# THE USE OF ADSORBENTS
# in
# NATURAL GAS ANALYSIS.

Thesis

by

Richard Pomeroy

In partial fulfillment of the

requirements for the degree of

Master of Science

in Chemistry.

Written in collaboration

with J. Stuart Campbell.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1927.

# USE OF ADSORBENTS IN NATURAL GAS ANALYSIS.

## INTRODUCTION

The separation of the members of the parrafin series in the analysis of natural gas presents many difficulties. Chemical methods are of negligible value because of the close series relationship of the compounds. Combustion methods are fairly satisfactory for determining a mixture of two hydrocarbons, and theoretically can be used to determine a ternary mixture, but in the latter case it is impossible to attain an accuracy of any useful significance. Fractional combustion is of limited value: it permits the determination of $H_2$, $CH_4$, and $C_2H_6$, but cannot separate the higher hydrocarbons. The use of physical properties, such as density, viscosity, and optical constants 1), is also limited to the determination of a mixture of two gases.

The only methods of analysis in this field capable of making comprehensive and accurate determinations have depended upon some physical method of isolating the constituents and measuring them separately. Fractional distillations making use of the differences in boiling point

---

1) Seibert and Harpster: Interferometer in Natural Gas Analysis. U.S. Bureau of Mines, Tech. paper 185 (1918).

between the members of the paraffin series require the use of temperatures low enough to liquefy the compounds to be separated. This suggests the advantageous procedure of employing temperatures at which the vapor pressures in question are very small, since the ratio between the vapor pressures of the successive paraffins increases as the pressures are reduced, increasing the degree of fractionation possible. In this manner Lebeau and Damiens 1) fractionated natural gas into groups of two compounds, using single distillations. Later Burrell 2) employed low temperatures obtained with liquid air to make analytical separations of natural gas into constituents as high as butane, making multiple distillations with recombination of fractions. His method was very slow, requiring as much as a week of pumping with a Toepler pump. Shepherd and Porter 3) improved Burrell's procedure in point of speed, reducing the pumping necessary by making distillations between three bulbs in series. Through the use of an evacuated apparatus entirely of glass with mercury filled gas lines they were able to separate natural gas with three distillations into ($CH_4$, $N_2$, H), $C_2H_6$, $C_3H_6$, $C_3H_8$, $C_4H_{10}$ and higher fraction

1) Lebeau and Damiens: Compt. Rend. 156,325 (1913)
2) Burrell & Seibert; J.A.C.S. 36,1537 (1914)
Burrell & Robertson; J.Ind. & Eng.Chem. 7,209 (1915)
3) Shepherd & Porter; J.Ind. & Eng.Chem. 15,1143 (1923)

to an accuracy of approximately 0.1%.

Shepherd and Porter's procedure would leave little to be desired had it not three serious defects from the standpoint of practical application. It requires an accurate control of rather widely separated temperatures in the neighborhood of the boiling point of liquid air. It moreover requires extreme care in manipulation and in making cuts to secure the accuracy stated above. Finally, the separation extends only to butane, whereas in the very important application of such analyses to testing natural gas for recoverable gasoline the percentages of the still heavier compounds are of great interest.

A. J. L. Hutchinson, working in this laboratory in 1925, applied the effect of selective adsorption to the problem of natural gas analysis. One of the most noticeable characteristics of the adsorption of gases on solid adsorbents is the fact that different gases are adsorbed to different extents. In general, and with the major exception of hydrogen, a gas is the more strongly bound to the adsorbent the higher its boiling point. The relation between degree of adsorption and critical temperature is even more exact and of deeper theoretical significance. Thus the paraffin hydrocarbons are adsorbed in the order of their boiling points, which increase with the molecular weight as the series is ascended; in other words, at a given equilibrium pressure and temperature a greater quantity will be retained in the adsorbed state in the case of a heavier paraffin compound than of a lighter one.

Hutchinson proceeded to test the separations attainable by distillation from activated charcoal at each of an ascending series of temperatures. A sample of natural gas was adsorbed on charcoal and put into communication with a bulb surrounded with liquid air for a period of several hours. The distillate corresponding to each temperature of the charcoal was separately measured and analysed by combustion.

On the basis of these experiments Hutchinson found a series of temperatures at each of which the lightest compound adsorbed on the charcoal, the still lighter compounds having been already removed, came over completely, leaving the heavier compounds in their entirety on the charcoal. At least this was the indication of his combustion analyses of the fractions. The conclusion drawn was that at the selected temperatures the ratio between the partial pressure of the lightest member present and that of the next higher is so large that the pressure of the former can become high enough to produce flow away from the charcoal without danger of appreciable contamination with the more strongly adsorbed compounds.

The analytic procedure employing these empirically determined temperatures was briefly as follows: $O_2$ and $CO_2$ were removed and measured by means of KOH and pyrogallol absorption pipettes. The sample was then liquefied at the temperature of liquid air and methane pumped off with a Toepler pump. The remainder was adsorbed on charcoal at liquid air temperature and the succeeding cuts made as described above, starting with the ethane distillation at 45° and ending with pentane at 230°. Higher temperatures caused cracking, so that compounds heavier than pentane could not be drawn off intact but were estimated by subtraction.

The accuracy of the method of combustion analysis to determine the purity of the fractions taken off is rather questionable, and inasmuch as Hutchinson did not work with pure hydrocarbons or known mixtures, there is some uncertainty as to just how accurate the method is. The research on the Standard Oil Co. Fellowship at the California Institute of Technology during the past year has been directed toward a more thoro investigation of the method of analysis and toward an improvement of the apparatus and proceedure. In particular, a study has been made of the properties of silica gel with a view to substituting it for charcoal as the adsorbent.

# EXPERIMENTAL INVESTIGATIONS

The experimental work has been concerned with a study of some of the basic principals underlying the method of analysis. The results are not complete in themselves, and additional experimental data will be required before the results can be applied in a general way to the proceedure of analysis. However, we have been able to suggest a number of improvements in the analytical apparatus and proceedure, and these will be found in the concluding section of this paper.

The experiments are divided into ~~three~~ two groups; adsorption of pure hydrocarbons; ~~adsorption of a mixture of hydrocarbons~~; and rate of flow measurements.

## Apparatus.

The apparatus used in all of our work is shown in chart #I. It is a modification of Hutchinson's original apparatus, embodying bulb #3, filled with silica gel, and bulb #4, empty, in addition to bulbs #1 and #2 of the original set-up. All of the bulbs except #2, are provided with large bore manometers a meter in length. Gas samples may be admitted to any one of the bulbs, and may be transferred from one to another. Bulbs #3 and #4 may be placed in communication thru the mercury cut-off. A Toepler pump is used to pump out fractions of gas and return them to the burette for measurement, and a Hyvac pump may also be used to evacuate the apparatus when the gas which it contains is to be discarded. The tubing connecting the bulbs is between 5 and

-X-

8 mm. internal diameter. The mercury cut-off is 199 cm. in length, with an average internal diameter of 5.96 mm.

Temperature control around the bulbs was maintained by surrounding them with baths of paraffin, water, or alcohol, which were mechanically stirred. The paraffin bath was in an electrically heated container. A rheostat control made it possible to maintain fairly constant any temperature from 60° to 240°. Temperatures from 0° to 90° could be maintained with a water bath in a Dewar flask. In order to hold the temperatures above 30° constant, a small resistance element was immersed in the water. Between -110° and 0°, a bath of chilled alcohol was used. With this arrangement the temperature would not change more than 4° in an hour at the lower temperatures. By adding a little colder alcohol from time to time, the temperature could be kept within 0.5° of any desired value.

The thermometers used above 0° were standardized against a Bureau of Standards thermometer up to 60°, and against the boiling points of water and aniline. For the lower temperatures a toluene thermometer was used which was calibrated by comparison with a standard mercury thermometerat -20°, and with the melting points of chlor-benzene and ammonia, and the boiling point of ethane.

Pressures below 100 mm. were read to 0.1 mm. with a Leitz microscope cathetometer. Higher pressures were read on meter sticks attached to the manometers.

-X-

## Materials.

The silica gel used in the research was prepared essentially according to the proceedure of Holmes, Metcalf, and Sullivan, (Ind. and Eng. Chem., 18, 388, Apr. 1926.) except that after adding the specified amount of ferric chloride solution to the sodium silicate, the solution was quite acid and no gel formed until the acidity was reduced by means of ammonia. The final product was crushed and screened between 10 and 20 mesh screens. By weighing the gel dry and again when saturated with water, it was possible to determine the pore volume. The porosity found in this way was 63% of the volume of the gel. The same sample of gel was used throughout the experiments described in this paper. Its weight was 26 grams after moderate ignition. Before making adsorption measurements, the gel was out gassed by heating to about 500° in vacuum for several hours.

The charcoal used in the research was commercial activated charcoal. The adsorption bulb has been filled with the same sample in all of the experiments; the weight of the charcoal has not yet been determined.

Ethane and ~~Butane~~ Propane were prepared by treating ethyl and isopropyl bromides, mixed with alcohol, with a magnesium-copper couple. They were purified by washing with fuming sulphyric acid, potassium permanganate solution, and sodium hydroxide solution, and were distilled several times. Butane was obtained by fractionating casing-head gasoline, and isopentane from ordinary gasoline. The vapor pressures of the four hydrocarbons in the vicinity of the boiling points were measured, and by drawing off successive fractions and observing the change in the vapor pressure the boiling point range could be estimated. In this way the boiling points were found to be as follows:

| Hydrocarbon | B.P. range | Average B.P. |
|---|---|---|
| Ethane | about 2° | (used to calibrate therm.) |
| Propane | about 2° | -43.0 |
| Butane | | — |
| Isopentane | 0.1° | 27.9° |

Incidentally, there does not appear to be in the literature any record of a determination of the vapor pressure curve of isopentane. Consequently it appeared worth while for us to determine as accurately as possible the vapor pressure of our sample at several temperatures. The measurements were made in bulb #4 of the apparatus. A mercury thermometer which had just been calibrated by comparison with a Bureau of Standards thermometer was used to measure the temperatures. The following values were obtained. Each value is a mean of several readings.

| Temperature | Pressure | Temperature | Pressure |
|---|---|---|---|
| -21.0 | 93.3 | 10.0 | 387.9 |
| 10.0 | 163.0 | 19.1 | 552 |
| 0.0 | 256.6 | | |

Pressures are in milimeters of mercury at 0°. This data will be found plotted logarithmically against the reciprocal of the absolute temperature on chart IX.

Our experiences in our attempts at a synthetic preparation of ethane, propane, and butane lead us to believe that any of these hydrocarbons can better be obtained by purification of the naturally occurring products.

-X-

## Adsorption Measurememts.

The adsorption of ethane on silica gel has been measured between $-100^\circ$ and $160^\circ$, and between 1 mm. and 800 mm. The proceedure adopted was to measure a quantity of the gas into the apparatus and draw it into the silica bulb by applying a liquid air temperature. The bulb was then closed off, and readings off the pressures were made at various temperatures, generally $20^\circ$ apart. Measurements below $0^\circ$ were made by placing the cold bath around the warm bulb; allowing the alcohol to warm up as it would, and following the pressure until it became a minimum, at which point the temperature was read. The minimum pressure must necessarily be the equilibrium pressure corresponding to the temperature of the adsorbent; the only error involved is in the assumption that the adsorbent is at the same temperature as the bath. The rate of change of temperature of the bath was slow enough so that errors from this source could not be very great. For readings above $0^\circ$, the same method was sometimes used, or else the temperature was held constant until the pressure became constant. A half hour was generally sufficient for this.

Runs of this sort were made with 15 different quantities of ethane. Each run was plotted separately, and smooth curves were drawn through the points. These curves do not have any fundamental significance, because the quantity of gas actually adsorbed is not constant throughout the run.

In order to correct for the unadsorbed portion of the gas, a measured quantity of helium, which is practically unadsorbed, was admitted to the bulb and the pressure read. With this data the corrections could easily be made. The intercepts of the curves with the various temperature ordinates were next read off, and the corresponding adsorbed volumes calculated. The isothermal data obtained in this way will be found in the appended tables. When the isotherms are plotted, it is possible to read off the intercepts with various volume lines, and from this data to plot isosters corresponding to the original data but corrected for the unadsorbed portion of the gas. Some of these isosters will be found plotted in chart II as log p against $\frac{1}{T}$, where T is the absolute temperature. The points up to 80 cc. are seen to correspond quite closely to a series of parallel straight lines, which furthermore are spaced logarithmically with respect to the volume. This makes it possible to represent the data by an equation of the form

$$\log p = a + b \log v - \frac{c}{T}$$

Upon avaluating the constants the equation becomes

$$\log p = 4.555 + 1.181 \log v - \frac{1298}{T}$$

The full lines drawn on the graph fit this equation. The deviations along the 1 cc. isoster are probably due to experimental errors in the measurements of the small quantities, while the deviations near the upper ends of some of the lines may be accounted for by the uncertainty in making large corrections for unadsorbed volume. The fair agreement of the data with such a simple equation over such a wide range of conditions is quite remarkable. It will be seen from thermodynamic considerations that the constant -c (1298 in this case) is numerically equal to the heat of adsorption times $\frac{\log e}{R} = .2188$. Thus the heat of adsorption of ethane on silica under the conditions investigated is $1298 \div .2188 = 5933$ calories per mol.

In measuring the adsorption of ethane on charcoal, successive quantities of ethane were run on while the temperature was kept approximately constant. Small differences of temperature between successive readings were corrected for after determining approximately the temperature coefficient. In making adsorption measurements with charcoal, it was found necessary to allow 12 to 24 hours for equilibrium to be attained. The data with the volumes corrected for the unadsorbed portion of the gas is included in the appended tables, and the isotherms will be found plotted logarithmically on chart III. The data can be represented fairly well by an equation of the same form as was applied to the adsorption of ethane on silica. When the constants are evaluated, the equation is

$$\log p = 3.86 + 1.18 \log v - \frac{1770}{T.}$$

The lines on the chart are drawn in accordance with this equation.

A limited amount of data was collected on the adsorption of propane on silica, the proceedure being similar to that used in the case of ethane on charcoal. The data will be found in the tables and plotted logarithmically on chart IV. The previous type of adsorption equation does not fit this data quite as well as the date for ethane; nevertheless average values of the constants of the equation were determined giving the equation

$$\log p = 4.69 + 1.40 \log v - \frac{1600}{T} .$$

Lines calculated from this equation are plotted on the graph.

In the measurement of the adsorption of propane on charcoal, the quantities of gas in the bulb were kept constant while the temperature was varied. The corrections for unadsorbed gas were always small, and after the relationship between the volume adsorbed and the pressure had been approximately determined, the pressures were corrected to correspond to a constant adsorbed volume for each run. The original data will be found in the tables, and the corrected isosters are plotted on chart V. as log p against $\frac{1}{T}$.
The lines drawn on the graph fit the equation

$$\log p = 4.08 + 1.40 \log v - \frac{2440}{T} .$$

It is an interesting fact that in the case of both ethane and propane, the constant b (coefficient of log v) is the same whether the gas is adsorbed on silica or charcoal.

The adsorption of butane on silica was measured between 6° and 60°, and the results are shown graphically on chart VI. It will be seen that the slope of the log isotherms (corresponding to the constant b of the adsorption equation) is fairly constant at a constant temperature, but decreases with rise of temperature. The values of the constants of the adsorption equation are given on the chart for

-X-

various ranges of temperature.

Investigations of the adsorption of butane by silica have also been carried out by Patrick and Long. (J. Phys. Chem. 29, 1925, 336.) For the purposes of comparisons we have shown on chart VII the log isotherms for 0° and 40° as determined by Patrick and Long, and also as we have determined them. The gel which they were using had a slightly higher adsorptive capacity than ours, and also shows a somewhat smaller value of the constant b of the adsorption equation, indicated by the fact that slope of the lines is less.

The data for isopentane on silica gel is even less adaptable to the simple adsorption equation, for not only does the coefficient b change but also the quantity c. Values of the constants for the temperature intervals investigated are given along with a plot of the data on chart VIII.

A comprehensive discussion of adsorption equations and a complete bibliography of the subject will be found in a paper by Swan and Urquhart in the Journal of Phys. Chem., 31, 1927, 251.

## Rate of Flow Measurements.

Rate of flow measurements were made by thoroly evacuating the apparatus, admitting a measured sample of the gas into the silica bulb, applying liquid air to bulb #4, and then opening the mercury cut-off. After the gas had been allowed to flow for a measured length of time, the cut-off was closed, bulb #4 was surrounded with water at

20°, and the pressure which resulted was measured. By measuring the pressure produced in the bulb by a known volume of gas, a factor was obtained by which the pressures could be converted to volumes.

When the flow is interrupted, the adsorbed gas will have an opportunity to fill the connecting tubes and free spaces of the bulb at the equilibrium pressure of the gas, and upon opening the cut-off again, the initial rate of flow would be too high. Hence, in order to avoid an error due to the interruption of the flow, when the equilibrium pressure was appreciable, the gas was run back on to the adsorbent after measurement and successively longer intervals of time were allowed for the flow. When the equilibrium pressure is very low, that is when the rate of flow is less than 0.2 cc per minute, this precaution was found to be unnecessary. Measurements were made with butane at 0° and with isopentane at 19.1° and 29.1°. The data is included in the tables, and will be found plotted on charts X, XI, and XII.

If we assume that the rate at which the gas comes over is determined by the rate at which the gas under equilibrium pressure can make its way up thru the body of the gel, then conditions of hydrodynamic flow would prevail and the rate would be proportional to the square of the pressure, or, since the equilibrium pressure is proportional to $v^b$, where v is the volume of gas adsorbed and b is the coefficient of log v in the adsorption equation, the rate of flow would be given by

$$-\frac{dv}{dt} = k\ v^{2b}.$$

If, on the other hand, the flow were determined by the rate at which the gas could pass thru the connecting tubes, the pressure in the connecting tubes would be so low for the rates experimentally determined that the mean free path of the molecules would be greater than the diameter of the tube and the flow would be proportional to the first power of the pressure. If the equilibrium pressure were maintained in the bulb, the rate would be given by

$$-\frac{dv}{dt} = k\ v^{b}.$$

The data is not sufficient to determine very accurately the coefficient of b in the exponent of v, but its value is undoubtedly very close to 2. The best values that could be obtained were 1.9 for butane at 0°, 1.9 for isopentane at 19°, and 2.2 for isopentane at 29°. Assuming the constant to be 2.0, curves have been drawn on the charts, and it is seen that they fit the experimental data reasonably well.

By extrapolating the isopentane adsorption isotherms of chart VII down to a volume of 3cc., which was the average quantity of isopentane vapor on the gel when the rate of flow measurements were made, it is found that the ratio of the pressure at 29.1° to the pressure at 19.1° is 2.12. If the rate of flow is really determined by the equilibrium pressure of the gas on the gel, then the rate at 29.1° should be $(2.12)^2$ or 4.5 times the rate at 19.1°. The increase in the velocity of the thermal agitation of the molecules at the higher temperature would also come in to increase the ratio, and should bring it up to 4.6. The ratio of the rate constants as determined experimentally is $\frac{.00109}{.000257} = 4.23$, a very satisfactory check with the theoretical value. From the data available it is not possible to make comparisons of the flow of butane and isopentane with sufficient accuracy to be of any significance.

The rate of flow equations make it possible to calculate the time which will be required at any temperature for any volume of a pure gas to be drawn over. For instance, by integrating the equation for isopentane at 29.1°, we obtain

$$\frac{1}{V^{2.2}} - \frac{1}{V_0^{2.2}} = .00240\ (t-t_0)$$

For the case that all but a small fraction of the sample is drawn off, $\frac{1}{V_0^{2.2}}$ is negligible compared to $\frac{1}{V^{2.2}}$ and we may write $\frac{1}{V^{2.2}} = .00240t$ (That is, we may set $v_0 = \infty$) In this case, the time required to draw off all but 0.1 cc. is 66,000 minutes or 1100 hours. The time required at 19.1° would be 1100 times 4.23 (the ratio of the rate constants) or 46,500 hours. At 50° the time would be approximately 60 hours; at 70° about 3 hours. These calculations of course involve the assumption that the same equation holds over all conditions. The extrapolation to time intervals of the order of 100 to 1000 hours is quite likely not justifiable, but there is no evident reason why the equation should not hold for small values of v if the temperature is high enough so that the pressure does not become extremely small. The rate of flow measrements present an attractive field for further investigations.

The rate of flow data may be applied to the analytical proceedure by deciding arbitrarily on a time interval which will be allowed for drawing off a fraction and also determining arbitrarily how much of a fraction will be allowed to remain behind. With the help of the rate of flow equations it then will be possible to calculate the temperature which must be used to remove the gas within the limits allowed. If other gases are present on the adsorbent at the same time, the rate of flow will, of course, not be the same, but the difference will be in the direction to insure a more complete removal of the fraction. This is because the presence of one adsorbed gas hinders the adsorption of another, or in other words increases the equilibrium pressure of the other. This fact is born out by the experiments of several investigators; in particular Homfray. (Z. fur Phys. Chem., 74, 136-143) A measurement which we have made on a mixture of butane and isopentane also verifies the fact. A quantity of butane adsorbed alone on the silice produced a pressure of 7.6 mm., another quantity of isopentane gave a pressure of 1.1 mm. When the two samples were put on together, the pressure was 10.7 mm.

Before the conditions and the efficiency of a separation can be fully determined, it will be necessary to know how much of a higher fraction of a mixture will come over when a lower fraction is being removed. Additional data will be necessary before this can be calculated with any certainty. It is possible with the help of the data obtained thus far, however, to make some qualitative observations on the separation of butane and isopentane. Let us assume that a gas sample of 100 cc. is used, and that it is desired in the separation of each hydrocarbon to leave not more than 0.1 cc. of that hydrocarbon behind. The time necessary to remove butane at 0° down to the volume v is given by $\frac{1}{v^{1.9}}$ .00163t. Substituting v = 0.1, t = 49,000 min. = 810 hours. Taking the constant c of the butane adsorption equation to be 1690, the increase of the equilibrium pressure for 10° rise in temperature in the vicinity of 20° is 1.56 fold. The increase of the rate of flow should be $(1.56)^2$ = 2.5 fold. In order for the butane to be drawn over in a space of one hour, which we will take arbitrarily as the standard time interval, a temperature somewhere in the vicinity of 60° would be required. The total amount of pentane (isopentane + normal pentane) in a 100 cc. sample would not likely exceed 3cc. But if we assume that 3 cc. of isopentane are present and assume that it would come over just as tho the other gases were not present, we should expect that at least 2.7 cc. would be removed along with the butane. At first sight this seems hopeless. There is a redeeming feature, however, in the fact that if the gas is admitted at the bottom of the bulb and is forced to rise up through the adsorbent before escaping, as is the case in the apparatus of Hutchinson, and if the pressure is kept low at all times, the gas will undergo a fractionation as it passes thru the gel and the quantity of the higher constituent coming over will be greatly reduced, although probably not to a negligible quantity. Furthermore, if the fraction which has been drawn over is run thru another adsorption bulb and fractionated again, much less of the diminished volume of pentane will come over with the butane. The apparatus proposed in the concluding section of this paper has two silica bulbs to provide for this sort of refractionation. Additional experimental work needs to be done in order to determine more accurately just how much of the higher fraction will come over when a lower fraction is being removed.

If the accuracy requirements are reduced, the separation becomes much easier. If we allow a residue of 0.3 cc. of butane to remain on the bulb, a temperature of 45° will suffice to remove it, and the quantity of pentane coming over would consequently be considerably reduced. In general it appears that the method of analysis is not suitable for work of a high degree of accuracy. Its value lies in the fact that it is a simple and rapid method of making analyses with a moderate degree of precision.

## RECOMMENDATIONS REGARDING THE METHOD OF ANALYSIS.

In considering the advisability of substituting silica gel for charcoal as an adsorbent in the analysis of natural gas, the first consideration that arises is how the efficiency of the separations obtained would compare in the two cases. Data is not available which would enable a calculation of how much of a heavier member of the paraffin series would come over when a lighter fraction is being removed, but there is little doubt that the ratio of the equilibrium pressures of two hydrocarbons could at least be used as an approximate measure of the sharpness of their separation. The adsorption equations of ethane and propane on silica and charcoal give us an opportunity to calculate the ratio of the pressures of these two gases. Let $a_1$, $b_1$, and $c_1$ be the constants of the adsorption equation for ethane on silica, and $a_2$, $b_2$, and $c_2$ be the corresponding constants for propane. The adsorption equation $\log p = a + b \log v - \frac{c}{T}$ may be rewritten in the form $p = 10^{a} \times V^{b} \times 10^{-\frac{c}{T}}$ The ratio of the pressures of samples of ethane and propane on silica is then $R = \frac{10^{a_1} \times V_1^{b_1} \times 10^{-\frac{c_1}{T_1}}}{10^{a_2} \times V_2^{b_2} \times 10^{-\frac{c_2}{T_2}}}$ If we consider the case where the volumes are equal, and consider the temperatures to be equal, $R = 10^{a_1 - a_2} \times v^{b_1 - b_2} \times 10^{\frac{c_2 - c_1}{T}} = 10^{.14} \times v^{.22} \times 10^{\frac{302}{T}}$ If we let primed letters refer to ethane and propane on charcoal, $R' = 10^{.22} v^{.22} 10^{\frac{670}{T}}$ For the case of the volumes being equal, $\frac{R}{R_1} = 10^{.06} \times 10^{\frac{302}{T} - \frac{670}{T}} = 1.15 \times 10^{\frac{302}{T} - \frac{670}{T}}$ It is seen from this that at the same temperature the ratio of the ethane pressure to bhe propane pressure has a higher value for charcoal than for silica. However, it must be born in mind that the temperatures at which separations would be made would not be the same. For instance, if ethane and propane were to be separated by the use of silice gel, the temperature would be in the vicinity of -70° or 203° Abs. The removal of ethane from charcoal is carried out at 45° or 313° Abs. Substituting these values, $R = 1,15 \times 10^{,149 - ,226} = ,986$ Hence it is seen that from the standpoint of the ratio of pressures, there is not much choice between silica and charcoal.

How the charcoal would behave regarding rates of flow and how the separations would be effected thereby, is yet to be determined. Charcoal has the disadvantage that it is necessary to go to quite high temperatures, which are difficult to control accurately, in order to remove butane and pentane, and higher fractions cannot be removed without decomposition. On the other hand, a separation of ethane from propane by means of silica would require very low temperatures, which are also difficult to control. The best plan seems to be to develop a proceedure using both adsorbents. This can be done with an apparatus constructed as shown in chart XIII. It includes six bulbs in series, as follows: 1, empty; 2, silica gel; 3, silica gel; 4 charcoal; 5, empty;, 6, empty bulb for determining quantities of gas by measurement the pressure. A gas sample may be passed thru all of the bulbs in series, or it may be by-passed around the charcoal bulb or all of the adsorption bulbs. The apparatus may be amplified by the addition of more silica and charcoal bulbs for the purpose of more accurate separations. The ~~bubes~~ bulbs are connected by means of mercury cut-offs instead of stopcocks. Stopcocks are apt to become partly clogged with grease, in which case the rate of flow conditions would be altered, and the grease also appreciably absorbs the heavier hydrocarbons. The tubing connecting the bulbs should be at least 8 mm internal diameter in order that it may not offer any appreciable resistance to the flow of the gases during separations. The adsorption bulbs must be arranged with a view to eliminating unnecessary resistance to the flow, for the more rapid the flow which can be obtained, the lower will be the temperatures which may be used for the separations, and hence the sharper will be the cuts. In the interest of reducing resistance, it would probably be better to use a coarser gel, for a 10 to 20 mesh gel packs down so as to make it quite difficult for the gas to rise from the bottom of the bulb. If the particles are too large, then the time for the gas to flow out of the interior of the gel particles will cause difficulty. We would suggest trying a gel of 5 to 10 mesh particles.

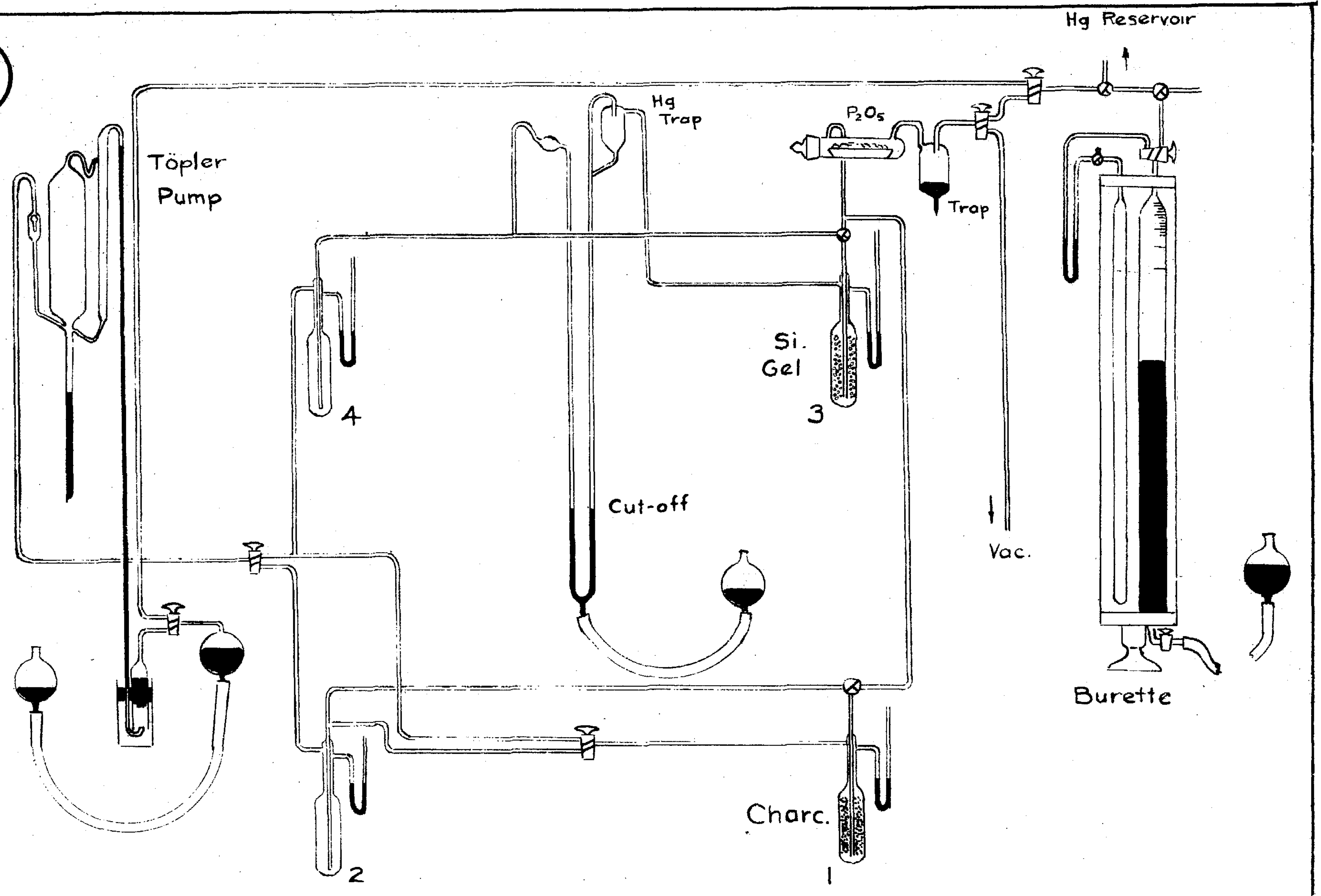
The adsorption equations allow us to calculate the effect of the size of the sample on the efficiency, provided that we assume the ratio of the pressures of two hydrocarbons is a measure of the sharpness of the separation. If we consider equal quantities of two hydrocarbons to be adsorbed on the gel at the same temperature, the ratio of the equilibrium pressures will be given by: $\frac{p_1}{p_2} = v^{b_1-b_2}$ If the subscript 2 refers to the higher hydrocarbon, then the quantity b1-b2 will be negative in value for a mixture of any of the substances which we have investigated. Consequently the smaller the value of v, the larger will be the ratio of the pressures. However except in the case of a mixture of ethane and propane, the difference in the values of b would be small, and the ratio of the pressures would not be affected very much by the size of the sample. Furthermore, the use of a smaller sample would require applying higher temperatures to draw off the same fraction of the total amount of each hydrocarbon, and this would tend to counteract any advantage gained from the first considerations. (The fractionation with the use of adsorbents is affected by the temperature in the same way as ordinary fractionations.) Apparently the choice of the size of the sample should be made with reference to convenience in measuring. We would suggest 100 cc., instead of a sample of 500 - 1000 cc. as used by Hutchinson. This would require only one reading of the burette for the measurement of the sample, and one reading to measure the methane. Furthermore, the time required to pump off the methane would be materially reduced. The measurement of the higher fractions which are present in small amounts can be made as accurately as desired by drawing them by means of liquid air temperature into bulb #6 of the proposed apparatus and measuring the pressure. If the volume of the bulb is made about 76 cc., a pressure of 1mm. will correspond to a volume of 0.1 cc.

Until the proposed analytical apparatus is actually set up and tried out, it will not be possible to determine fully the analytical proceedure. We can, however, outline it in a general way as follows: The apparatus is thoroughly evacuated, and a liquid air flask is placed around bulb #1. The line to the Toepler pump thru bulb #5 is opened, all other cut-offs being closed, when the sample is measured in. The methane and lighter gases may be pumped off quantitatively by the Toepler pump and run back to the burette for measurement. The sample is then run in to the first silica bulb. The cut-off should not be opened before the liquid air is removed from the first bulb. Otherwise, if the pressure becomes more than a few millimeters before the cut-off is opened, the sudden rush of gas will cause the sample to distribute itself evenly thruout the silica bulb and the advantage of a fractionation as the gas rises slowly thru the adsorbent under low pressure will be lost. This same precaution should be observed whenever the sample is transfered from one bulb to another.

The ethane, propane, and butane are removed to the second silica bulb by surrounding it with liquid air and maintaining the first silica bulb at a temperature, to be determined later, somewhere in the vicinity of room temperature. One hour should be allowed for the separation of the fractions. The first fraction is then drawn off a second time, in this case to the charcoal bulb, where the three gases are separated. The higher members of the series are separated by means of the silica, two successive fractionations being made in each case. In all cases, the final fractions are collected in bulb #5, and then transfered to bulb #6, where the pressures at $20^{\circ}$ are read. The standard volume of each fraction can be calculated from the pressure.

The experimental work described in this paper was made possible by a grant from the Standard Oil Company of California, to whom we are very grateful. Especial thanks is also tendered to Dr. Robert Millikan and to A.J.L. Hutchinson for the advise and assistance given in the research.

I.


Hg Reservoir
Töpler
Pump
Hg
Trap
$P_2O_5$
Trap
Si.
Gel
4
3
Cut-off
Vac.
Burette
Charc.
2
1

# EXPERIMENTAL DATA.

## 1. Adsorption of ethane on silica gel.

| Press. | Total vol. | Vol.Ads. |
|---|---|---|
| | -100° | |
| 2.0 | 163.2 | 162.8 |
| 3.1 | 227.4 | 226.9 |
| | -90° | |
| 4.3 | 163.2 | 162.6 |
| 7.0 | 227.4 | 226.5 |
| | -80° | |
| 1.4 | 74.4 | 74.2 |
| 2.1 | 105.0 | 104.6 |
| 8.2 | 163.2 | 161.8 |
| 14.5 | 227.4 | 224.9 |
| | -70° | |
| 1.0 | 49.7 | 49.5 |
| 2.8 | 74.4 | 73.9 |
| 5.2 | 105.0 | 104.1 |
| 14.3 | 163.2 | 161.8 |
| 26.0 | 227.4 | 223.0 |
| | -60° | |
| 1.7 | 33.2 | 32.9 |
| 2.8 | 49.7 | 49.2 |
| 5.3 | 74.4 | 73.5 |
| 10.2 | 105.0 | 103.3 |
| 24.0 | 163.2 | 159.3 |
| 44.0 | 227.4 | 220.2 |
| | -50° | |
| 2.0 | 22.5 | 22.2 |
| 3.0 | 33.2 | 32.7 |
| 5.3 | 49.7 | 48.9 |
| 9.8 | 74.4 | 72.8 |
| 18.0 | 105.0 | 102.2 |
| 42.0 | 163.2 | 156.6 |
| 72 | 227.4 | 215.9 |
| 123 | 317.9 | 298.0 |

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| | -40° | |
| 1.8 | 10.5 | 10.2 |
| 2.1 | 15.0 | 14.7 |
| 3.7 | 22.5 | 21.9 |
| 5.3 | 33.2 | 32.4 |
| 9.4 | 49.7 | 48.3 |
| 16.9 | 74.4 | 71.8 |
| 30.0 | 105.0 | 100.4 |
| 60.0 | 163.2 | 153.9 |
| 108 | 227.4 | 210.6 |
| 190 | 318 | 288 |
| | -30° | |
| 0.22 | 2.2 | 2.2 |
| 1.6 | 7.4 | 7.2 |
| 2.4 | 10.5 | 10.1 |
| 3.2 | 15.0 | 14.5 |
| 6.3 | 22.5 | 21.6 |
| 9.2 | 33.2 | 31.8 |
| 15.7 | 49.7 | 47.4 |
| 32.0 | 74.4 | 69.6 |
| 47 | 105.0 | 97.9 |
| 97 | 163.2 | 148.5 |
| 158 | 227.4 | 203.2 |
| 290 | 318 | 273 |
| | -20° | |
| .36 | 2.2 | 2.1 |
| 1.0 | 3.8 | 3.7 |
| 1.2 | 4.5 | 4.3 |
| 2.5 | 7.4 | 7.0 |
| 3.9 | 10.5 | 9.9 |
| 5.8 | 15.0 | 14.2 |
| 9.9 | 22.5 | 21.1 |
| 14.8 | 33.2 | 31.1 |
| 25.5 | 49.7 | 46.0 |
| 43.5 | 74.4 | 68.1 |
| 71.5 | 105.0 | 94.5 |
| 138 | 163.2 | 142.8 |
| 224 | 227.4 | 193.8 |
| 398 | 317.9 | 225.6 |
| 196 | | 186.7 |

Ethane on silica (cont.)

| Press. | Total vol. | Vol.ads. | Press. | Total vol. | Vol.ads. |
|---|---|---|---|---|---|
| | -10° | | | 20° | |
| .76 | 2.2 | 2.1 | 1.1 | 1.1 | 1.0 |
| 1.8 | 3.8 | 3.5 | 2.8 | 2.2 | 1.8 |
| 2.3 | 4.5 | 4.2 | 5.6 | 3.8 | 2.9 |
| 3.7 | 7.4 | 6.9 | 6.7 | 4.5 | 3.6 |
| 5.7 | 10.5 | 9.7 | 10.1 | 7.4 | 6.1 |
| 8.6 | 15.0 | 13.8 | 15.2 | 10.5 | 8.5 |
| 14.5 | 22.5 | 20.7 | 24.9 | 15.2 | 11.7 |
| 23.1 | 33.2 | 29.9 | 38.6 | 22.5 | 17.4 |
| 39.5 | 49.7 | 44.1 | 60.6 | 33.2 | 25.1 |
| 65.0 | 74.4 | 65.1 | 93.8 | 49.7 | 37.2 |
| 97 | 105.0 | 91.1 | 149.8 | 74.4 | 54.8 |
| 185 | 163.2 | 136.3 | 221 | 105.0 | 74.9 |
| 305 | 227.4 | 182.1 | 389 | 163.2 | 108.5 |
| 500 | 318 | 242 | 568 | 227.4 | 145.0 |
| | | | 831 | 317.9 | 192.6 |
| | 0.0° | | | 30° | |
| .56 | 1.1 | 1.0 | | | |
| 1.2 | 2.2. | 2.0 | 1.6 | 1.1 | .9 |
| 2.9 | 3.8 | 3.4 | 3.5 | 2.2 | 1.7 |
| 3.4 | 4.5 | 4.0 | 7.3 | 3.8 | 2.8 |
| 5.5 | 7.4 | 6.6 | 9.0 | 4.5 | 3.3 |
| 8.6 | 10.5 | 9.3 | 13.2 | 7.4 | 5.7 |
| 13.0 | 15.0 | 13.2 | 19.8 | 10.5 | 7.9 |
| 21.3 | 22.5 | 19.6 | 32.2 | 15.2 | 11.0 |
| 33.9 | 33.2 | 28.5 | 51.0 | 22.5 | 15.8 |
| 55.2 | 49.7 | 42.0 | 77.7 | 33.2 | 23.1 |
| 89.6 | 74.4 | 61.9 | 117 | 49.7 | 34.3 |
| 140 | 105.0 | 85.2 | 185 | 74.4 | 49.7 |
| 250 | 163.2 | 127.3 | 270 | 105.0 | 68.4 |
| 390 | 227.4 | 170.1 | 455 | 163.2 | 100.0 |
| 605 | 317.9 | 226.3 | 658 | 227.4 | 131.1 |
| | 10° | | | 40° | |
| .9 | 1.1 | 1.0 | 1.9 | 1.1 | .9 |
| 2.0 | 2.2 | 1.9 | 4.4 | 2.2 | 1.6 |
| 4.2 | 3.8 | 3.2 | 9.4 | 3.8 | 2.6 |
| 5.1 | 4.5 | 3.8 | 11.4 | 4.5 | 3.1 |
| 7.7 | 7.4 | 6.4 | 16.4 | 7.4 | 5.3 |
| 11.8 | 10.5 | 8.9 | 24.5 | 10.5 | 7.4 |
| 18.5 | 15.0 | 12.5 | 40.2 | 15.0 | 9.9 |
| 29.2 | 22.5 | 18.6 | 62.1 | 22.5 | 14.6 |
| 46.0 | 33.2 | 27.0 | 93.5 | 33.2 | 21.2 |
| 72 | 49.7 | 39.9 | 145.0 | 49.7 | 30.9 |
| 117 | 74.4 | 58.3 | 223 | 74.4 | 45.2 |
| 175 | 105.0 | 80.7 | 320 | 105.0 | 62.4 |
| 318 | 163.2 | 118.1 | 545 | 163.2 | 87.7 |
| 477 | 227.4 | 157.9 | 754 | 227.4 | 119.3 |
| 725 | 318 | 208.0 | | | |

Ethane on silica (cont.)

| Press. | Total vol. | Vol.ads. | Press. | Total vol. | Vol.ads. |
|---|---|---|---|---|---|
| | 50° | | | 80° | |
| 2.4 | 1.1 | .8 | 3.6 | 1.1 | .7 |
| 5.3 | 2.2 | 1.5 | 8.8 | 2.2 | 1.2 |
| 11.5 | 3.8 | 2.4 | 18.2 | 3.8 | 1.7 |
| 14.0 | 4.5 | 2.8 | 22.2 | 3.8 | 1.7 |
| 19.9 | 7.4 | 4.9 | 31.4 | 7.4 | 3.7 |
| 29.7 | 10.5 | 6.9 | 46.3 | 10.5 | 5.1 |
| 48.3 | 15.0 | 8.9 | 73.0 | 15.0 | 6.3 |
| 73.7 | 22.5 | 13.2 | 108.1 | 22.5 | 9.5 |
| 114.8 | 33.2 | 18.6 | 163.5 | 33.2 | 13.4 |
| 169 | 49.7 | 28.0 | 239 | 49.7 | 20.3 |
| 260 | 74.4 | 40.5 | 362 | 74.4 | 28.9 |
| 368 | 105.0 | 56.4 | 502 | 105.0 | 40.2 |
| 594 | 163.2 | 81.2 | 788 | 163.2 | 53.8 |
| 887 | 227.4 | 117.2 | | | |
| | 60° | | | 90° | |
| 2.9 | 1.1 | .7 | 4.1 | 1.1 | .6 |
| 6.5 | 2.2 | 1.4 | 9.8 | 2.2 | 1.1 |
| 14.0 | 3.8 | 2.1 | 20.6 | 3.8 | 1.4 |
| 16.6 | 4.5 | 2.5 | 24.7 | 4.5 | 1.6 |
| 23.3 | 7.4 | 4.6 | 34.7 | 7.4 | 3.4 |
| 35.5 | 10.5 | 6.2 | 51.3 | 10.5 | 4.5 |
| 56.6 | 15.0 | 8.0 | 81.0 | 15.0 | 5.4 |
| 85.0 | 22.5 | 11.9 | 119.8 | 22.5 | 8.4 |
| 128.6 | 33.2 | 17.2 | 179 | 33.2 | 11.8 |
| 198 | 49.7 | 24.7 | 262 | 49.7 | 17.9 |
| 295 | 74.4 | 36.5 | 381 | 74.4 | 27.1 |
| 418 | 105.0 | 50.0 | 538 | 105.0 | 63.0 |
| 665 | 163.2 | 72.0 | | | |
| 918 | 227.4 | 96.2 | | | |
| 918 | | | | | |
| | 70° | | | 100° | |
| 3.1 | 1.1 | .7 | 4.8 | 1.1 | .6 |
| 7.5 | 2.2 | 1.3 | 10.9 | 2.2 | 1.0 |
| 16.1 | 3.8 | 1.9 | 22.9 | 3.8 | 1.2 |
| 19.4 | 4.5 | 2.2 | 27.0 | 4.5 | 1.4 |
| 27.4 | 7.4 | 4.1 | 37.7 | 7.4 | 3.1 |
| 41.0 | 10.5 | 5.6 | 56.0 | 10.5 | 4.0 |
| 64.8 | 15.0 | 7.1 | 88.3 | 15.0 | 4.8 |
| 96.7 | 22.5 | 10.7 | 131.0 | 22.5 | 7.2 |
| 146.3 | 33.2 | 15.2 | 194 | 33.2 | 10.2 |
| 217 | 49.7 | 22.7 | 285 | 49.7 | 15.4 |
| 332 | 74.4 | 32.2 | 420 | 74.4 | 22.6 |
| 461 | 105.0 | 45.0 | 570 | 105.0 | 32.5 |
| 722 | 163.2 | 64.7 | | | |

Ethane on silica (cont.)

110°

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| 5.4 | 1.1 | .5 |
| 11.9 | 2.2 | .9 |
| 25.0 | 3.8 | 1.0 |
| 29.1 | 4.5 | 1.2 |
| 40.5 | 7.4 | 2.9 |
| 60.0 | 10.5 | 3.7 |
| 95 | 15.0 | 4.1 |
| 142 | 22.5 | 6.1 |
| 209 | 33.2 | 8.8 |
| 306 | 49.7 | 13.3 |
| 446 | 74.4 | 19.1 |

120°

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| 6.1 | 1.1 | .4 |
| 12.8 | 2.2 | .8 |
| 27.0 | 3.8 | .9 |
| 31.0 | 4.5 | 1.1 |
| 43.1 | 17.4 | 2.6 |
| 63.7 | 10.5 | 3.4 |
| 101.9 | 15.0 | 3.6 |
| 150.7 | 22.5 | 5.4 |
| 222 | 33.2 | 7.6 |
| 325 | 49.7 | 11.4 |
| 446 | 74.4 | 17.3 |

130°

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| 6.5 | 1.1 | .4 |
| 13.4 | 2.2 | .7 |
| 28.7 | 3.8 | .8 |
| 32.7 | 4.5 | .9 |
| 45.8 | 7.4 | 2.4 |
| 67.0 | 10.5 | 3.1 |
| 108.0 | 15.0 | 2.9 |
| 158.2 | 22.5 | 4.6 |
| 235 | 33.2 | 6.4 |
| 343 | 49.7 | 9.7 |
| 494 | 74.4 | 14.9 |

160°

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| 15.0 | 2.2 | .6 |
| 37.1 | 4.5 | .6 |
| 52.0 | 7.4 | 1.9 |
| 76.6 | 10.5 | 2.4 |
| 122 | 15.0 | 1.9 |
| 180 | 22.5 | 2.9 |
| 264 | 33.2 | 4.0 |
| 383 | 49.7 | 6.2 |
| 556 | 74.4 | 8.9 |

140°

| Press. | Total vol. | Vol.ads. |
|---|---|---|
| 6.8 | 1.1 | .4 |
| 14.0 | 2.2 | .7 |
| 30.0 | 3.8 | .6 |
| 34.2 | 4.5 | .8 |
| 48.0 | 7.4 | 2.1 |
| 70.1 | 10.5 | 2.9 |
| 113.2 | 15.0 | 2.5 |
| 165 | 22.5 | 4.2 |
| 246 | 33.2 | 5.4 |
| 357 | 49.7 | 8.9 |
| 517 | 74.4 | 12.8 |

2. Adsorption of ethane on charcoal.

| Temp. | Pres. | Tot.vol. | Vol.ads. | Temp. | Pres. | Tot.vol. | Vol.ads. |
|---|---|---|---|---|---|---|---|
| 18.6 | 1.03 | 85.0 | 84.9 | 78.0 | 56.5 | 56.5 | 55.6 |
| 82.2 | .25 | 3.0 | 3.0 | 80.8 | 12.6 | 79.8 | 78.4 |
| 79.0 | 1.70 | 15.3 | 15.1 | 86.2 | 15.7 | 78.2 | 76.5 |
| 78.8 | 1.70 | 15.5 | 15.3 | 119.0 | 30.4 | 40.1 | 37.0 |
| 82.0 | .73 | 7.5 | 7.4 | 167.1 | 168.1 | 131.6 | 115.5 |
| 77.0 | 4.7 | 35.7 | 35.2 | 162.9 | 28.9 | 28.9 | 26.1 |
| 20.7 | 2.8 | 170.8 | 170.5 | 123.0 | 86.5 | 170.8 | 162.0 |

3. Adsorption of propane on silica gel.

| Temp. | Press. | Vol. ads. | Temp. | Press. | Vol. ads. |
|---|---|---|---|---|---|
| 17.2 | 28.2 | 46.4 | 0.0 | 2.6 | 13.1 |
| 95.8 | 187.0 | 27.8 | " | 4.4 | 20.0 |
| 139.4 | 292 | 18.6 | " | 7.7 | 26.3 |
| -33.6 | 1.6 | 49.8 | " | 11.4 | 43.6 |
| -44.0 | 16.5 | 203.3 | " | 17.1 | 51.1 |
| 19.6 | 228 | 174.6 | " | 21.0 | 58.9 |
| 80.4 | 708 | 111.0 | " | 27.7 | 70.9 |
| 81.7 | 569 | 12.6 | " | 35.6 | 82.6 |
| 19.8 | 10.0 | 17.9 | " | 41.0 | 91.5 |
| 150.3 | 137.2 | 4.6 | " | 3.9 | 16.2 |
| 49.6 | 28.0 | 15.7 | " | 6.9 | 24.6 |
| 0.0 | 9.3 | 32.6 | " | 9.7 | 36.8 |
| 90.4 | 98.5 | 22.5 | " | 16.4 | 45.5 |
| 21.1 | 4.9 | 10.7 | " | 24.9 | 61.2 |
| 0.0 | 2.0 | 11.0 | " | 42.6 | 89.1 |

4. Adsorption of propane on charcoal.

| Temp. | Press. | Vol.ads. | Temp. | Press. | Vol. ads. |
|---|---|---|---|---|---|
| 79.1 | .73 | 80.6 | 161.8 | 70.5 | 271.5 |
| 153.6 | 10.7 | 79.7 | 123.5 | 2.1 | 49.6 |
| 231.5 | 56.4 | 75.6 | 156.7 | 6.0 | 49.1 |
| 230.1 | 58.0 | 75.5 | 175.5 | 9.9 | 48.8 |
| 188 | 25.8 | 78.3 | 205.5 | 21.2 | 47.8 |
| 116.0 | 3.5 | 80.3 | 133.5 | 2.7 | 49.4 |
| 123.1 | .57 | 24.1 | 162.0 | 3.0 | 23.9 |
| 19.6 | 1.07 | 278.1 | 182.9 | 5.4 | 23.7 |
| 79.1 | 6.8 | 277.5 | 154.6 | 61.6 | 272.2 |
| 109.1 | 17.1 | 276.4 | | | |

5. Adsorption of butane on silica gel.

Temperature = 17.5°

| Pressure | Volume adsorbed | Pressure | Vol. adsorbed |
|---|---|---|---|
| .60 | 8.2 | ~~36.8~~ 18.4 | 83.5 |
| 1.4 | 14.5 | ~~52.9~~ 33.3 | 122.1 |
| 2.6 | 23.7 | ~~78.8~~ 60.0 | 176.7 |
| 5.1 | 36.9 | ~~113.8~~ 101 | 254.0 |
| 9.6 | 55.7 | 177 | 363.4 |

Butane on silica (cont)

| 0.0° |  | 40.0° |  | 60.0° |  |
|---|---|---|---|---|---|
| Press. | Vol.ads. | Press. | vol. Ads. | Press. | Vol. Ads. |
| .57 | 12.9 | 1.6 | 8.4 | .90 | 1.5 |
| .87 | 19.6 | 3.2 | 14.0 | 1.7 | 3.0 |
| 1.6 | 29.1 | 7.25 | 24.3 | 2.9 | 4.7 |
| 2.9 | 45.0 | 16.2 | 43.1 | 4.6 | 8.1 |
| 5.7 | 64.2 | 35.15 | 69.2 | 8.1 | 11.9 |
| 10.4 | 94.3 | 97.5 | 135.7 | 12.8 | 17.1 |
| 19.6 | 140.0 | 208 | 221.7 | 21.1 | 25.4 |
| 36.9 | 205.1 | 268 | 262.2 | 34.1 | 37.2 |
| 67.6 | 297.9 |  |  | 55.0 | 53.2 |
| 126 | 429.9 |  |  | 88 | 75.5 |
| 210 | 626.8 |  |  | 143 | 1o6.2 |
| 327 | 920.1 |  |  | 234 | 151.0 |
|  |  |  |  | 368 | 209.8 |

6 Adsorption of isopentane on silica gel.

| Temp. | Press. | Vol. | Temp. | Press. | Vol. | Temp. | Press. | Vol. |
|---|---|---|---|---|---|---|---|---|
| 20.1 | 2.4 | 41.2 | 20.1 | 10.0 | 89.7 | 20.1 | .9 | 23.5 |
| 29.1 | 4.4 | 4o.8 | 29.1 | 15.8 | 88.5 | 29.1 | 1.9 | 23.4 |
| 39.2 | 7.0 | 40.2 | 39.2 | 23.8 | 86.8 | 39.2 | 3.2 | 23.1 |
| 49.3 | 11.0 | 39.4 | 49.3 | 34.5 | 84.6 | 49.3 | 4.8 | 22.7 |
| 62.2 | 15.8 | 38.5 |  |  |  |  |  |  |

7. Rate of flow data

<u>Butane, 0°</u>

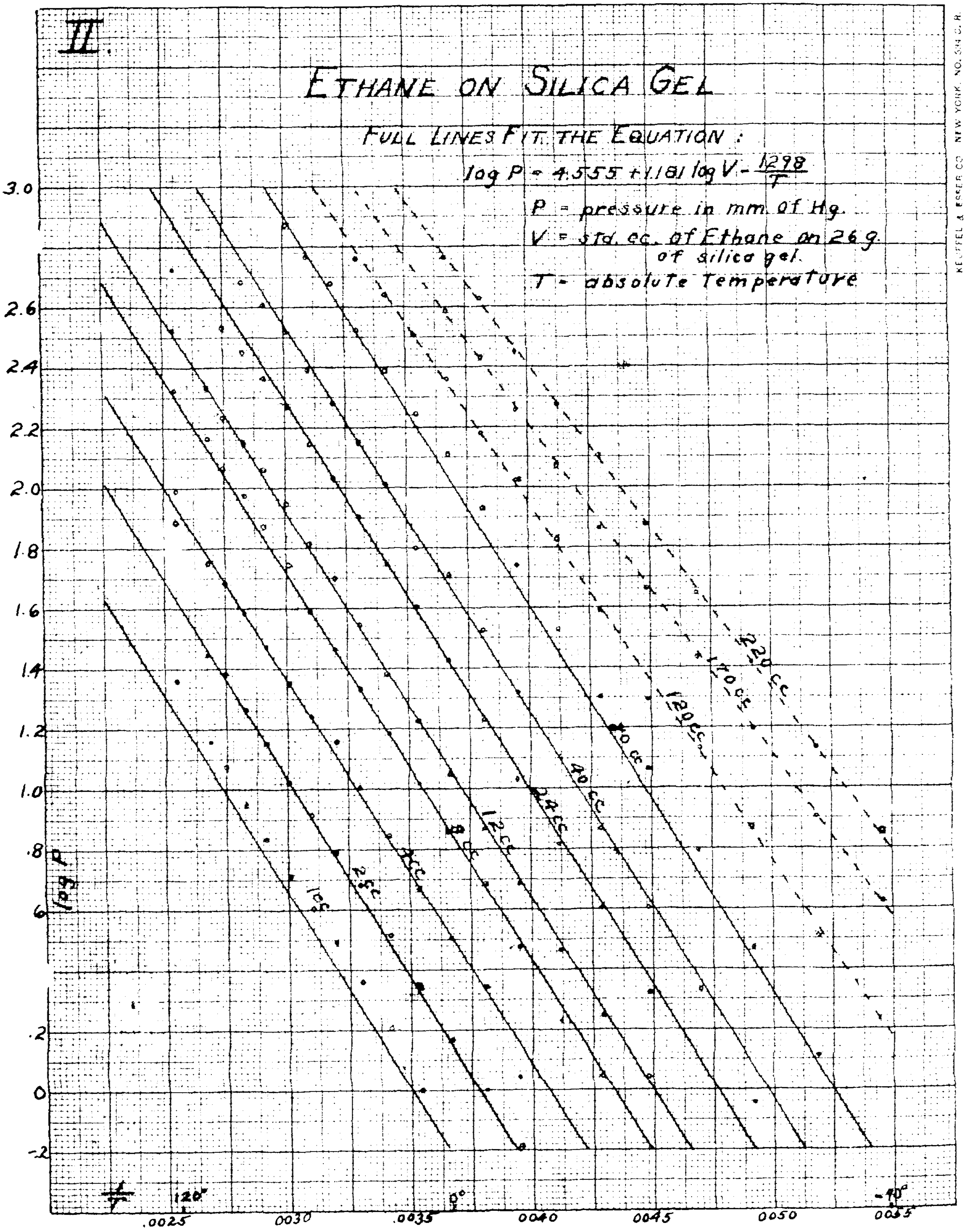
| Time (min) | Vol.on gel |
|---|---|
| 0 | 29.9 |
| 2 | 21.4 |
| 3 | 19.36 |
| 4 | 17.52 |
| 4.2 | 17.52 |
| 5 | 16.27 |
| 5.2 | 16.27 |
| 6.2 | 15.45 |
| 7.2 | 14.42 |
| 8.2 | 13.64 |
| 9.2 | 13.06 |
| 10.2 | 12.48 |
| 13.2 | 11.36 |
| 13.4 | 11.22 |
| 17.2 | 10.03 |
| 17.4 | 9.91 |
| 22.2 | 8.84 |
| 29.4 | 7.57 |

<u>Isopentane, 19.1°</u>

| Time (min) | Vol. on gel |
|---|---|
| 0 | 6.80 |
| 16 | 5.23 |
| 30 | 4.59 |
| 75 | 3.38 |
| 154 | 2.88 |
| 274 | 2.53 |
| 1234 | .93 |
| 790 | 1.56 |
| 880 | 1.23 |
| 2oo | 2.57 |

<u>Isopentane, 29.1°</u>

| Time (min) | Vol. on gel |
|---|---|
| 0 | 7.29 |
| 13 | 4.03 |
| 5 | 5.47 |
| 30 | 2.78 |
| 90 | 2.22 |



II.

ETHANE ON SILICA GEL

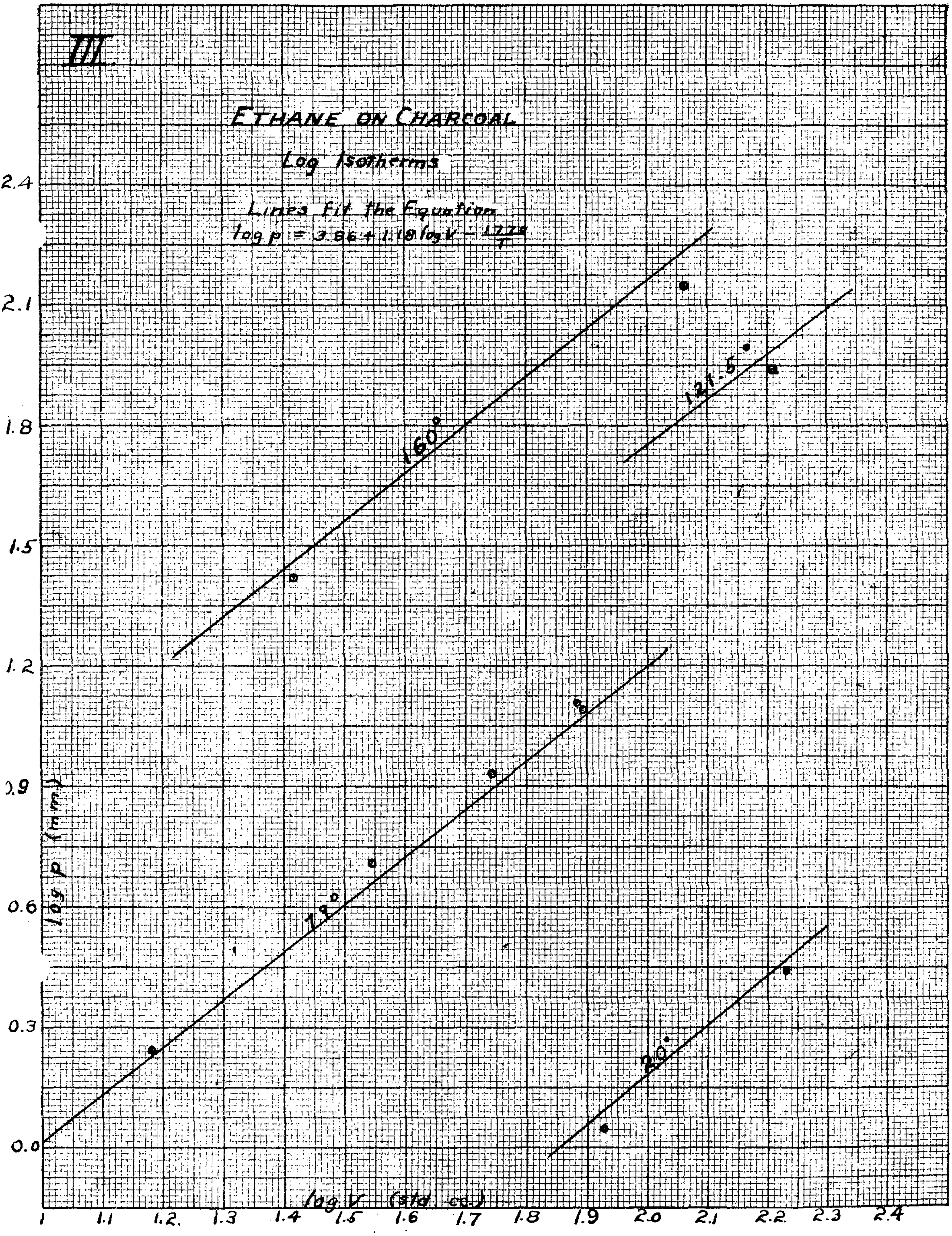
FULL LINES FIT THE EQUATION :

$$\log P = 4.555 + 1.181 \log V - \frac{1298}{T}$$

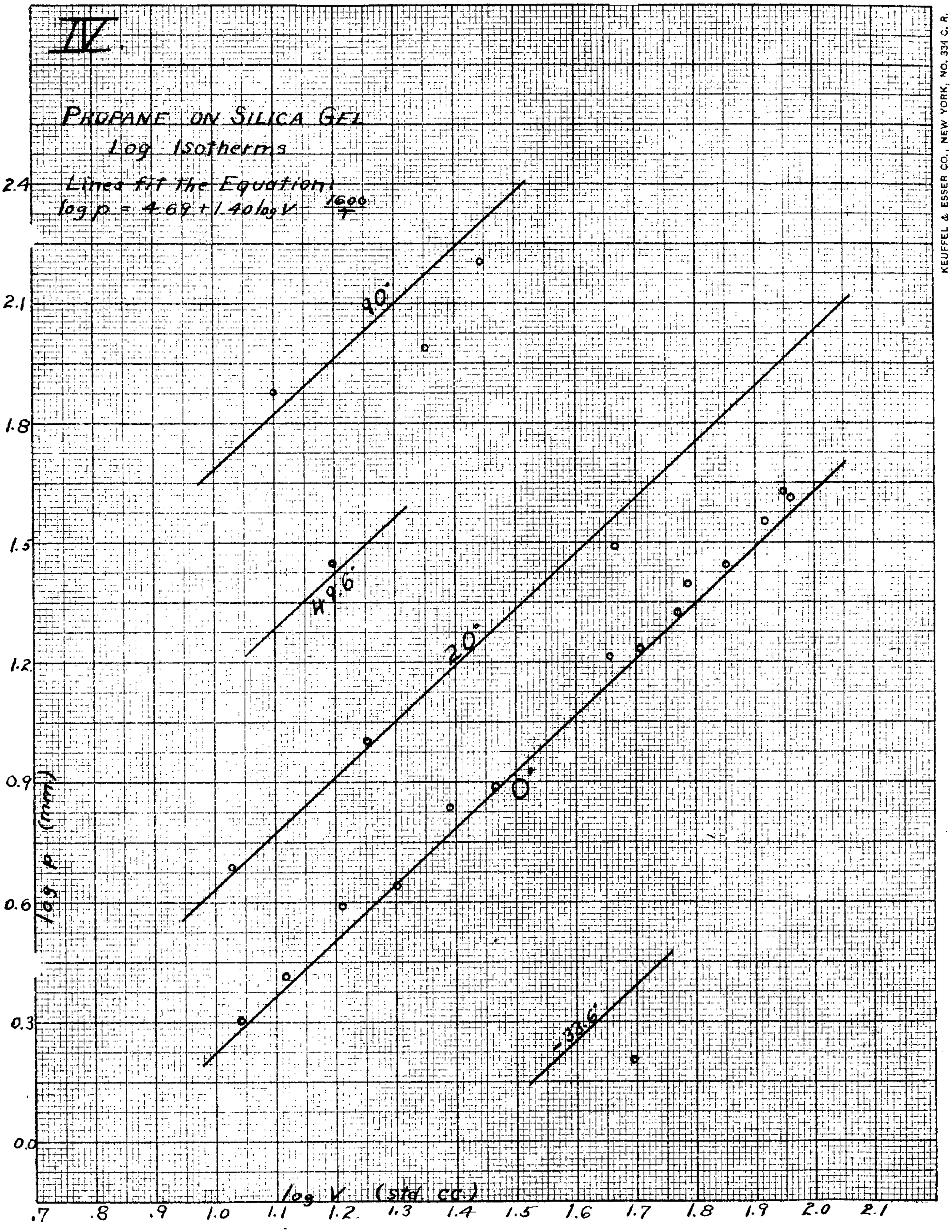
P = pressure in mm. of Hg.

V = std. cc. of Ethane on 26 g. of silica gel.

T = absolute Temperature



KEUFFEL & ESSER CO., NEW YORK, NO. 334 C. R.



IV

PROPANE ON SILICA GEL

Log Isotherms

Lines fit the Equation:

$\log p = 4.69 + 1.40 \log V - \frac{1600}{T}$

KEUFFEL & ESSER CO., NEW YORK, NO. 334 C. R.

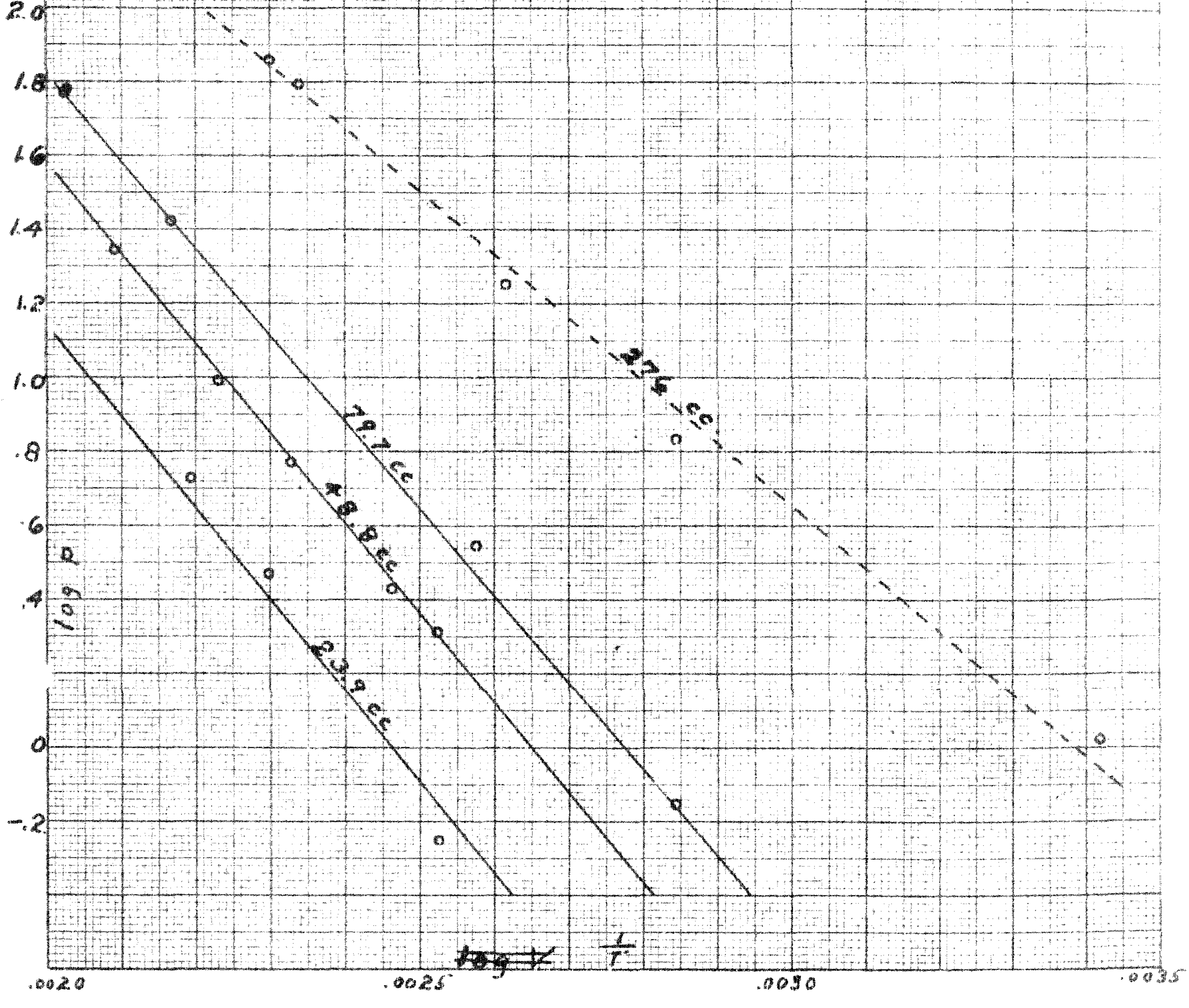
# V

## PROPANE ON CHARCOAL

Log isasters.

FULL LINES Fit the Equation

$$\log p = 4.08 + 1.40 \log V - \frac{2440}{T}$$



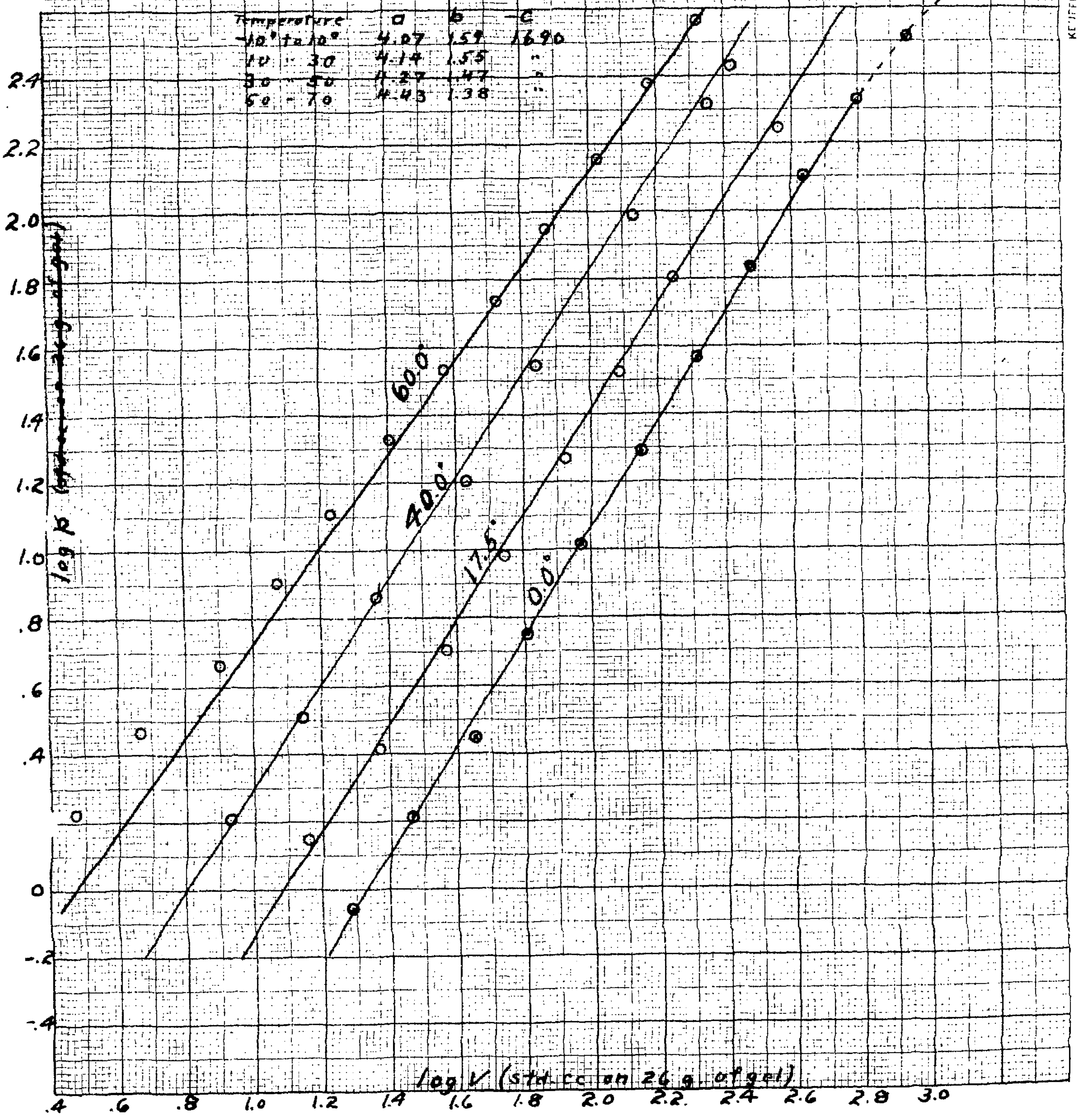
# VI

# BUTANE ON SILICA

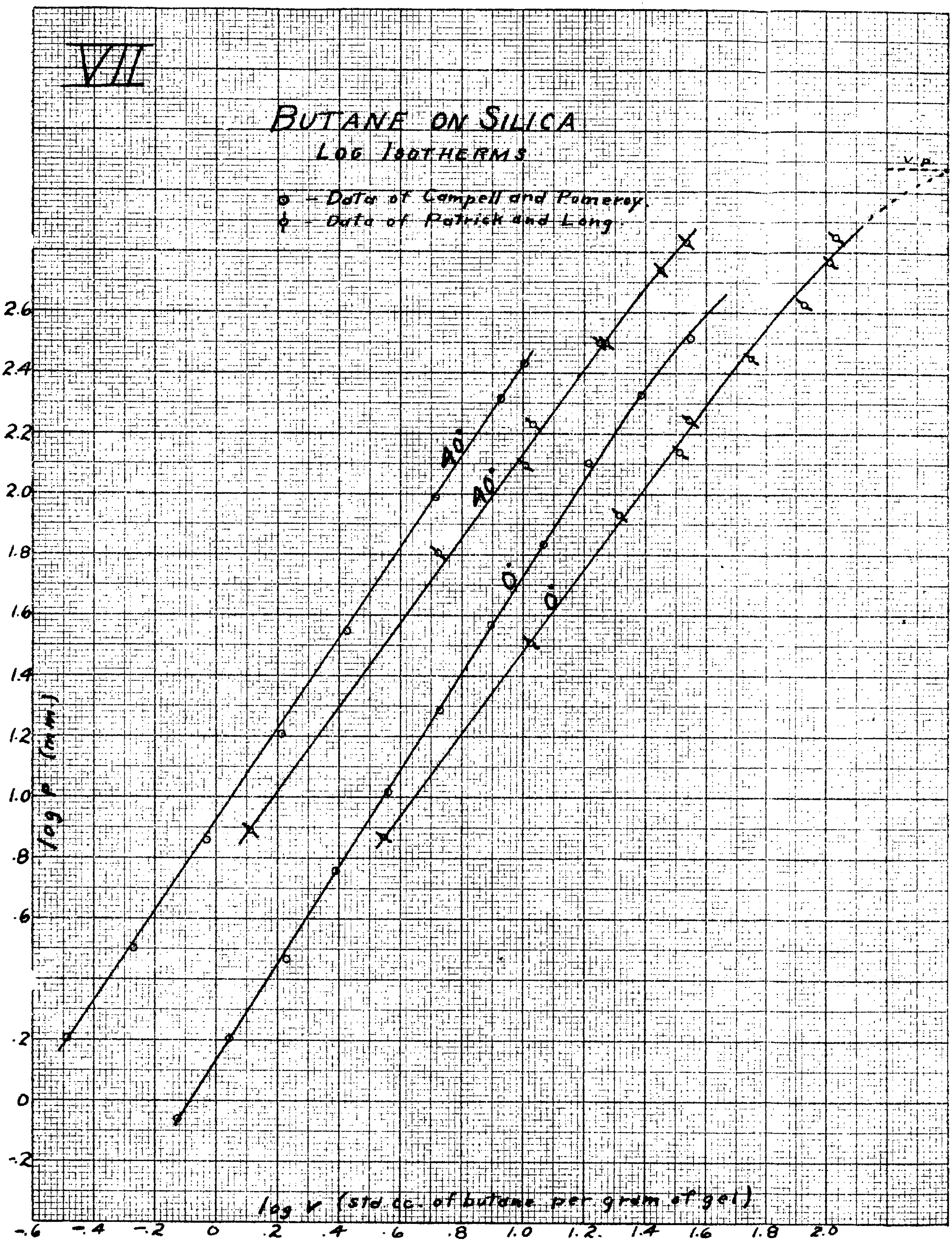
## Log Isotherms

$$\log p = a + b \log v - \frac{c}{T}$$

| Temperature | a | b | -c |
|---|---|---|---|
| -10° to 10° | 4.07 | 1.59 | 1690 |
| 10 - 30 | 4.14 | 1.55 | " |
| 30 - 50 | 4.27 | 1.47 | " |
| 50 - 70 | 4.43 | 1.38 | " |



KEUFFEL & ESSER CO., NEW YORK, NO. 334 C. R.



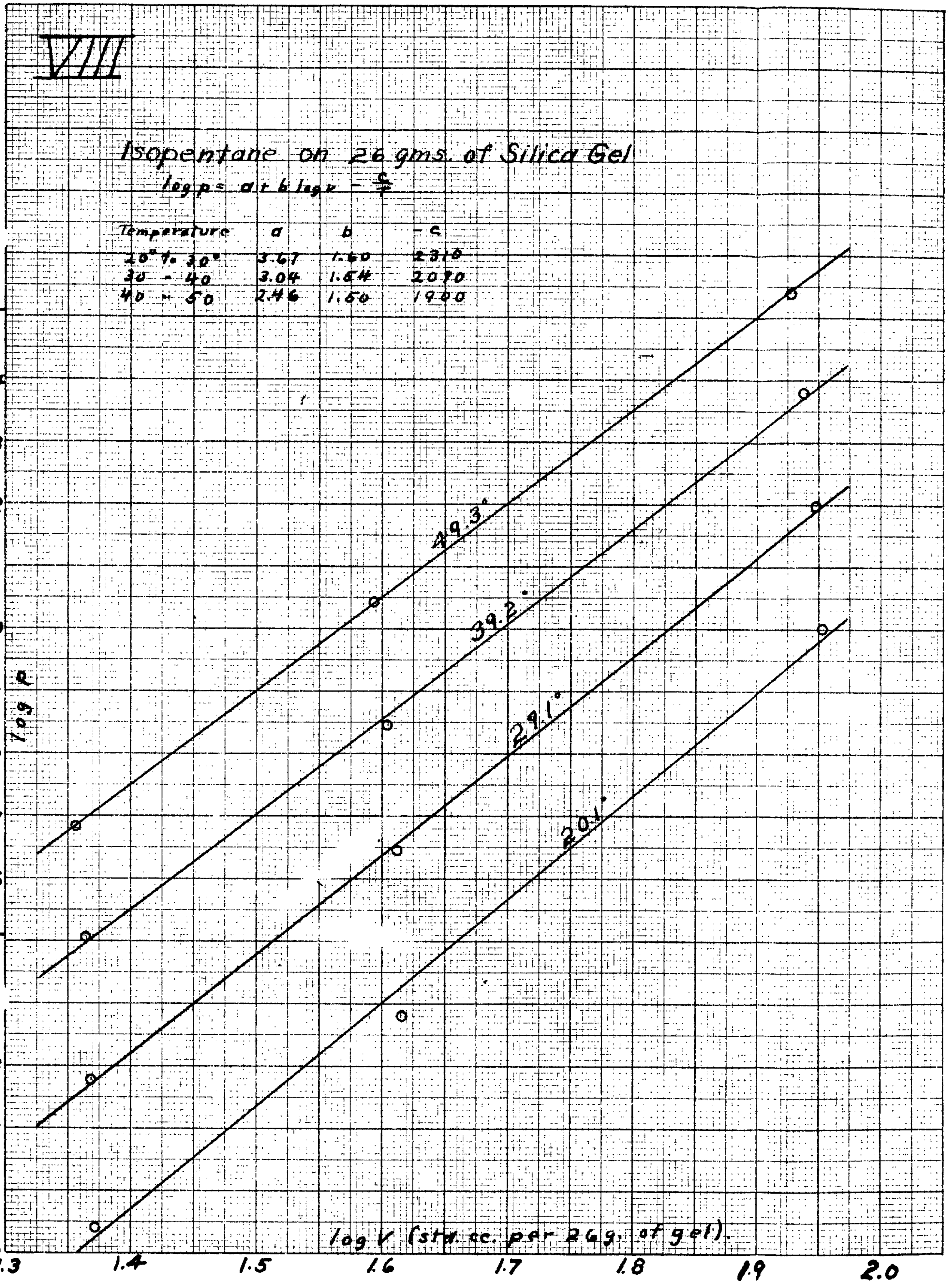
KEUFFEL & ESSER CO. NEW YORK, NO. 334 C. R.

VIII

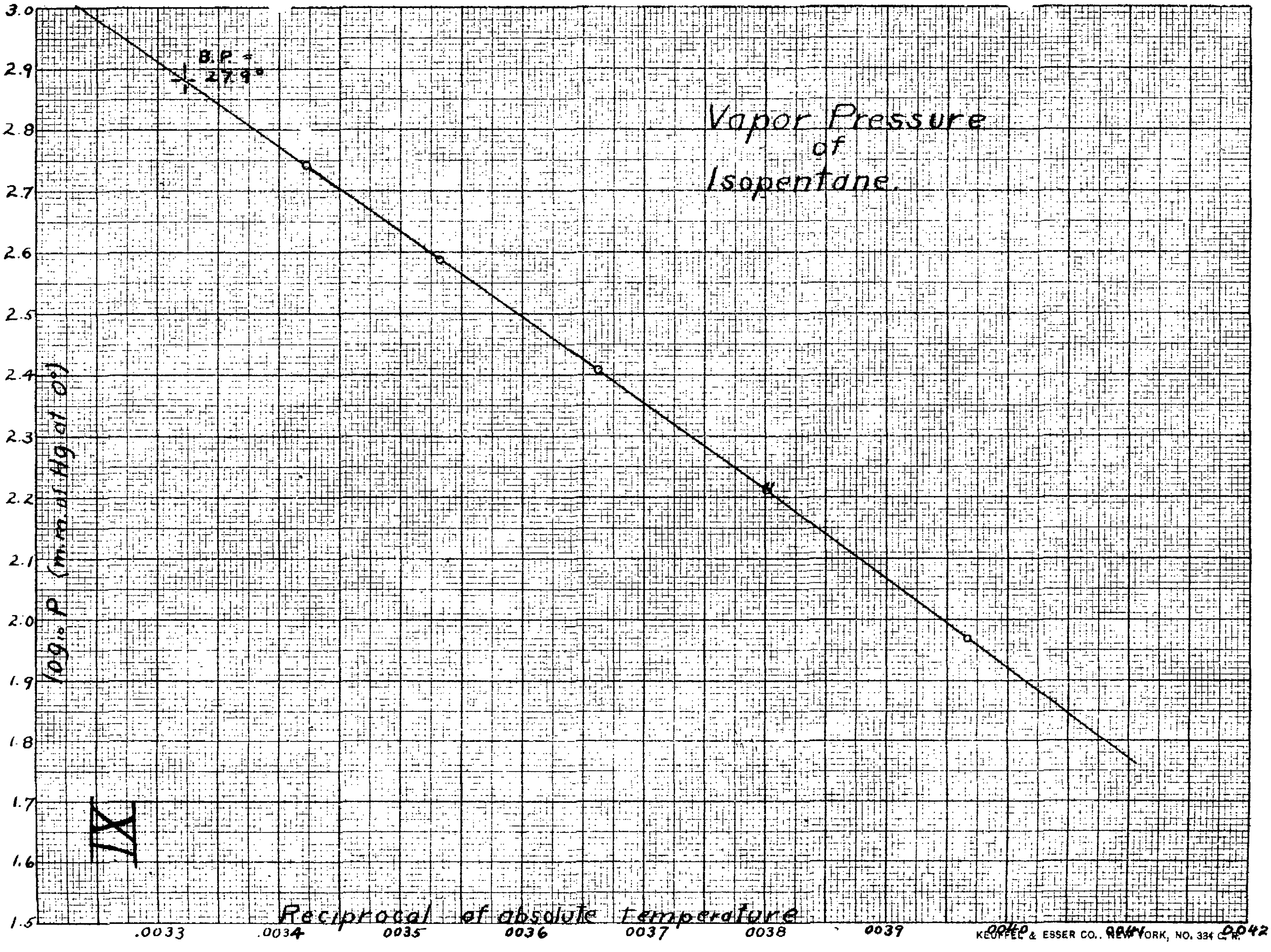
## Isopentane on 26 gms. of Silica Gel

$$\log p = a + b \log v - \frac{c}{T}$$

| Temperature | a | b | − c |
|---|---|---|---|
| 20° to 30° | 3.67 | 1.60 | 2310 |
| 30 - 40 | 3.04 | 1.54 | 2070 |
| 40 - 50 | 2.46 | 1.50 | 1900 |

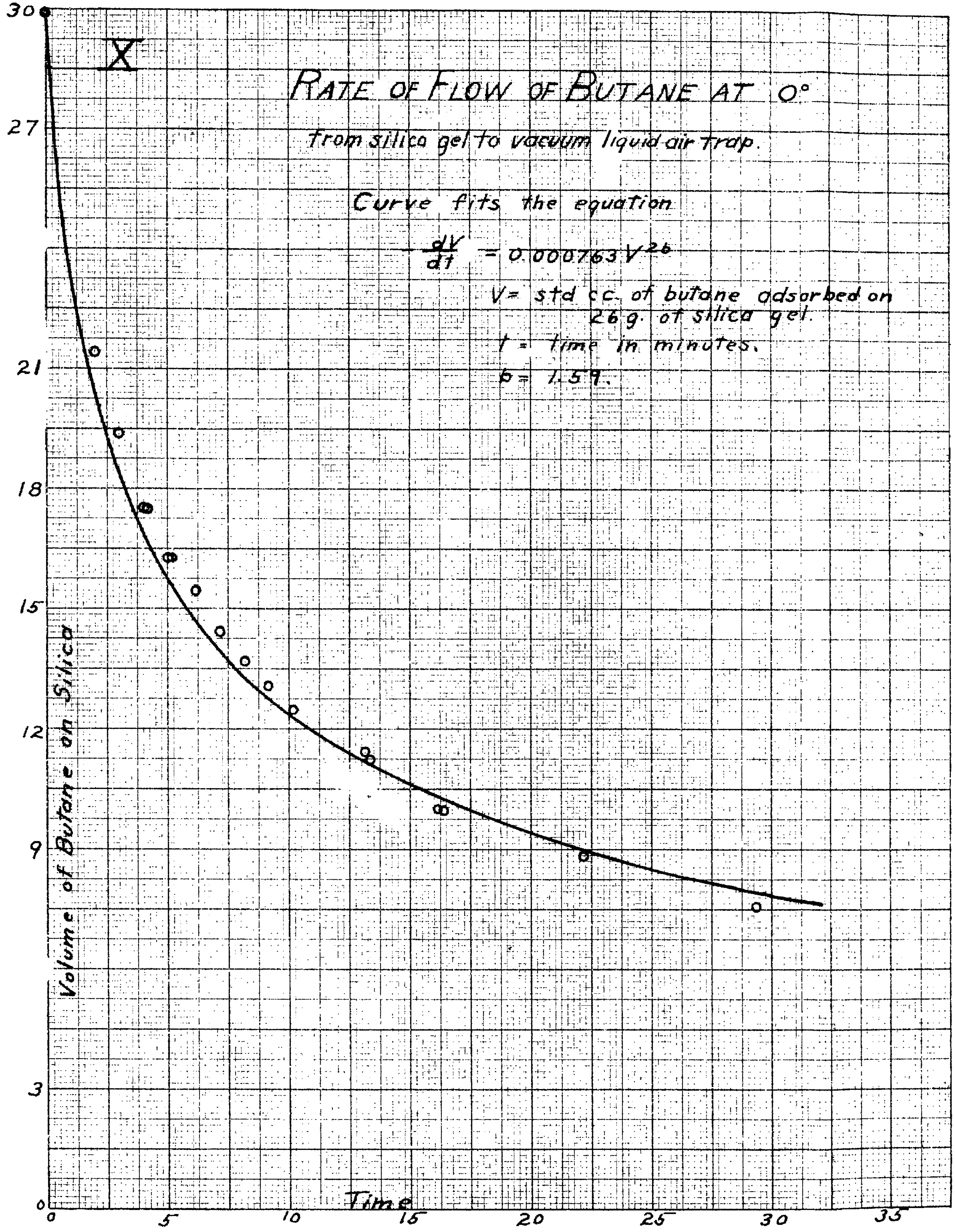


KEUFFEL & ESSER CO., NEW YORK, NO. 334 C. R.



IX

Vapor Pressure of Isopentane.



X

RATE OF FLOW OF BUTANE AT 0°

from silica gel to vacuum liquid air trap.

Curve fits the equation

$$-\frac{dV}{dt} = 0.000763\,V^{2b}$$

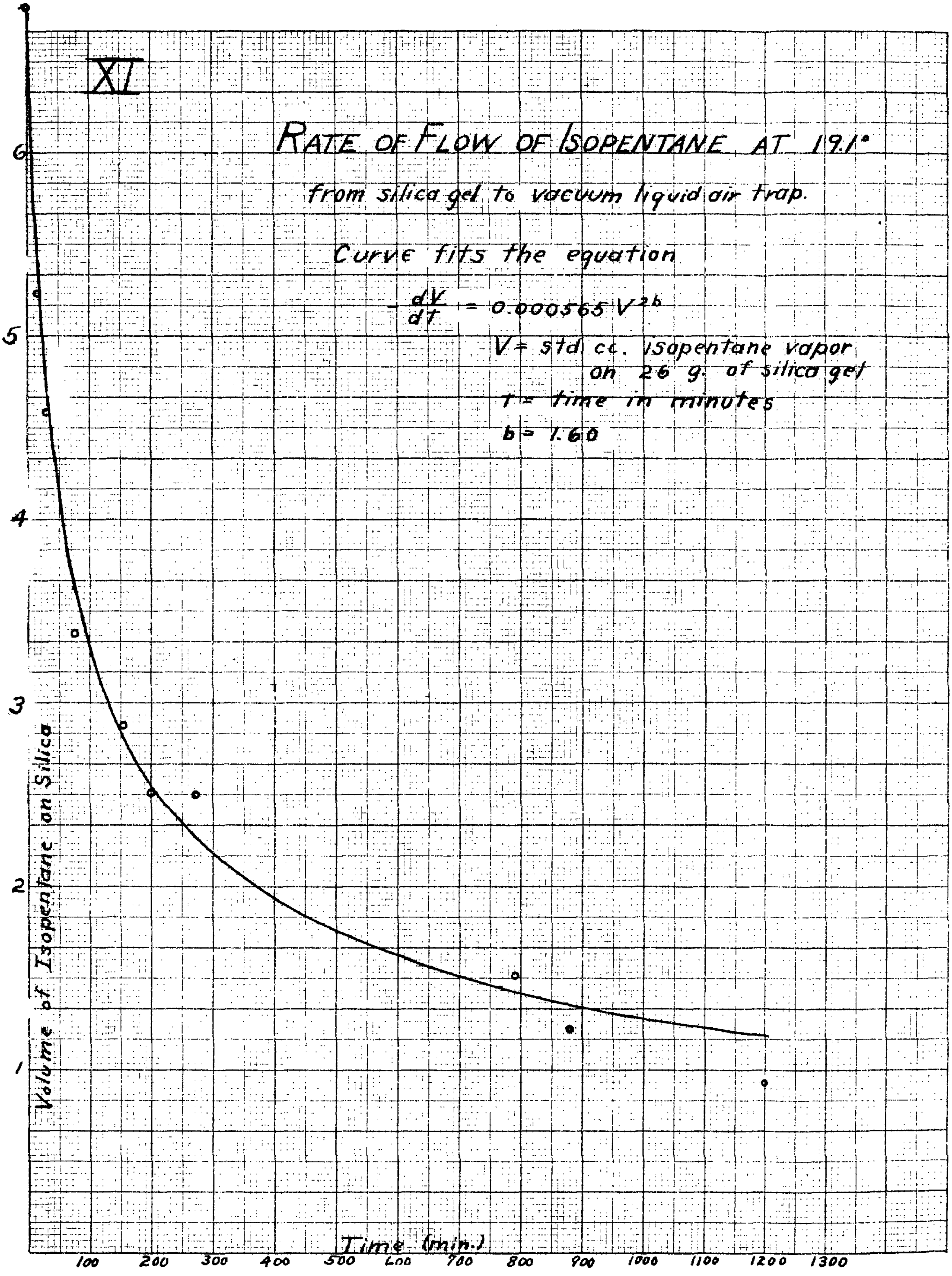
V = std cc. of butane adsorbed on 26 g. of silica gel.

t = time in minutes.

b = 1.59.

KEUFFEL & ESSER CO., NEW YORK, NO. 331 C. R.

XI



RATE OF FLOW OF ISOPENTANE AT 19.1°

from silica gel to vacuum liquid air trap.

Curve fits the equation

$$-\frac{dV}{dt} = 0.000565\,V^{2b}$$

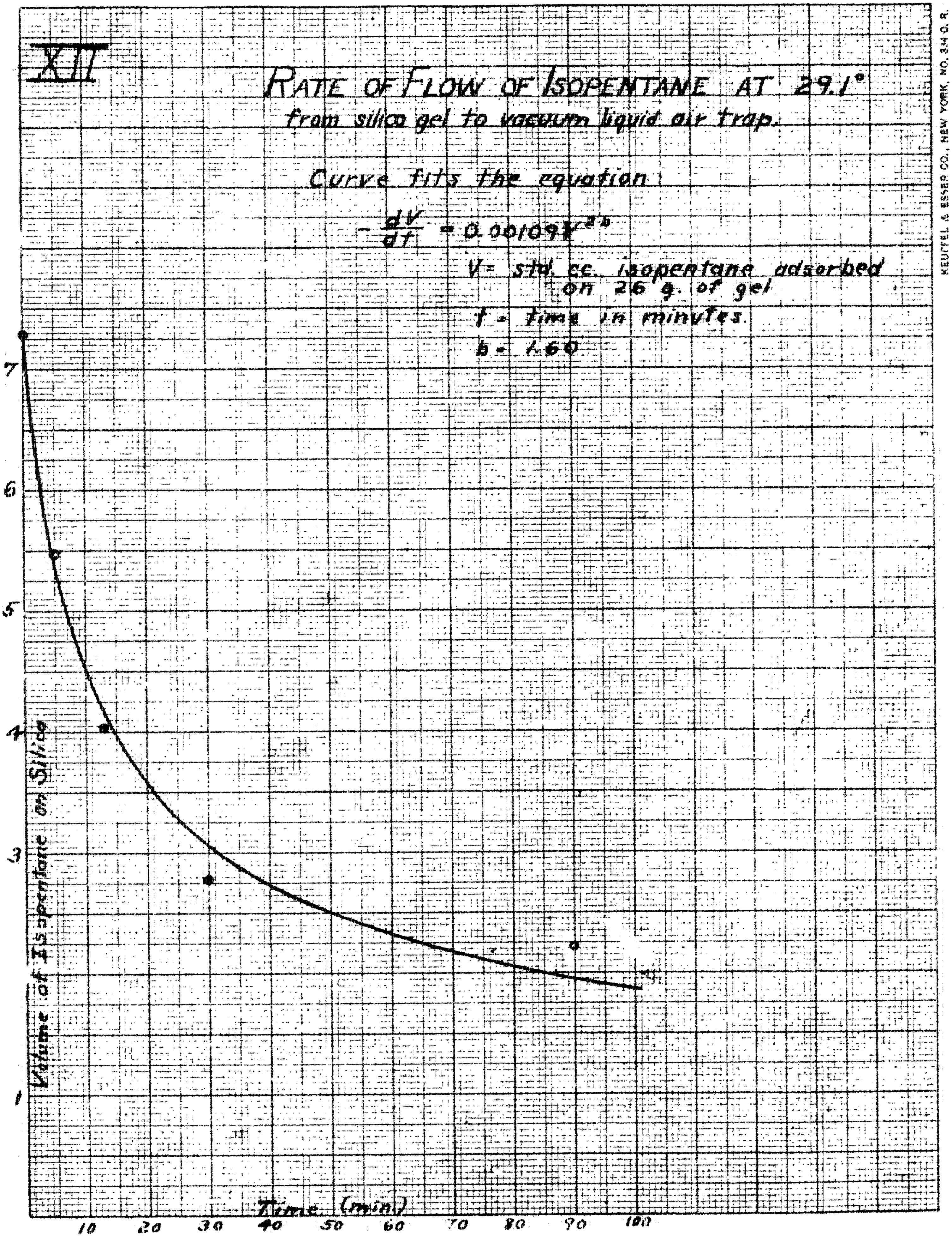
V = std. cc. isopentane vapor on 26 g. of silica gel

t = time in minutes

b = 1.60

KEUFFEL & ESSER CO., NEW YORK, NO. 334 C. R.

XII



## RATE OF FLOW OF ISOPENTANE AT 29.1°

from silica gel to vacuum liquid air trap.

Curve fits the equation

$$-\frac{dV}{dt} = 0.00109V^{2b}$$

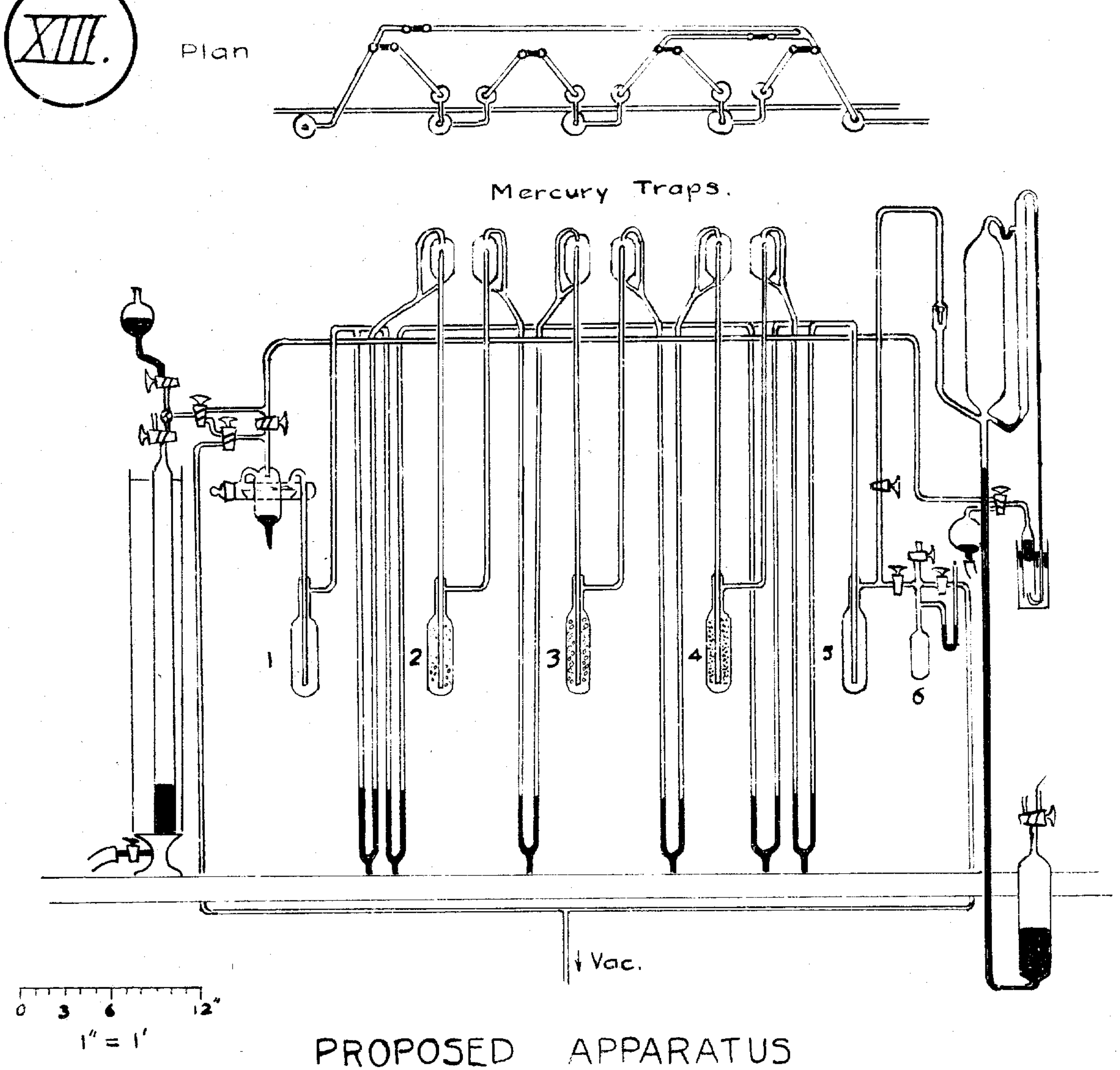
V = std. cc. isopentane adsorbed on 26 g. of gel

t = time in minutes.

b = 1.60

KEUFFEL & ESSER CO., NEW YORK, NO. 314 O.R.

XIII.



PROPOSED APPARATUS
FOR ADSORPTION ANALYSIS.