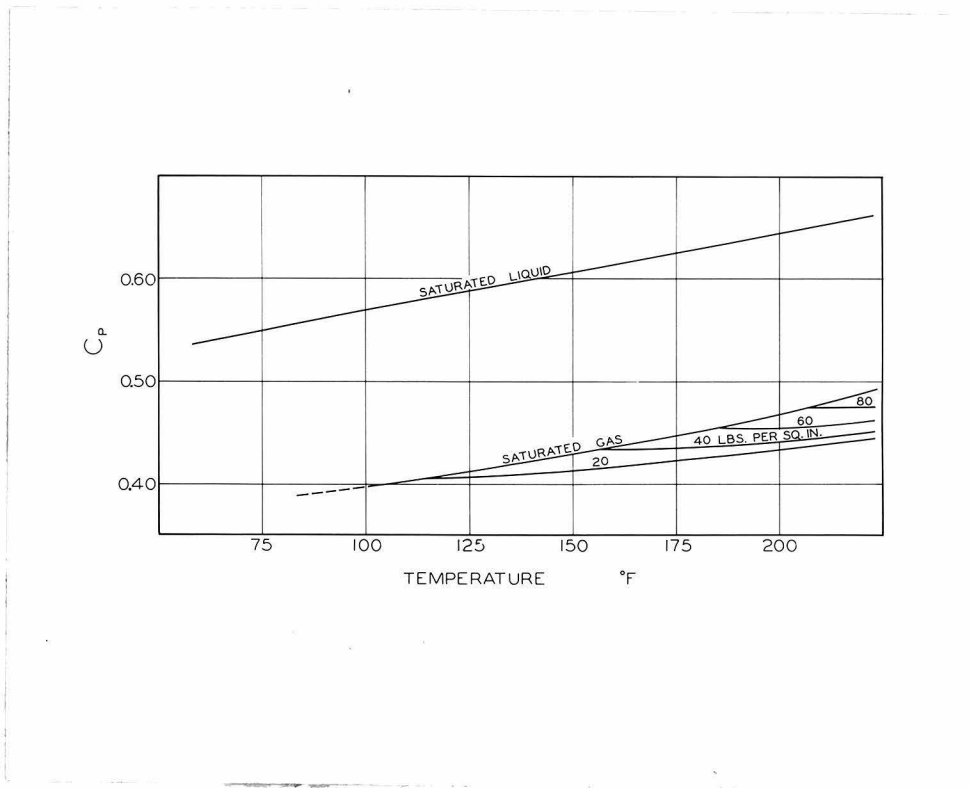


Figure 12.
Specific Heat at Constant Pressure for n-Pentane Gas

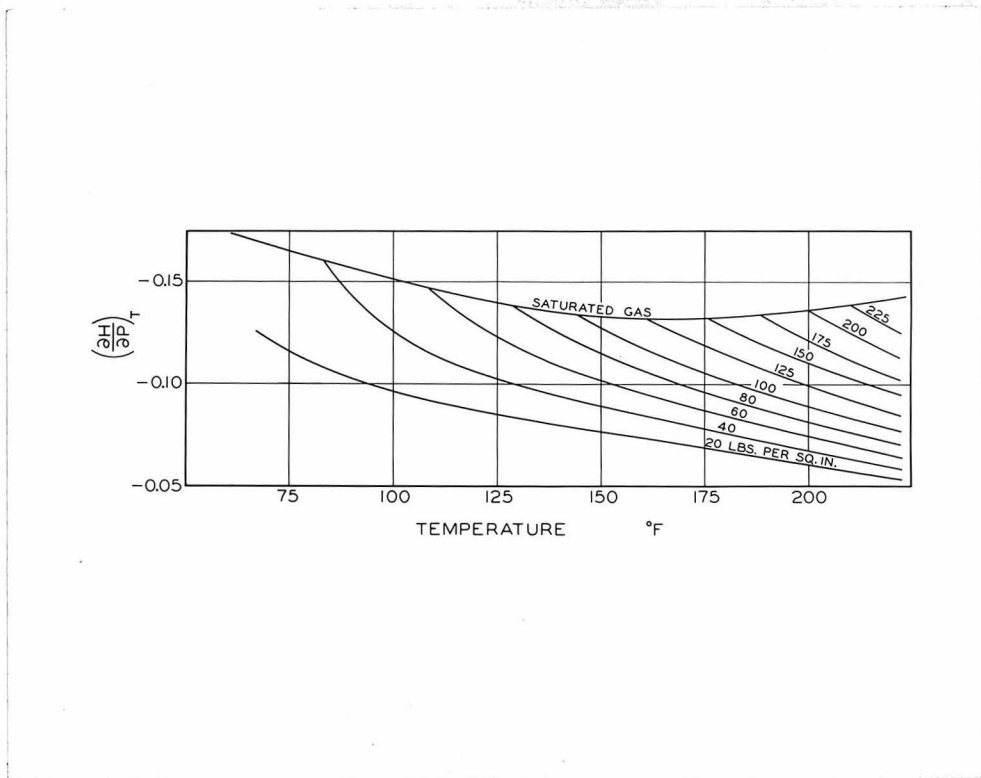


Figure 13.
Isothermal Change in Heat Content of n-Butane Gas with Change of Pressure, in Btu per pound / pound per square inch

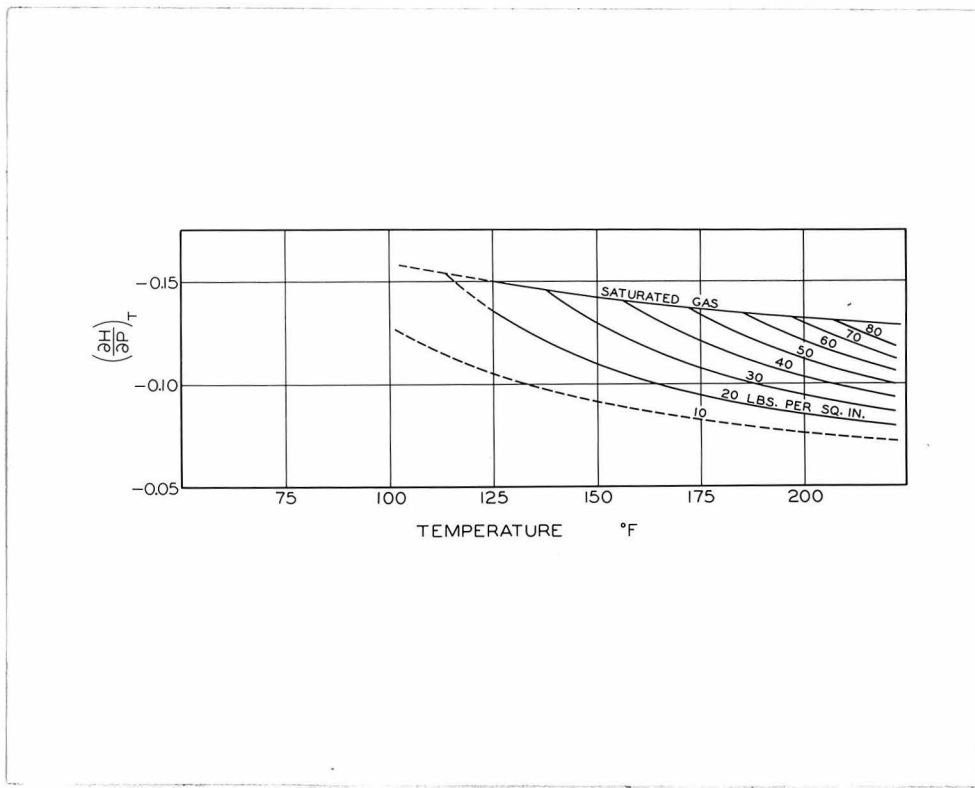


Figure 14.
Isothermal Change in Heat Content of n-Pentane Gas with Change of Pressure, in Btu per pound / pound per square inch

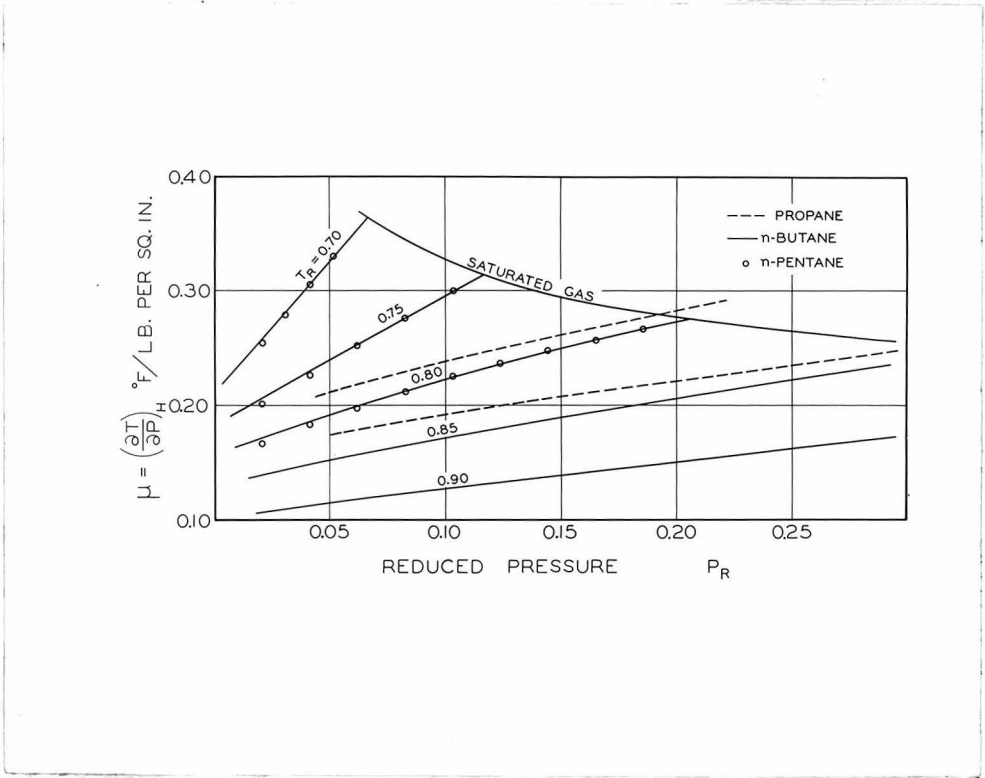


Figure 15.
Comparison of Coefficients for Three Gases at the Same
Reduced Pressures and Temperatures

Acknowledgments

The authors wish to acknowledge indebtedness to the American Petroleum Institute for financial support of the investigation, which was carried on under its Research Project 37.

J.A.Davies assisted materially by making a number of the experimental measurements. D.C.Webster contributed to the preparation of the figures.

Literature Cited

1. Pattee, E.C. and Brown, G.G., Ind.Eng.Chem., 26, 511(1934).
2. Sage, B.H., Backus, H.S., and Vermeulen, T.,
 ibid., 28, 489 (1936).
3. Sage, B.H., Kennedy, E.R. and Lacey, W.N.,
 ibid., 28, (1936).
4. Sage, B.H. and Lacey, W.N., ibid., 27, 1484 (1935).
5. Sage, B.H. and Lacey, W.N., ibid., 28, 106 (1936).
6. Sage, B.H., Schaafsma, J.G. and Lacey, W.N.,
 ibid., 27, 48 (1935).

Appendix to Part II

This section comprises tables of the values presented as curves in Figures 5, 6, 11, 12, 13 and 14. Tables IV to VI inclusive contain values of specific heat in Btu per pound per °F for propane, n-butane and n-pentane respectively. Atmospheric pressure values are tabulated in red to emphasize the fact that these values are the basis for the calculation of all others in the same table. As mentioned previously the atmospheric values for n-pentane result from extrapolation rather than from experimental measurement. Tables VII to IX inclusive present values of $(\partial H/\partial P)_T$ for the three hydrocarbons calculated from measured values of μ previously tabulated and values of C_p given in Tables IV to VI. The tabulated values have an estimated accuracy of 2 percent.

For convenience vapor pressure and critical data for the three hydrocarbons are here listed and are taken from work of the A.P.I. Research Project 37 (except the critical data of n-butane and n-pentane, which are from I.C.T.).

Temperature	Saturation Pressure Lbs./ Sq.In.		
	Propane	n-Butane	n-Pentane
70°F	126.0	31.67	8.49
100	189.5	52.81	15.62
130	273.8	82.59	26.37
160	380.0	123.7	42.15
190	522.7	178.5	64.13
220	--	249.2	94.02
212.2	643.3*	--	--
307.8	--	551.4*	--
387.0	--	--	484.8*

*critical

TABLE IV

Specific Heat at Constant Pressure of Gaseous Propane

Abs. Pressure Lb./ Sq. In.	C_p , Btu per pound per °F					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. gas	0.473	0.529	0.620	0.761	--	--
Atmos.	0.383	0.396	0.408	0.420	0.433	0.445
25	0.387	0.401	0.410	0.422	0.434	0.447
50	0.401	0.410	0.418	0.428	0.440	0.453
100	0.442	0.438	0.437	0.442	0.454	0.466
150	--	0.479	0.465	0.462	0.470	0.482
200	--	--	0.508	0.490	0.492	0.500
250	--	--	0.576	0.525	0.518	0.522
300	--	--	--	0.580	0.552	0.546
350	--	--	--	0.677	0.595	0.575
400	--	--	--	--	0.676	0.609
450	--	--	--	--	0.775	0.653
500	--	--	--	--	--	0.712
550	--	--	--	--	--	0.796

TABLE V

Specific Heat at Constant Pressure of Gaseous n-Butane

Abs. Pressure Lb./ Sq. In.	Cp, Btu per pound per °F					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. gas	0.404	0.424	0.450	0.485	0.536	0.615
Atmos.	0.378	0.390	0.403	0.416	0.429	0.442
20	0.383	0.392	0.405	0.417	0.431	0.444
40	--	0.406	0.413	0.425	0.438	0.451
60	--	--	0.428	0.436	0.447	0.460
80	--	--	0.447	0.447	0.457	0.469
100	--	--	--	0.463	0.469	0.480
125	--	--	--	--	0.486	0.496
150	--	--	--	--	0.506	0.513
175	--	--	--	--	0.532	0.533
200	--	--	--	--	--	0.556
225	--	--	--	--	--	0.582

TABLE VI

Specific Heat at Constant Pressure of Gaseous n-Pentane

Abs. Pressure Lb./ Sq. In.	C _p , Btu per pound per °F					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. Gas	--	--	0.416	0.437	0.458	0.488
Atmos.	--	--	(0.402)	(0.413)	(0.427)	(0.441)
20	--	--	0.407	0.416	0.428	0.442
30	--	--	--	0.424	0.432	0.445
40	--	--	--	0.434	0.438	0.450
50	--	--	--	--	0.445	0.455
60	--	--	--	--	0.454	0.461
70	--	--	--	--	--	0.468
80	--	--	--	--	--	0.476
90	--	--	--	--	--	0.484

TABLE VII

Isothermal Change in Heat Content of Propane Gas
with Change of Pressure

Abs. Pressure Lb./ Sq. In.	$(\partial H/\partial P)_T$, Btu per pound / pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. Gas	-0.1438	-0.1416	-0.1604	-0.1917	--	--
25	-0.0832	-0.0731	-0.0649	-0.0567	-0.0510	-0.0448
50	-0.0966	-0.0810	-0.0693	-0.0613	-0.0541	-0.0471
100	-0.1251	-0.0984	-0.0813	-0.0703	-0.0610	-0.0513
150	--	-0.1183	-0.0955	-0.0799	-0.0675	-0.0558
200	--	--	-0.1144	-0.0908	-0.0738	-0.0613
250	--	--	-0.1421	-0.1043	-0.0819	-0.0672
300	--	--	--	-0.1248	-0.0918	-0.0734
350	--	--	--	-0.1594	-0.1037	-0.0808
400	--	--	--	--	-0.1230	-0.0888
450	--	--	--	--	-0.1492	-0.1069
500	--	--	--	--	--	-0.1225

TABLE VIII

Isothermal Change in Heat Content of n-Butane Gas
with Change of Pressure

Abs. Pressure Lb./ Sq. In.	$(\partial H/\partial P)_T$, Btu per pound / pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. Gas	-0.1680	-0.1511	-0.1379	-0.1315	-0.1341	-0.1412
Atmos.	-0.1091	-0.0905	-0.0802	-0.0710	-0.0614	-0.0520
20	-0.1214	-0.0965	-0.0843	-0.0742	-0.0640	-0.0534
40	--	-0.1241	-0.0996	-0.0840	-0.0714	-0.0592
60	--	--	-0.1166	-0.0949	-0.0788	-0.0649
80	--	--	-0.1355	-0.1064	-0.0866	-0.0710
100	--	--	--	-0.1169	-0.0948	-0.0773
125	--	--	--	--	-0.1059	-0.0855
150	--	--	--	---	-0.1179	-0.0940
175	--	--	--	--	-0.1317	-0.1038
200	--	--	--	--	--	-0.1149
225	--	--	--	--	--	-0.1274

TABLE IX

Isothermal Change in Heat Content of n-Pentane Gas
with Change of Pressure

Abs. Pressure Lb./ Sq. In.	$(\partial H / \partial P)_T$, Btu per pound / pound per square inch					
	70°F	100°F	130°F	160°F	190°F	220°F
Sat. Gas	--	--	-0.1484	-0.1398	-0.1341	-0.1299
Atmos.	--	--	-0.1149	-0.0950	-0.0835	-0.0795
20	--	--	-0.1290	-0.1028	-0.0886	-0.0797
30	--	--	--	-0.1190	-0.0988	-0.0869
40	--	--	--	-0.1360	-0.1093	-0.0939
50	--	--	--	--	-0.1195	-0.1007
60	--	--	--	--	-0.1297	-0.1073
70	--	--	--	--	--	-0.1137
80	--	--	--	--	--	-0.1202
90	--	--	--	--	--	-0.1269

III

THE HYDRATION OF ACETYLENE

THE HYDRATION OF ACETYLENE

Abstract

An analytical method for the determination of acetylene in aqueous solution is described together with tests to ascertain its validity. Rates of homogeneous reaction were experimentally determined for the mercuric sulfate catalysed hydration of acetylene in sulfuric acid solution. The dependence of rate upon acetylene and mercuric sulfate is established and the effect of acetaldehyde is discussed.

A well known industrial method for the production of acetaldehyde involves the hydration of acetylene in sulfuric acid solutions containing mercuric sulfate. Other acids besides sulfuric likewise hydrate acetylene in the presence of their mercury salts. Ordinarily, when this process is carried out, there is present an amorphous white precipitate of some organic mercury compound.

The nature of the compounds present as precipitates during the reaction is not known but several investigators have proposed various formulas which agree with empirical data. Whitmore (7) indicates that the precipitate probably varies in composition with varying conditions of formation. He believes it probable that the organic compounds are not the real catalysts but may be products of side reactions and that the reaction is catalysed by mercuric ions in acid solu-

tion. Vogt and Nieuwland (6) point out that it is impossible to detect any inorganic salts of mercury in the catalytic mixture after the absorption of acetylene. They propose a mechanism which involves an organo-mercury compound as a carrier.

In view of the importance of the hydration reaction it is strange that nothing can be found in the literature concerning the reaction rate and the factors influencing it. The work here reported is a continuation of work on this problem started by Frieman (3). His initial work in dilute acid solutions was not consistent with itself due mainly to the fact that precipitates were present and also due to the partial reduction of the mercuric salt in dilute acid solutions. He found first order rate dependence upon acetylene in a given experiment, but no two rate measurements agreed. In order to prevent the formation of precipitates it was necessary to use quite strong acid (5 weight-formal) and rather dilute mercuric salt concentrations (5×10^{-5} wf.). It should be emphasized that the reaction under these conditions is homogeneous and may not correspond to the rate under heterogeneous conditions.

Analytical Method

For the purpose of determining the rate of hydration of acetylene in sulfuric acid solution it is necessary to have a rapid reliable method for the analysis of acetylene. It is usually determined by absorption in ammoniacal cuprous chloride solution, in which reddish-brown copper acetylde is precipitated. Rapid and accurate determinations are difficult

to accomplish. Davis, Crandall and Higbee (1) have attempted to apply to acetylene the bromide-bromate method of determining unsaturated hydrocarbons. They found that oxygen interferes and described a procedure for excluding oxygen. Their method is too long however, and of doubtful accuracy. Mulliken and Wakeman (5) applied the bromide-bromate method to liquid alkynes and found that the bromine taken up under the conditions of their analysis was but 30-50% of the theoretical value.

It was noticed by the authors cited above (1) that aluminum, nickel, and mercury salts aid in the quantitative bromination of acetylene. Frieman found that aluminum and nickel were entirely unsatisfactory. When mercury is used he found that consistent results could be obtained if the mercury salt was in excess of the total amount of halide present. With an excess of mercury salt present the endpoint in the iodometric determination of the excess bromine is uncertain, but this may be remedied satisfactorily by adding sodium chloride before converting the excess bromine to iodine.

The procedure finally adopted by the present author is as follows: 25 ml. of 0.0500 N KBr-KBrO₃ solution is added to a flask which has a stopcock sealed through the stopper (1). The flask is evacuated by means of a water aspirator; 5 ml. of 6 N sulfuric acid is added and the solution given time for the bromine to develop. 10 ml. of 0.2 formal mercuric sulfate solution is now added, followed by 25 ml. water. The sample is then rinsed into the flask from a special pipet of the type described by Eberz and Lucas (2). Still under vacuum the

flask, wrapped in a black cloth for the purpose of excluding light, is shaken mechanically for 5-7 minutes. 5 ml. of 2.0 formal sodium chloride solution is added, followed by 10 ml. of freshly prepared 20% potassium iodide solution. Shaking is continued for another 5-7 minutes, after which the vacuum is broken, the solution diluted with water, and titrated using 0.03 N sodium thiosulfate solution. The acetylene present in the solution being analysed is calculated from the difference with a blank run at the same time.

Tests of the Analytical Method

The above procedure is essentially that of Davis, Crandall and Higbee, as modified by Lucas and Eberz (4), with the addition of mercuric sulfate as an aid in the bromination of acetylene, and of sodium chloride to prevent the interference of mercury in the iodine endpoint with starch. Lucas and Eberz found that good results were obtainable in the analysis of isobutene and that the amount of substitution taking place was negligible.

In order to see if the same were true for acetylene, tests were made which would indicate the amount of substitution taking place. Identical samples of an aqueous acetylene solution were shaken with bromine for various lengths of time as in the first part of the procedure described above. This was followed by the addition of sodium chloride and potassium iodide solutions, and the analysis was completed as described. The results are shown in Figure 16. They indicate that within experimental accuracy and constancy of the aqueous acetylene

solution involved, there is no appreciable substitution; and, that concordant results may be obtained provided time is allowed for complete addition of bromine to the triple bond.

To discover the excess bromine required in order to secure quantitative bromination, various volumes of aqueous acetylene solutions were analysed using the same amount of bromine. If the apparent concentration of the acetylene solutions used for these tests changed with the molal ratio of acetylene to bromine, a straight line would not be obtained on plotting bromine used up against the amount of acetylene solution taken for analysis. Such a plot, embodying the results of experiments on four solutions of different concentrations is shown in Figure 17. In order to put all experiments on the same basis the percent of total bromine used up has been plotted as ordinates and molal ratios of acetylene to bromine as abscissas. The 45° angle line represents the theoretical curve expected in case the acetylene present always reacts with the stoichiometrical amount of bromine. In placing the experimental points on this plot one titration of each series, chosen as being most nearly correct, was used to establish the concentration of the solution used for that series. Since these chosen titrations would automatically fall upon the 45° angle line they are not shown.

As may be seen, deviations from the theoretical curve exist where more than half of the bromine is used up and seem to be inversely proportional to the bromine concentration at the completion of the bromination. Excellent agreement, well within estimated experimental error, is

obtained with the theoretical curve when the bromine initially present is 2-3 times the amount required to react with the acetylene.

A final test of the validity of the analytical method lies in the analysis of gaseous acetylene. Unfortunately the volume of gaseous acetylene which could be used was so small (2-3 ml.) that its volume could be determined to but 1-2%. Add to this the necessity of transferring quantitatively such a small volume and the problem is indeed difficult. The acetylene available was the commercial product and of doubtful purity. Such analyses were made however, and with somewhat surprising results. In practically all cases the gaseous acetylene used up more bromine than would be expected. The amount, although variable, was about 114% of the expected value. Efforts made to purify the acetylene by the usual reagents (page 50) did not change this value appreciably unless the acetylene was passed through the purification train very slowly. Phosphine was known to be present (from a qualitative test and from the characteristic odor). This, as well as polymers (vinylacetylene), would lead to high results. Gas density measurements indicated an apparent molecular weight of 26.60 (theoretical 26.02), which would be accounted for by the presence of 7% phosphine. The titration value of 114% also indicates 7% phosphine if it is assumed to be the only impurity. Efforts to obtain pure acetylene by a chemical reaction on a compound which would yield acetylene as the only gaseous product were unsuccessful.

In view of the excellent agreement secured in the

tests previously described and because similar methods of analysis give good results on other unsaturated hydrocarbons, the results of the tests on gaseous acetylene are taken to indicate an impurity in the acetylene used rather than a faulty procedure.

In the hydration of acetylene the product of the reaction is acetaldehyde, and a satisfactory analytical method for studying the rate of hydration should not be adversely affected by the presence of acetaldehyde. Unfortunately this is not the case with the above described procedure. Frieman used a very similar analytical procedure and believed that about 1% of the aldehyde was oxidized giving high results. He tried to remove aldehyde by oxidation before brominating the acetylene, but was unable to do so satisfactorily. The alternative was to apply a proportional correction factor, and that is what he did in his work.

Experiments carried out by the present author indicate that the effect of the aldehyde can not be corrected in this manner. Tests, made by varying the amount of aldehyde solution used in a blank, the time of shaking, the amount of light, and the amount of air left in the flask on evacuation, showed complete randomness. In such experiments, identical tests might show 100% variation. The only qualitative facts gained from the tests was that, in a rough way, the amount of bromine used up by the aldehyde was dependent upon the length of time the aldehyde solution had been prepared, and appeared to increase more rapidly in strong acid solution. This, perhaps, indicates that it is not the acetaldehyde, but some

condensation product of it which reacts with bromine under these conditions.

The erratic behavior of the aldehyde would seem to preclude the use of the analytical procedure in studying the rate of hydration of acetylene. However, in the initial stages of the hydration the concentration of the aldehyde is very small and the error would be of the same order of magnitude as the precision of measurement. By taking initial slopes of the curves obtained in a rate measurement a semi-quantitative picture of the hydration can thus be obtained.

Materials

The acetylene used was dispensed from a "Prestolite" cylinder and passed through a purifying train as follows: solutions of sodium acid sulfite, acid copper sulfate, chromic acid in 50% sulfuric acid, sodium hydroxide; towers packed with solid calcium chloride, calcium hypochlorite ("HTH"), flake sodium hydroxide. The acetylene issuing from this system still contained phosphine (or polymers) as indicated above, although the amount could be cut down somewhat by passing the gas through very slowly. That this impurity did not interfere with the hydration rate was shown by agreement of experiments using this material with similar experiments made by Frieman using acetylene prepared from calcium carbide, ^{water} and alcohol, indicating that the impurity either did not dissolve in the sulfuric acid used as a reaction medium or was very rapidly hydrolysed. Undoubtedly the acetylene prepared from calcium carbide was impure also, but there is no reason to believe

that the impurities would occur to the same extent in each source and thus give identical results in the hydration. Mercuric sulfate solutions used were prepared from mercuric oxide and sulfuric acid. Acetaldehyde was prepared from paraldehyde and was three times distilled before use.

Methods and Apparatus

The methods and apparatus used in making a hydration experiment have been described elsewhere (3,4). The hydrations were carried out by partially saturating a known volume of 5.00 weight-formal sulfuric acid solution at 25.0°C with acetylene. The hydration was started by pipeting in a known volume of mercuric sulfate solution and then transferring the solution to a containing vessel so designed as to minimize diffusion. In transferring the solution to the vessel it is necessary to prevent bubbles of acetylene from being transferred with the solution since they would cause a local variation of concentration on dissolving. That the hydration solutions as transferred to the vessel were homogeneous is shown by Figure 16, since the aqueous solution used for the test of bromine substitution was placed in the hydration vessel as in a hydration experiment. Samples of the hydrating solution were taken at intervals and the concentration of acetylene determined to establish the rate of disappearance of acetylene. In taking samples for analysis the special pipet mentioned above (2) was used so as to prevent the loss of acetylene from the sample while transferring to the flask for analysis.

Experimental Results

The results of three such experiments are shown in Figure 18, in which \log_e of C_0/C_t is plotted against time. C_0 is the initial acetylene concentration (obtained by extrapolation of the experimental results to zero time), and C_t is the concentration at the time t . The dash line in Figure 18 as well as that in Figure 19 represents the averages of the initial slopes of eight such experiments. The pertinent data of these and other experiments is shown in Table X. For first power rate dependence upon acetylene a straight line would be expected, whose slope would be the apparent specific reaction rate constant. If, due to an effect of the acetaldehyde, the apparent concentration of the acetylene does not decrease as rapidly as expected, C_0/C_t will be smaller, and the experimental points will form a curve rather than a straight line when plotted in this manner. Since the titration error due to aldehyde is dependent upon the length of time the aldehyde solution has been prepared, it is quite possible that there will not have been time for any bromine-reactive material to have been formed during the course of the reaction. If this were true it would seem to indicate some rate dependence other than first order upon acetylene, since reproducible curves are obtained.

A test of this hypothesis by plotting the experimental results according to the integrated rate expressions for the various powers gave excellent agreement with $4/3$ power rate dependence upon acetylene. This proved to be only

a coincidence of the concentrations involved since hydrations made with a low initial acetylene concentration, as well as ones with large initial acetaldehyde concentrations, failed to correspond. In fact, the hydrations with a large amount of aldehyde present showed but slight deviation from first power dependence upon acetylene, as shown in Figure 19. The results shown indicate that, when the aldehyde is freshly prepared and does not change more than 5-8% in the course of the hydration, the first power rate equation is obeyed. The curved line obtained in Figure 18 results then from the effect of the aldehyde upon the reaction itself, rather than from a titration error due to aldehyde or from a $4/3$ rate dependence upon acetylene. That erratic titrations will not explain the curved line was shown by carrying out hydrations with aldehyde solutions which had stood for 2-3 days (and which when freshly made up gave experimental results like those in Figure 19). Very erratic results were obtained which did not form a smooth curve nor show any resemblance to a first power rate dependence.

Before discussing the effect of the acetaldehyde further it will be well to investigate the effect of acid and mercuric sulfate upon the hydration. Sulfuric acid alone (i.e. no mercuric sulfate present) will not hydrate acetylene at an observable rate. This was shown by observing the decrease of acetylene in an acid solution over the period of 5-6 days. Such decrease as occurred (about 5%) was due to loss of acetylene from the apparatus as shown by comparison with an aqueous solution used as a control and by the inability to secure

a test for acetaldehyde in the acid solution. No systematic effort was made to determine the effect of the acid in the presence of the mercuric sulfate because of the difficulty of determining the hydrogen ion activity in such a concentrated solution. An experiment made by Frieman upon a 1.00 wf. sulfuric acid solution which was 5×10^{-5} wf. in mercuric sulfate had a rate of reaction too slow to measure, indicating that the acid strength undoubtedly has an effect.

To determine the effect of mercuric sulfate upon the hydration, initial slopes were measured on plots similar to Figure 18 for rate experiments upon two additional mercuric sulfate concentrations (4.00 and 6.00×10^{-5} wf.). The apparent specific reaction rate constant is proportional to the square of the mercuric sulfate concentration as shown by Figure 20. The curve drawn must pass through the origin since it was found that the sulfuric acid alone will not cause the hydration to take place. The range of mercury concentrations is somewhat limited by the necessity of avoiding the precipitation of organo-mercury compounds (which invalidated most of Frieman's work), and obtaining a sufficiently rapid reaction. It is noteworthy that the dependence of rate upon the square of the mercury also holds when aldehyde is present (runs 8 and 9, Table X).

In considering the effect of acetaldehyde upon the hydration reaction a complication arises, in that it is very difficult to secure aldehyde solutions of reproducible effect upon the reaction. For instance, runs 5 and 8 (Table X) had

initial aldehyde concentrations differing by a factor of two, yet the apparent specific reaction rates are practically identical. The best basis for considering the effect of the aldehyde lies in the runs which had no aldehyde added initially. In these cases the aldehyde concentration may be calculated at the time t and compared with the rate at that time. If this is done it is found that the rate varies approximately as the inverse $3/2$ power of the acetaldehyde. This is probably due to the formation of an un-ionized compound of acetaldehyde and mercury (since it is known that acetaldehyde reacts with an acid solution of mercuric sulfate (7)), but it is not possible to make a more definite statement at this time.

TABLE X

Hydration Experiments in 5.00 weight-formal Sulfuric Acid

Run	k initial hr ⁻¹	Initial Concentration		
		C ₂ H ₂ vf.	CH ₃ CHO vf.	HgSO ₄ wf. x 10 ⁵
1	0.302	0.0222	zero	5.00
2	0.288	.0215	"	"
3	.285	.0258	"	"
4	.260	.0123	"	"
10	.322	.0052	"	"
11	.293	.0245	"	"
12*	.292	.0225	"	"
14*	.285	.0252	"	"
average	0.290			
15*	.186	.0229	"	4.00
9	.415	.0275	"	6.00
6	zero	.0470	"	zero
5	.201	.0257	.042	5.00
8	.198	.0248	.083	"
9	.285	.0275	.083	6.00

*taken from Frieman's data

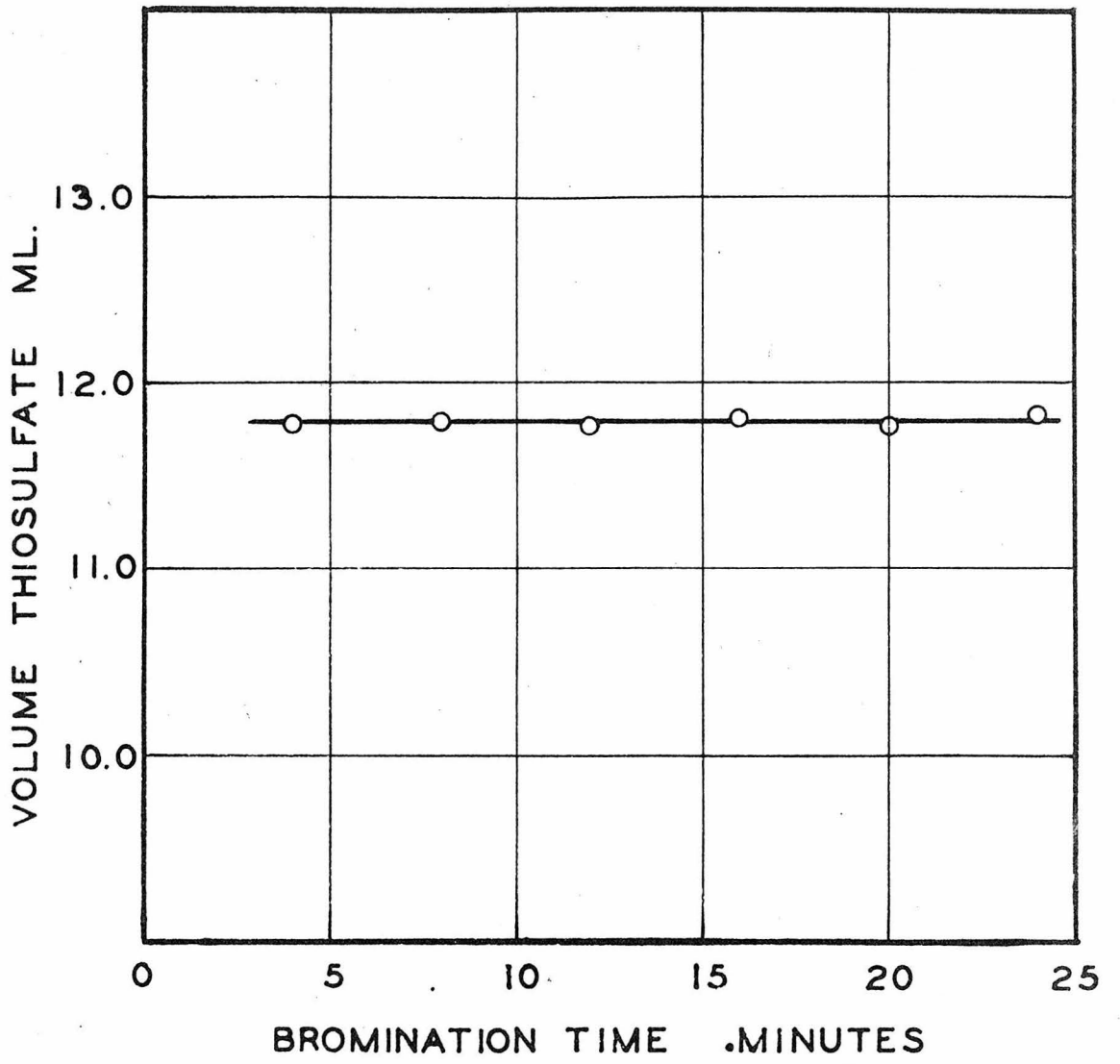


Figure 16

Test of Bromine Substitution

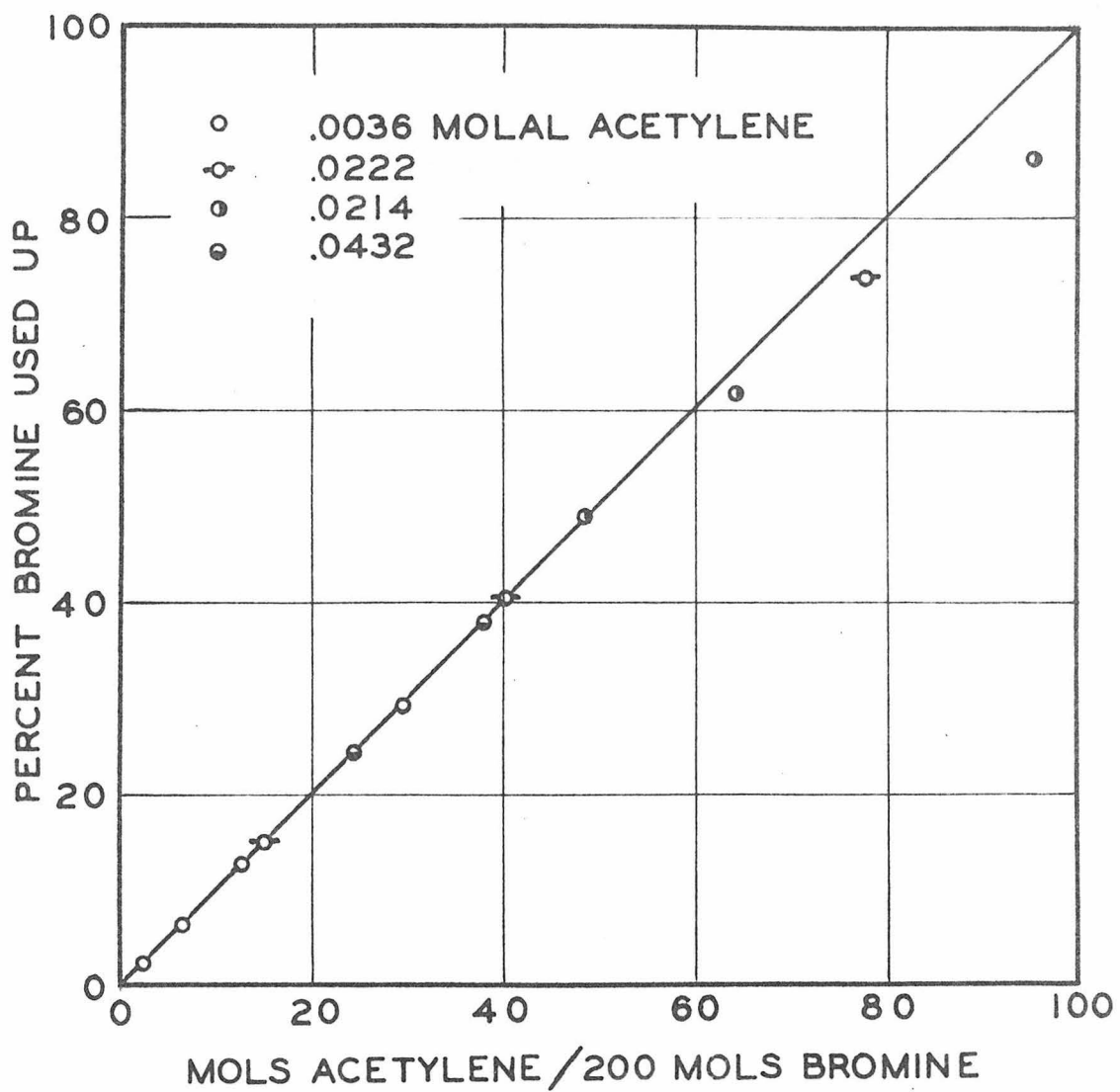


Figure 17

Limitations of the Analytical Procedure

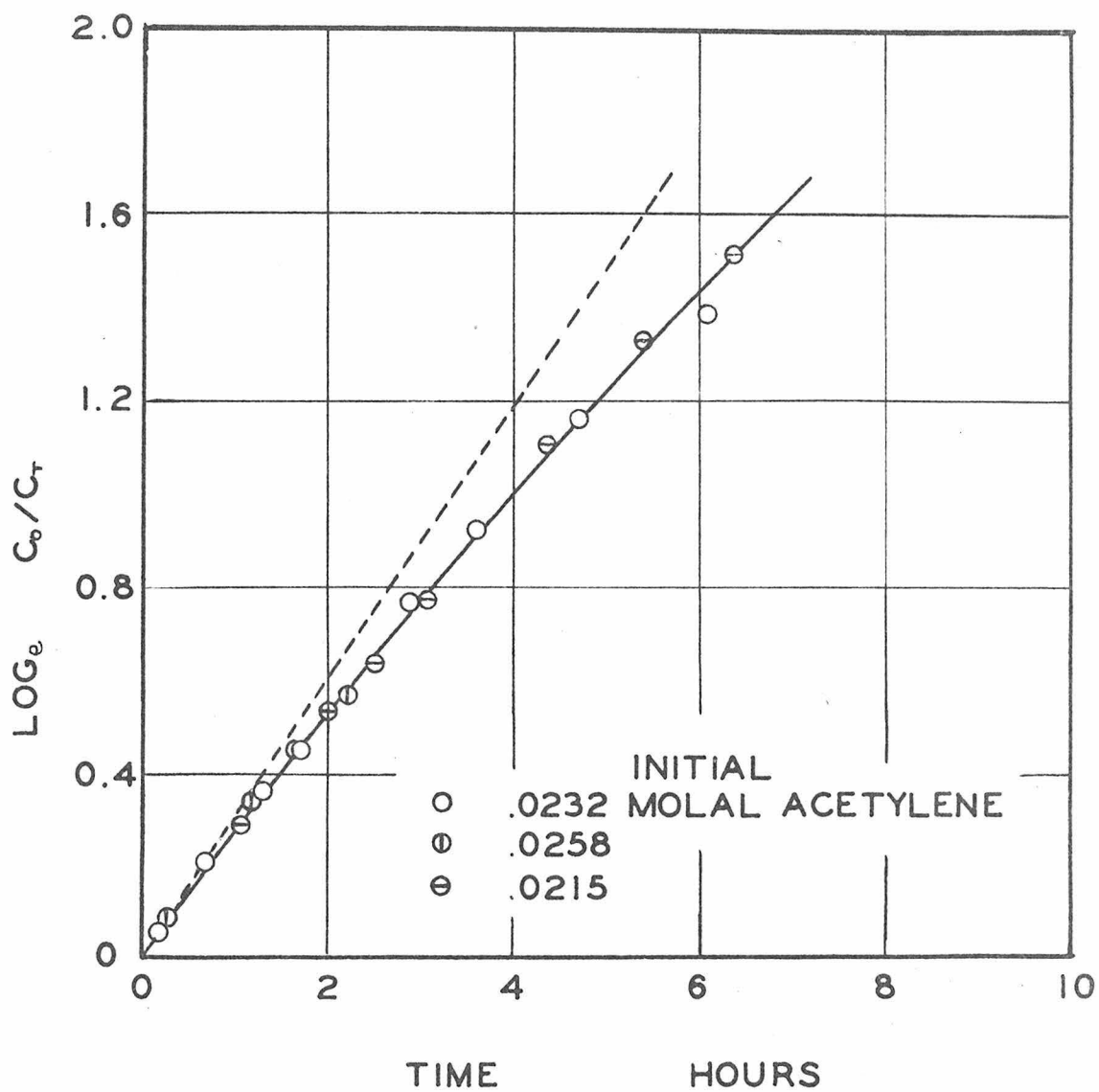


Figure 18

The Hydration of Acetylene in Sulfuric Acid Solution

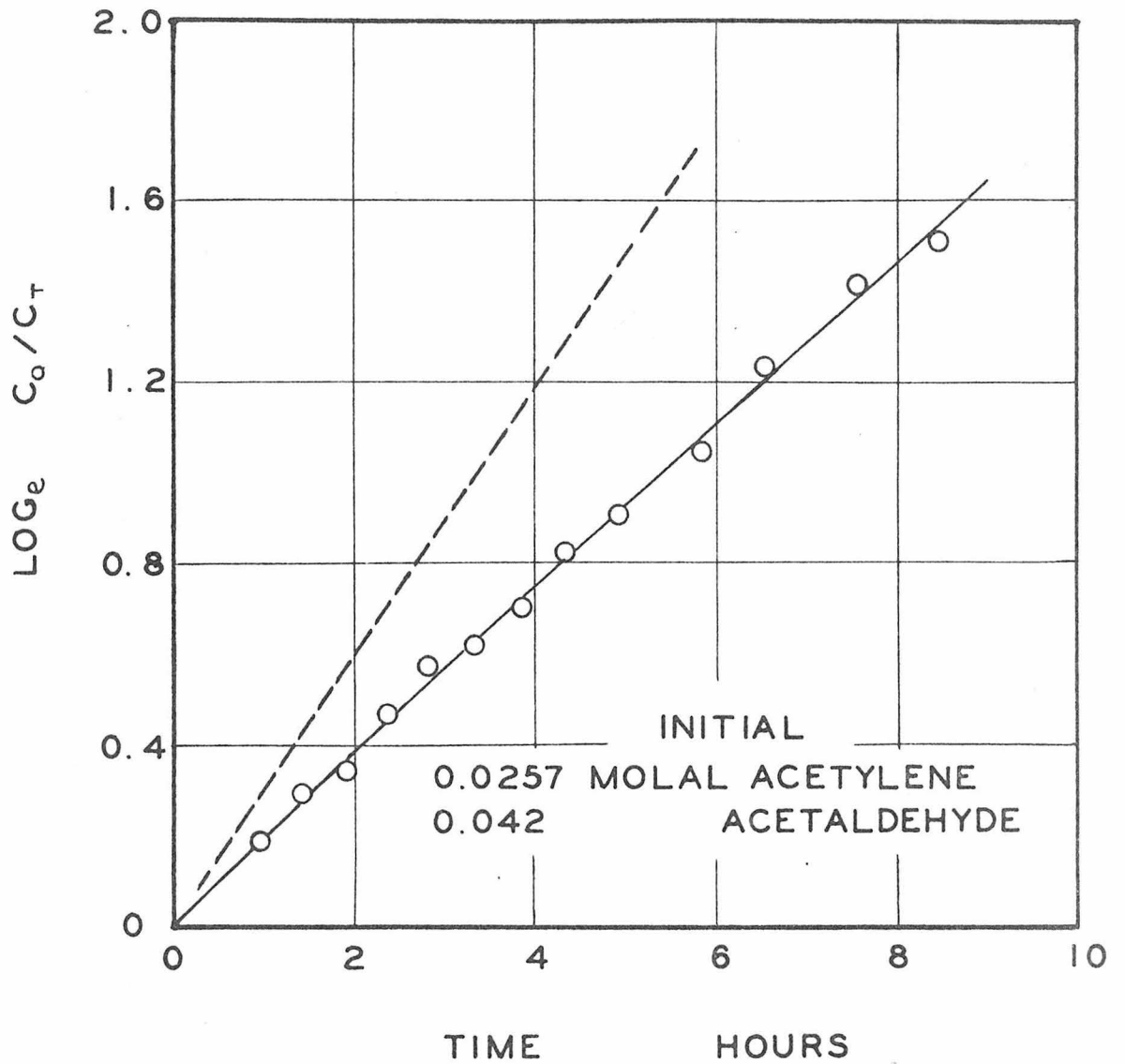


Figure 19

The Hydration of Acetylene in the Presence of
Acetaldehyde in Sulfuric Acid Solution

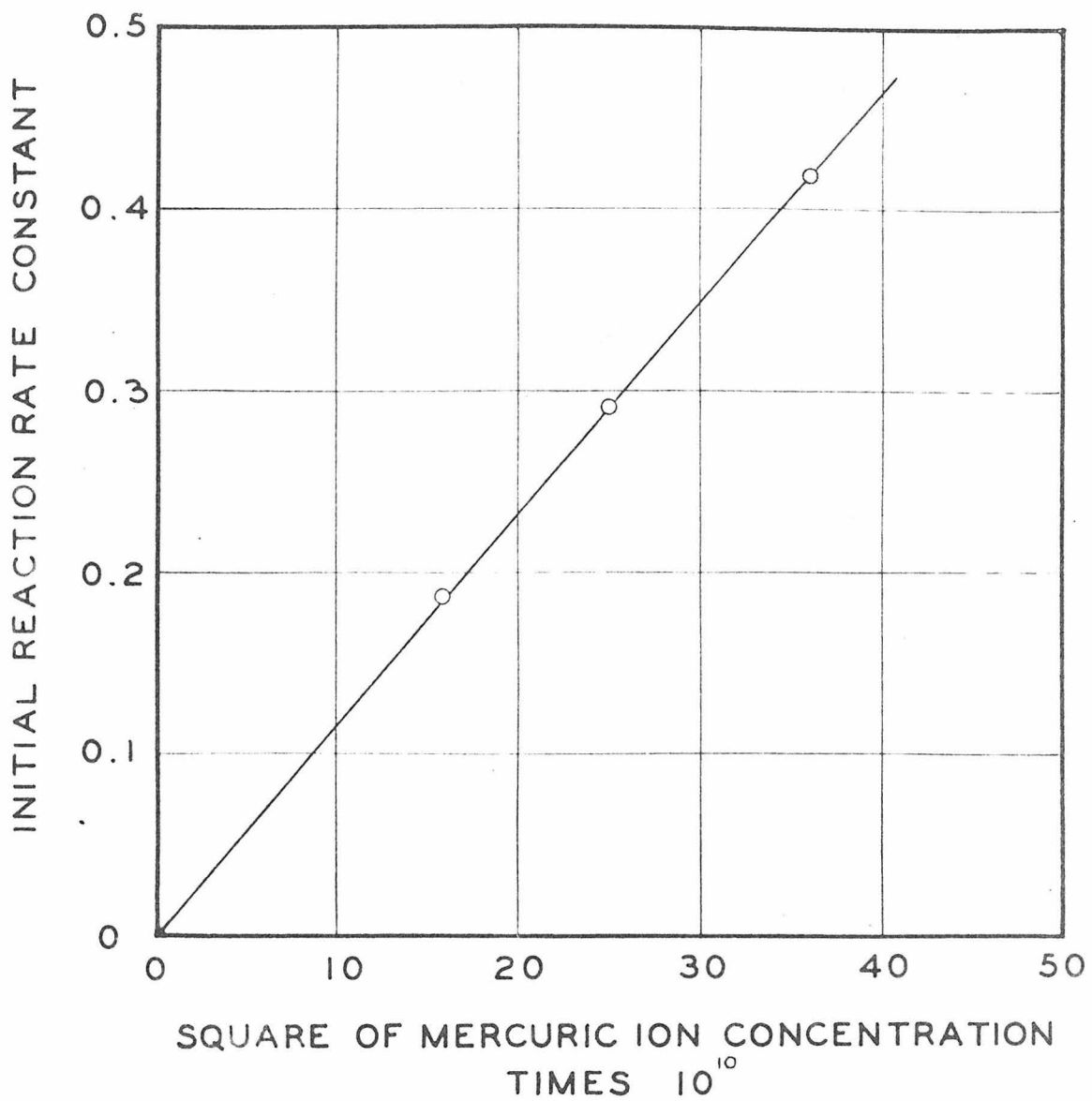


Figure 20

The Effect of Mercuric Sulfate upon the Hydration
Rate of Acetylene

Acknowledgments

The author wishes to express his sincere thanks to Professor H.J.Lucas for guidance and advice in carrying out this investigation. Credit is due the late R.H.Frieman for his pioneering work on this problem.

Literature Cited

1. Davis, Crandall and Higbee, Ind.Eng.Chem., Anal.Ed., 3, 108 (1931).
2. Eberz and Lucas, J.Amer.Chem.Soc., 56, 1232 (1934).
3. Frieman, R.H., Masters Thesis, Calif.Inst.Tech., (1934).
4. Lucas and Eberz, J.Amer.Chem.Soc., 56, 460 (1934).
5. Mulliken and Wakeman, Ind.Eng.Chem., Anal.Ed., 7, 59 (1935).
6. Vogt and Nieuwland, J.Amer.Chem.Soc., 43, 2071 (1921).
7. Whitmore, "Organic Compounds of Mercury" pp. 118-19, 155,
The Chemical Catalog Co., New York, (1921).

PROPOSITIONS

Submitted for defense April 9, 1936

Edwin Russell Kennedy

In a mixture of iodoso and iodoxy compounds suspended in water, an iodonium compound is not formed as a result of the interaction of an iodoso and an iodoxy compound, but results from the reduction of an iodyl compound.

In the mercuric sulfate catalysed hydration of acetylene in sulfuric acid solution, the effect of the acetaldehyde formed in the reaction explains the apparent $4/3$ power rate dependence upon acetylene.

Pattee and Brown incorrectly interpret their data in determining the Joule-Thomson coefficients of gaseous n-pentane.

Ind. Eng. Chem. 26 511 (1934)

$(\frac{dH}{dp})_T$ of actual gases does not approach zero as the gas is indefinitely expanded.

It is possible to predict with reasonable accuracy the thermal properties of straight-chain hydrocarbon gases above propane by means of the Law of Corresponding States.