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# ON PHYSICAL ADSORPTION

# IV - A COMPARISON OF TWO THEORIES OF MULTILAYER ADSORPTION

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# ON PHYSICAL ADSORPTION

## IV - A COMPARISON OF TWO THEORIES OF MULTILAYER ADSORPTION

Sydney Ross

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Since its publication ten years ago the multilayer adsorption theory of Brunauer, Emmett and Teller(3) has been the source of a prolific literature of both theoretic and practical importance. Although in its original and simpler form, the theory does not describe experimental adsorption isotherms above relative pressures of 0.3, various modifications have been suggested to enlarge its scope (2,8,1,4). In general, the modifications have dealt either with the summation of the adsorption to a limited number of layers, or to the variation of the heat of adsorption in the second and higher layers. In every case, it has been found necessary to add a third empirical constant to the two constants of the original equation.

Recently another treatment of the multilayer adsorption theory has been published by G. F. Hüttig(6), which challenges an implicit assumption of the B.E.T. theory not heretofore recognized. A comparison of the two treatments brings into prominence some important theoretical considerations, which it is my present purpose to point out.

The following brief derivation follows Hüttig's procedure but uses the symbols of the B.E.T. theory which are now familiar to U.S. chemists. As in the B.E.T. theory, Hüttig uses Langmuir's treatment of unimolecular adsorption applied to each layer. Let $S_0$, $S_1$, $S_2$ . . . $S_i$ . . . represent the surface area that is covered by 0, 1, 2, . . . i, . . . layers of adsorbed molecules, containing $n_1$, $n_2$, . . . $n_i$, . . . molecules respectively. The symbol $\chi$ represents the maximum number of molecules that is adsorbed on the first layer.

$$S_0 = \sigma_0 (\chi - n_1) \qquad 1$$
$$S_1 = \sigma_0 (n_1 - n_2) \qquad 2$$
$$S_2 = \sigma_0 (n_2 - n_3) \qquad 3$$
$$S_3 = \sigma_0 (n_4 - n_3) \text{ , etc.}$$

where $\sigma_0$ is the area per adsorbed molecule on a completely filled layer. The conditions for equilibrium are that on each layer the rate of condensation is equal to the rate of evaporation. In its most general form, for the first layer, this condition is expressed.

$$a_1 p\,(\chi - n_1) = b_1\,(n_1 - \gamma n_2)\,e^{-E_1/RT} \qquad 4$$

where p is the pressure, $E_1$ the heat of adsorption in the first layer, $a_1$, $b_1$ and $\gamma$ are constants. The right-hand side of this equation signifies that the rate of evaporation of molecules on the first layer is proportional to the total number of molecules on that layer minus a certain effect produced by those molecules that are covered by two or more higher layers. The B.E.T. theory assumes that this effect is powerful enough to prevent evaporation of first-layer molecules so covered ($\gamma = 1$), while the theory of G. F. Hüttig uses the other extreme viewpoint, namely, that molecules covered by second and higher layers still play their role in evaporation as freely as if the higher layers were not present ($\gamma = 0$). This is the only point of difference of the two theories. All the other assumptions made in the B.E.T. development are followed by Hüttig[3].

---

3) Up to this point, Hüttig's approach is identical with the much earlier paper of E. C. C. Baly, Proc. Roy. Soc. 160 A, 465, 1937. Hüttig's original contribution is to combine the ideas of Baly with the simplifying assumptions of Brunauer, Emmett and Teller. It is perhaps because of the disruption of the usual interchange of scientific journals between countries caused by the late war that Hüttig is apparently unaware of these earlier workers so well known in this country. At any rate, he makes no reference to them although his development runs so closely parallel. The mathematical formalism in the present paper follows that of the B.E.T. theory and will be found to differ from that employed either by Baly or by Hüttig.

Hüttig's mechanism for equilibrium on each layer gives:

$$a_1 p\ (\chi - n_1) = b_1 n_1 e^{-E_1/RT} \qquad 5$$

$$a_2 p\ (n_1 - n_2) = b_2 n_2 e^{-E_2/RT} \qquad 6$$

$$a_3 p\ (n_2 - n_3) = b_3 n_3 e^{-E_3/RT}, \text{ etc.} \qquad 7$$

Assume $E_2 = E_3 = \ldots E_i \ldots = E_L$

and assume $b_2/a_2 = b_3/a_3 \ldots\ldots = g$, as in the B.E.T. development.

Let $y = (a_1/b_1)\ p\ e^{E_1/RT}$ 8

$$x = (p/g)\ e^{E_L/RT} \qquad 9$$

and n, the total amount adsorbed, $= n_1 + n_2 + \ldots\ldots$

Equations 5, 6, and 7 then become

$$n_1 = y\ (\chi - n_1) \qquad 10$$

$$n_2 = x\ (n_1 - n_2) \qquad 11$$

$$n_3 = x\ (n_2 - n_3), \text{ etc.} \qquad 12$$

Hence $n = n_1 + n_2 + n_3 + \ldots\ldots$

$$= y\ (\chi - n_1) + xn_1 \qquad 13$$

Combined with Equation 10:

$$n = \chi\left(\frac{y}{1 + y}\right)\left(1 + x\right) \qquad 14$$

For condensation and evaporation on a liquid surface at its equilibrium vapor pressure $p_o$, Equation 7 can be applied:

$$ap_o\phi = be^{-E_L/RT}\phi \qquad 15$$

where $\phi$ is the extent of the liquid surface.

Combining Equations 9 and 15 gives

$$x = p/p_o \qquad 16$$

In the terminology of the B.E.T. theory (3)

$$C = \frac{y}{x} = \frac{a_1 g}{b_1}\ e^{(E_1 - E_L)/RT} \qquad 17$$

Hence $y = Cx = cp/po$

Equation 14 then becomes

$$\frac{n}{\chi} = \frac{V}{Vm} = \left(\frac{C\ p/po}{1 + C\ p/po}\right)\left(1 + p/po\right) \qquad 18$$

This is an expression of Hüttig's theory using constants whose physical significance is the same as the constants found in the B.E.T. theory. For comparison the B.E.T. equation is given

$$\frac{V}{Vm} = \frac{Cp}{(po - p)\left[1 + (C - 1)(p/po)\right]} \qquad 19$$

For the purpose of experimental testing of Equations 18 and 19, they may be written respectively

$$\frac{p}{V}\left(1 + p/po\right) = \frac{po}{C\ Vm} + \frac{p}{Vm} \qquad 20$$

and

$$\frac{p}{V(po - p)} = \frac{1}{C\ Vm} + \left(\frac{C - 1}{C\ Vm}\right) p/po \qquad 21$$

A graphical plot of $\frac{p}{V}(1 + p/po)$ against p is a straight line according to Equation 20, with a slope equal to $\frac{1}{Vm}$ and an intercept equal to $\frac{po}{C\ Vm}$. According to Equation 21, a plot of $\frac{p}{V(po - p)}$ against p/po is a straight line with a slope equal to $\frac{(C - 1)}{C\ Vm}$ and an intercept equal to $\frac{1}{C\ Vm}$. The experimental data used for testing and comparing Equations 20 and 21 are the results of low pressure ethane adsorption on sodium chloride samples at the temperature of liquid oxygen, using an apparatus similar to that described by Wooten and Brown (10). These isotherms have not been previously published. In addition, some published data by Hüttig and Pietzka (7) for the adsorption of ethanol and methanol on silica and rutile at room temperature are included. Figures 1 to 12 give the experimental data and their comparison with the straight line called for by Equations 20 or 21. Equation 20 is readily seen in all cases to describe the experimental data to higher relative pressures than is done by Equation 21.

Table I gives a comparison of the constants obtained by the use of each theory. The specific surface of the adsorbent, $\Sigma$, is obtained from the value of Vm by using an average value for the coverage per molecule of the adsorbate. For ethane the value used is 23 $\mathring{A}^2$ (9). For methanol and ethanol the values are calculated from the equation

$$S = 4 \times 0.866 \left[ \frac{M}{4\sqrt{2}\, N_0 D_\ell} \right]^{2/3}$$

given by Emmett and Brunauer (5) where S is the area per molecule, M the molecular weight, $N_0$ Avogadro's number and $D_\ell$ is the density of the liquid at the temperature of the adsorption experiment. For methanol, Equation 22 gives S = 18.0 $\mathring{A}^2$ and for ethanol S = 23.1 $\mathring{A}^2$.

Table I

Comparison of Two Theories of Multilayer Adsorption

| Isotherm | C Hüttig | C BET | $\Sigma$ $cm^2/gm$ Hüttig | $\Sigma$ $cm^2/gm$ BET |
|---|---|---|---|---|
| $C_2H_6$ on NaCl crystals at 90°K | 70.4 | 58.0 | 2300 | 2260 |
| $C_2H_6$ on pulverized NaCl at 90°K | 42.0 | 137 | 1020 | 915 |
| $CH_3OH$ on rock crystal $SiO_2$, at 298.5°K | 143 | 137 | 541 | 529 |
| $C_2H_5OH$ on rock crystal, $SiO_2$, at 298.5°K | 79.0 | 92.1 | 625 | 586 |
| $CH_3OH$ on glassy quartz, $SiO_2$, at 298.5°K | 78.0 | 77.1 | 451 | 449 |
| $C_2H_5OH$ on glassy quartz, $SiO_2$, at 298.5°K | 54.7 | 75.1 | 486 | 412 |
| $CH_3OH$ on rutile, $TiO_2$, at 298.5°K | 91.0 | 220 | 434 | 385 |
| $C_2H_5OH$ on rutile $TiO_2$, at 298.5°K | 54.7 | 58.8 | 313 | 296 |

Inasmuch as Hüttig's equation describes the isotherm throughout a longer range of pressures than the B.E.T. equation, more points are provided on the straight line to determine the values of the constants. For that reason, values of C and Vm derived from Hüttig's equation can be obtained with greater precision. In general, the values for the specific surface of the adsorbent agree rather well; Hüttig's equation usually gives larger values, but rarely more than ten per cent more than the B.E.T. equation. The values for C show greater differences, the B.E.T. values being usually greater, sometimes by a factor of between 2 and 3.

Hüttig's equation does not describe the experimental points beyond a relative pressure of about 0.85. Figure 13 shows Equations 18 and 19 for a hypothetical isotherm (C = 100, Vm = 0.5). The two equations are the same for low relative pressures and begin to deviate soon after the beginning of multilayer formation. This is quite in accord with the postulated mechanisms of the two theories, which are alike during the adsorption of the first layer. For second and successive layers, the B.E.T. theory predicts values for the amount adsorbed which are greater than those actually observed. In Figure 13, the evidence provided by the experiments quoted in Table I would enable one to visualize the experimental points of this imaginary isotherm lying along the Hüttig curve to about p/po = 0.8, and then leaving it to ascend as an asymptote to the line p/po = 1.

These observations are again in accord with the mechanism postulated. It seems reasonable enough that at low relative pressures one may neglect the effect of superposed layers on the evaporation of molecules from lower layers. But at higher relative pressures, beyond about 0.8, the number of superposed layers has increased to the extend that evaporation from the lower layers is

affected. Expressed mathematically with reference to Equation 4, the value of $\gamma$ remains close to zero up to relative pressures of eight-tenths. When $\gamma$ increases appreciably, the rate of evaporation is slowed down so that at equilibrium there are more molecules adsorbed. The more that are adsorbed will in turn assist in increasing the value of $\gamma$ still further, i.e. reducing still further the rate of evaporation from underlying adsorbed layers, so that the quantity adsorbed increases autocatalytically. Accordingly $\gamma$ approaches a value of 1 fairly rapidly once the effect of superposed layers on the evaporation of underlying layers has begun to assert itself. The rapid rise of the experimental curve of an adsorption isotherm at higher pressures does indeed suggest that some autocatalytic effect is operating. When $\gamma = 1$, the conditions of the BET theory are satisfied and the course of the isotherm would then become asymptotic to the line $p/po = 1$. This discussion suggests that a modification of Hüttig's theory would follow the lines of discovering the variation of $\gamma$ as a function of $p/po$, in order to describe the course of the isotherm with greater precision in the region of high relative pressure. The mathematical task of such an undertaking is complicated by the consideration that $\gamma$ has different values in each layer, becoming equal to 1 in the lower adsorbed layers first and ranging to a value of 0 for the upper layers.

It is interesting to find that an equation closely similar to Equation 18 has already been proposed and actually tested as an adsorption isotherm, although derived from a completely different physical concept. Both Pickett (8) and Anderson (1) have derived an equation for adsorption limited to n layers:

$$\frac{V}{Vm} = \frac{Cx\,(1 - x^n)}{(1 - x)(1 + (C - 1)\,x)} \qquad \underline{23}$$

For $n = 2$ and the assumption that $C - 1$ is approximated sufficiently by $C$, Equation 23 becomes the same as Equation 18.

Where Equation 23 has been tested experimentally, the best values of $n$ are found to be near $n = 2$. The mechanism on which Equation 23 is derived does not seem to be generally valid (i.e. adsorption limited to two layers) and it is suggested that the experimental tests of Equation 23, yielding values of $n$ close to 2, are better interpreted as tests of the more general multilayer theory of Hüttig as expressed by Equation 18.


## Summary

A new theory of multilayer adsorption published by G. F. Hüttig is compared with the B.E.T. theory, using experimental isotherms, some already published and some never before published. The new theory is shown to describe the experimental results with greater precision. The differences in the postulated physical mechanisms of the two theories are pointed out. The basis for a modification, designed to provide a still more precise description of the experimental observations, is suggested.

## References


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(6) Hüttig, G. F.: Monatsh. 78, 177 (1948).

(7) Hüttig, G. F. and Pietzka, G.: Monatsh. 78, 185 (1948).

(8) Pickett, G.: J. Am. Chem. Soc. 67, 1958 (1945)

(9) Ross, S.: J. Am. Chem. Soc. Submitted. Also see MDDC-1765, U.S. Atomic Energy Commission, Tech. Information Div., Oak Ridge, Tenn.

(10) Wooten, L. A. and Brown, J. R. C.: J. Am. Chem. Soc. 65, 113 (1943).

Figure I

BET Equation for Adsorption of Ethane on

Crystals of NaCl at 90°K.

dwg. # 5852

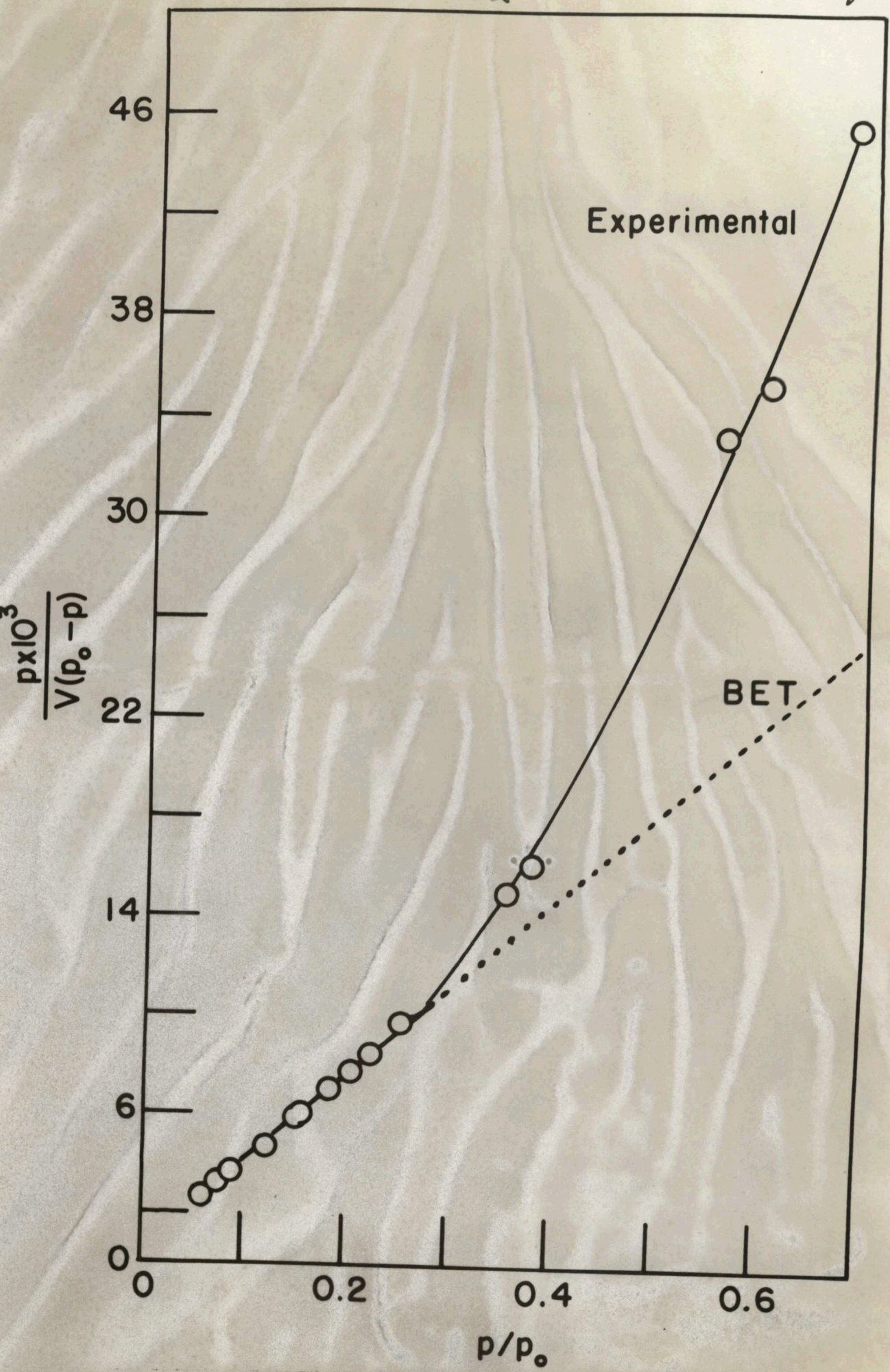

46
38
30
22
14
6
0
$\frac{p \times 10^3}{V(p_o - p)}$
Experimental
BET
0
0.2
0.4
0.6
$p/p_o$

Figure 2

Hüttig's Equation for Adsorption of Ethane on

Crystals of NaCl at 90°K.

Aug. #5853

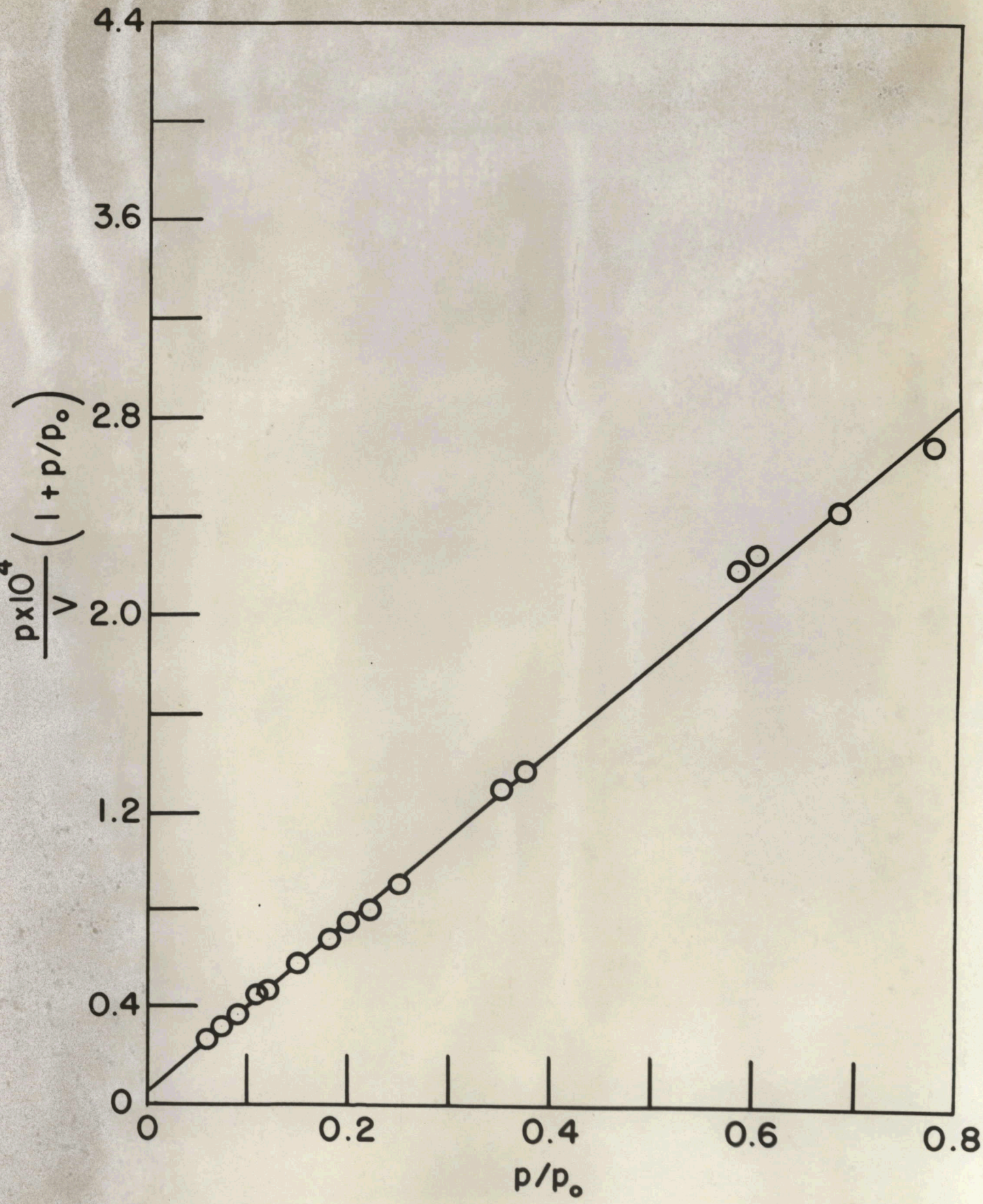

4.4
3.6
2.8
2.0
1.2
0.4
0
$\frac{p \times 10^4}{V}\left(1 + p/p_o\right)$
0
0.2
0.4
0.6
0.8
$p/p_o$

Figure 3

BET Equation for Adsorption of Ethane on

Pulverized NaCl at 90°K.

Dwg. 5854

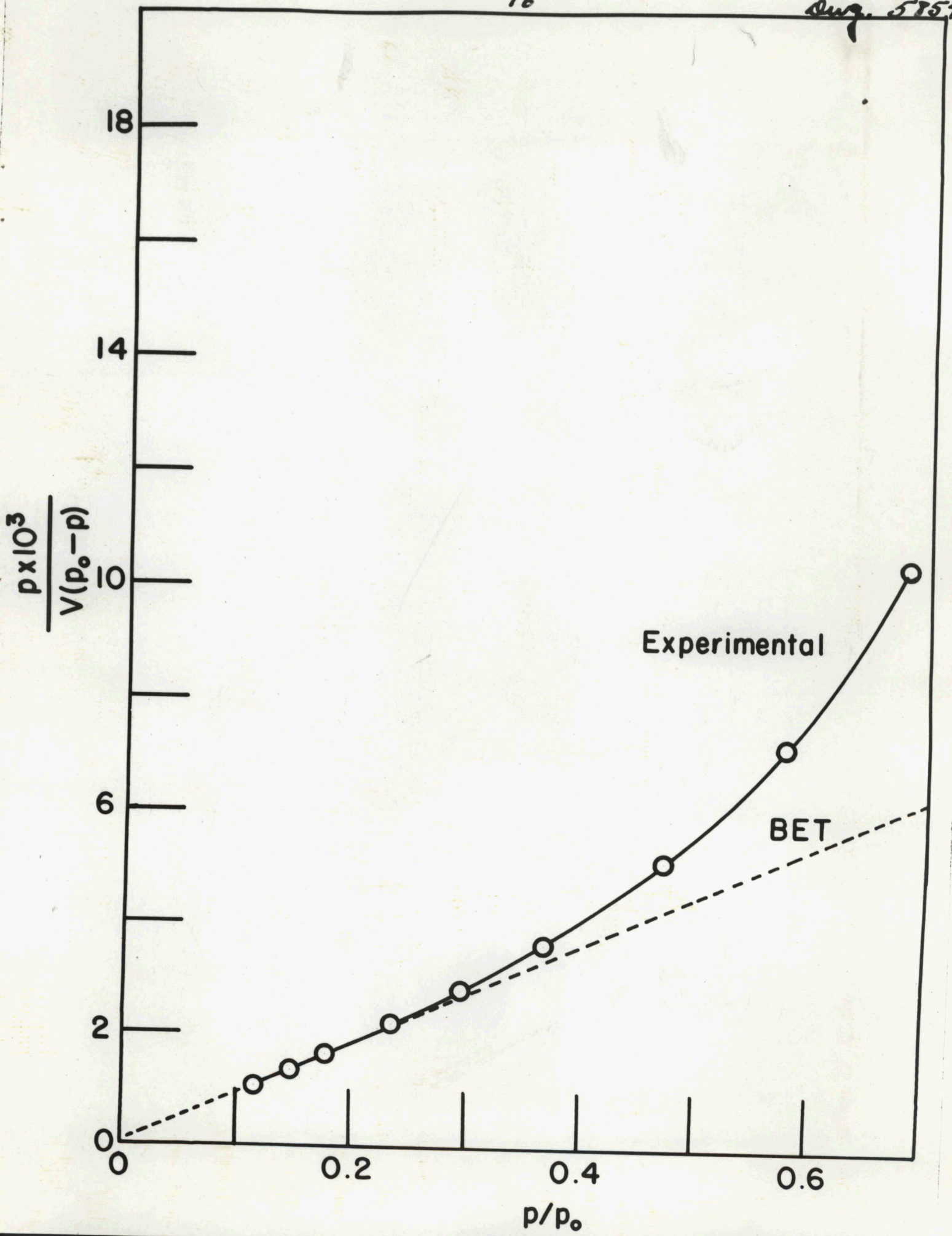
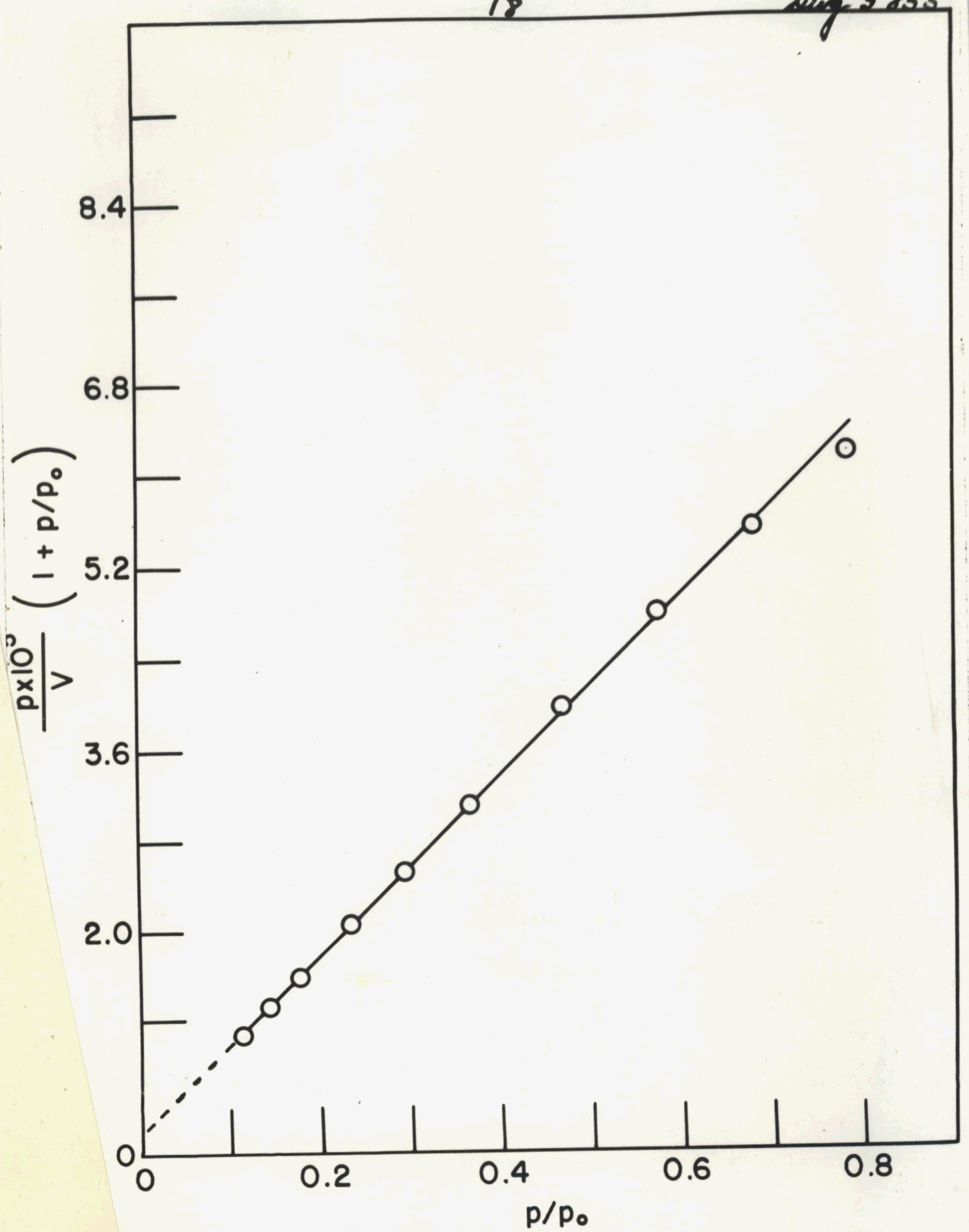

18
14
10
6
2
0
$\frac{p \times 10^3}{V(p_o - p)}$
Experimental
BET
0
0.2
0.4
0.6
$p/p_o$

Figure 4

Hüttig's Equation for Adsorption of Ethane on

Pulverized NaCl at 90°K.

Dwg. #5255


8.4
6.8
5.2
3.6
2.0
0
$\frac{p \times 10^5}{V}\left(1 + p/p_o\right)$
0
0.2
0.4
0.6
0.8
$p/p_o$

Dwg. #5 856

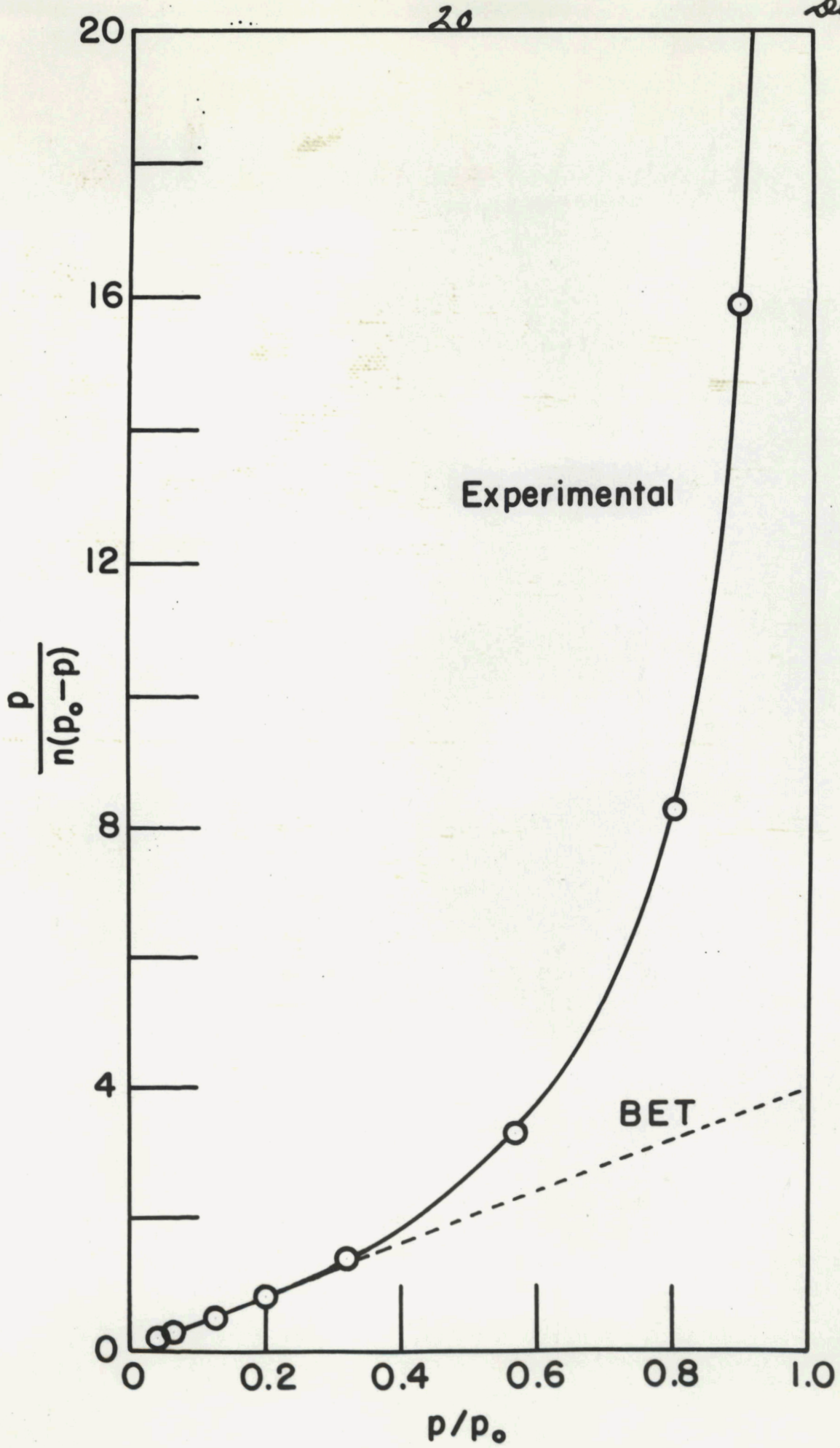


Figure 6

Hüttig's Equation for Adsorption of Ethanol on

Rock Crystal ($SiO_2$) at 298.5°K.

Dwg. #5857

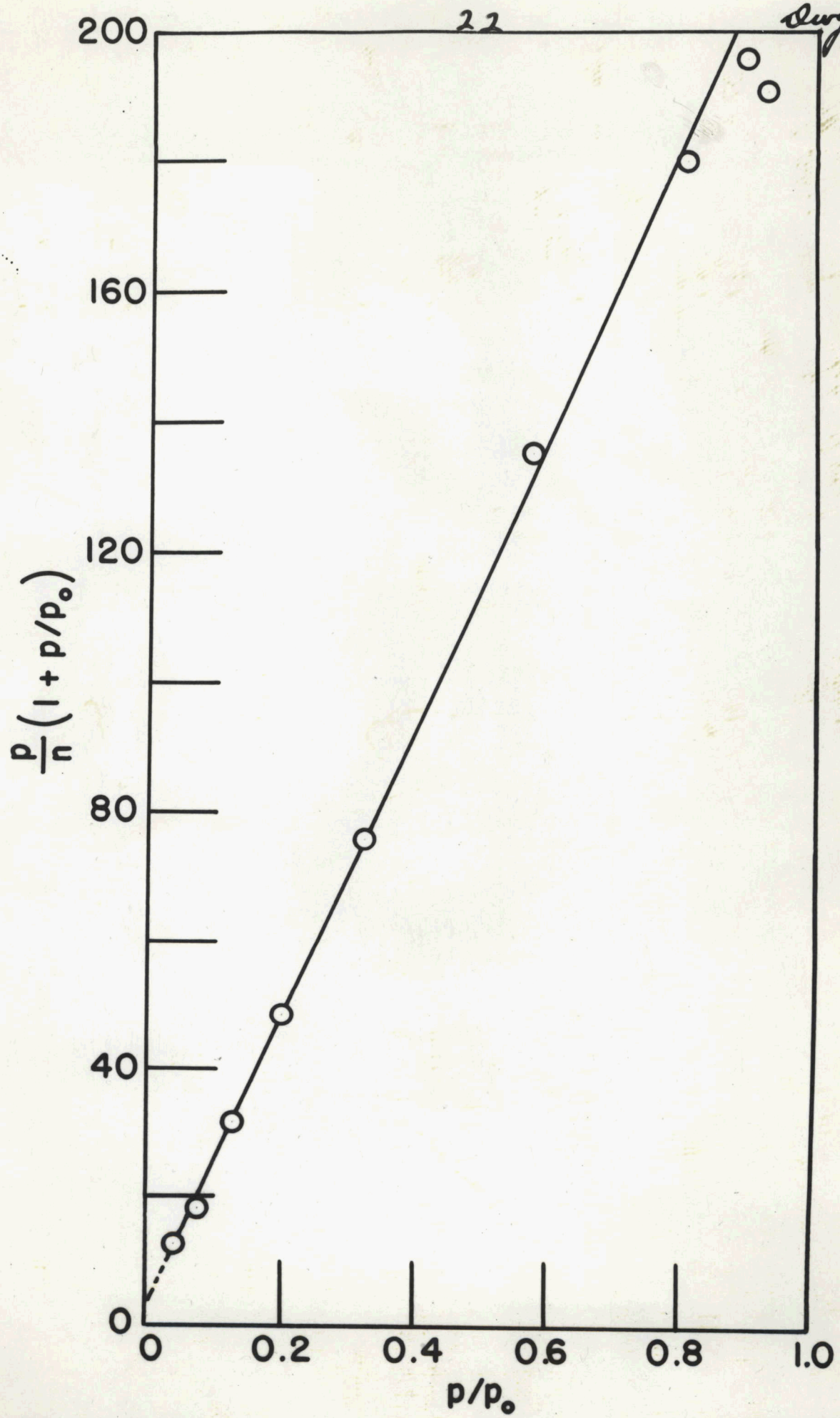


Figure 7

BET Equation for Adsorption of Ethanol on

Glassy Quartz ($SiO_2$) at 298.5°K.

Dwg. #5858

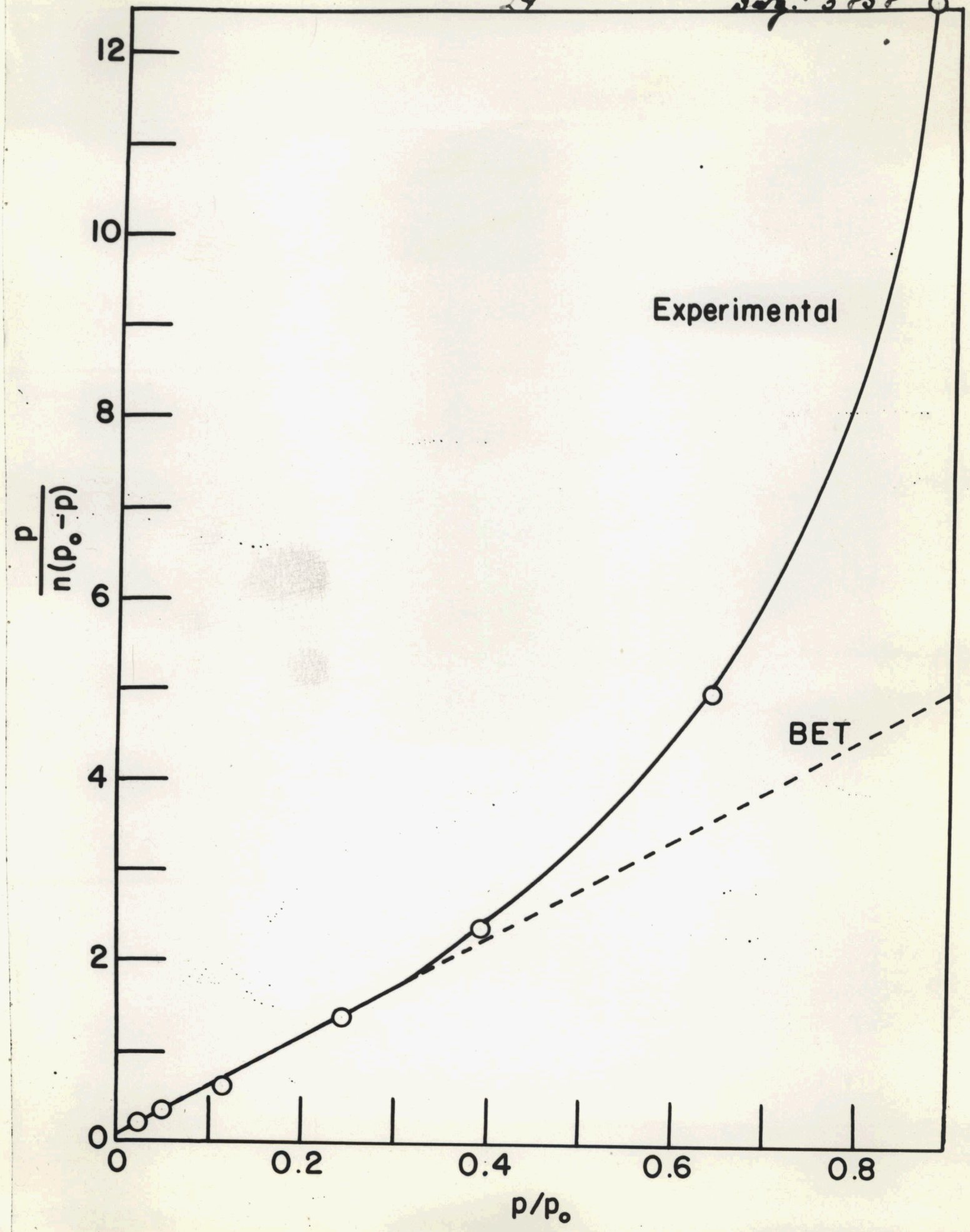


Figure 8

Hüttig's Equation for Adsorption of Ethanol on

Glassy Quartz ($SiO_2$) at 298.5°K.

Dwg. 5859

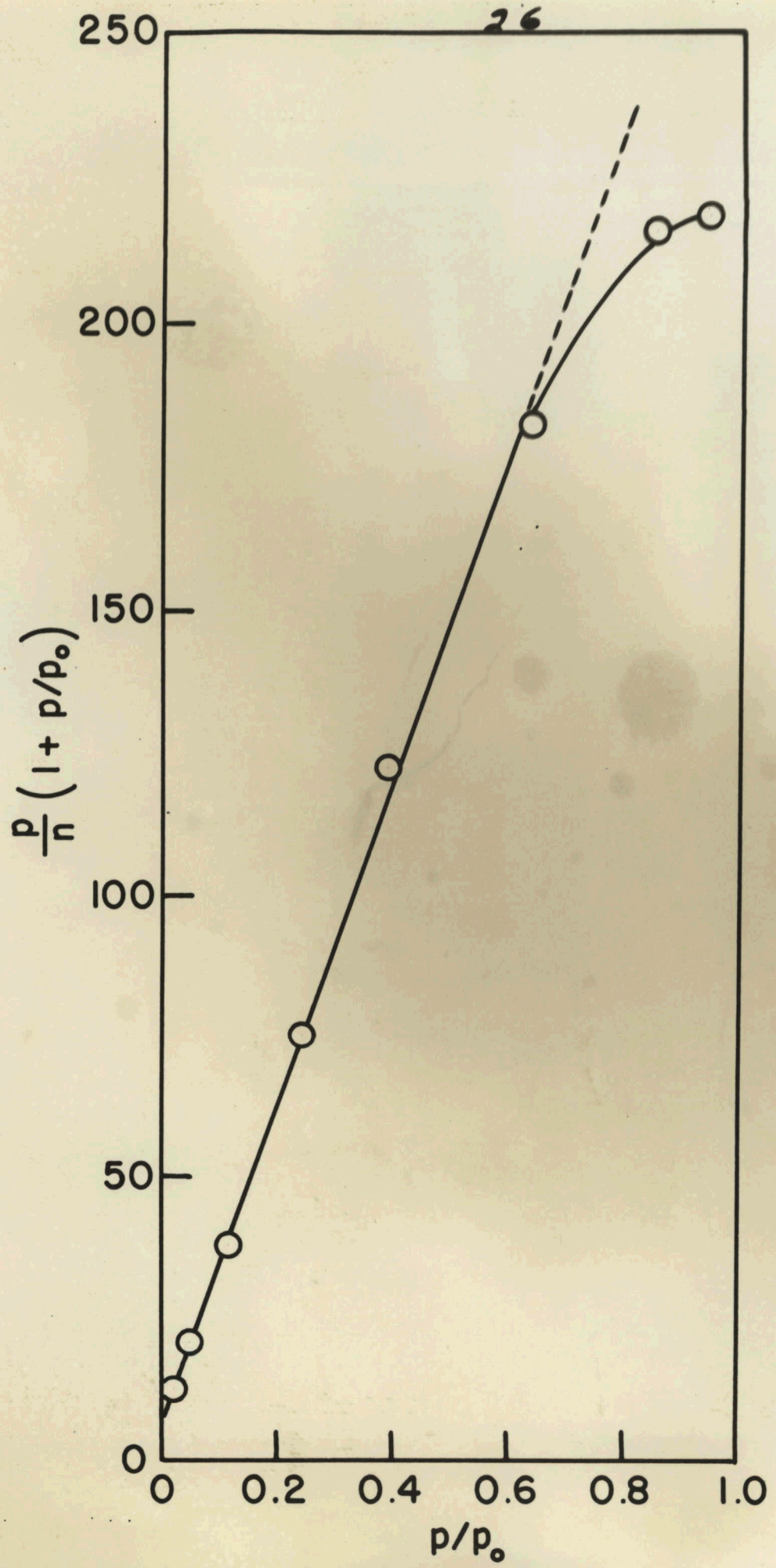


Figure 9

BET Equation for Adsorption of Methanol on

Rutile ($TiO_2$) at 298.5°K.

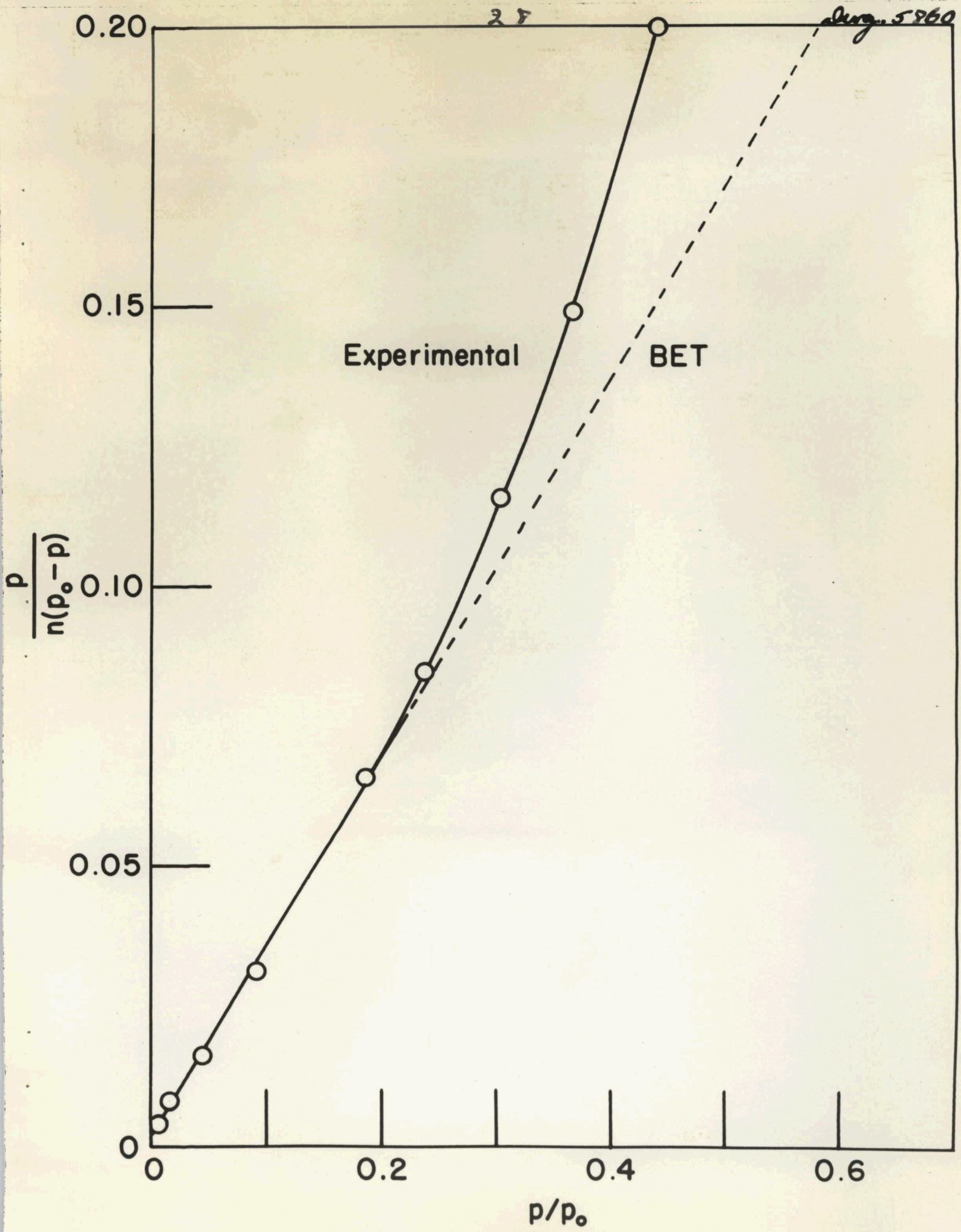

28
Dwg. 5860
0.20
0.15
0.10
0.05
0
Experimental
BET
$\frac{p}{n(p_o - p)}$
0
0.2
0.4
0.6
$p/p_o$

Figure 10

Hüttig's Equation for Adsorption of Methanol on

Rutile ($TiO_2$) at 298.5°K.

Dwg. 5861

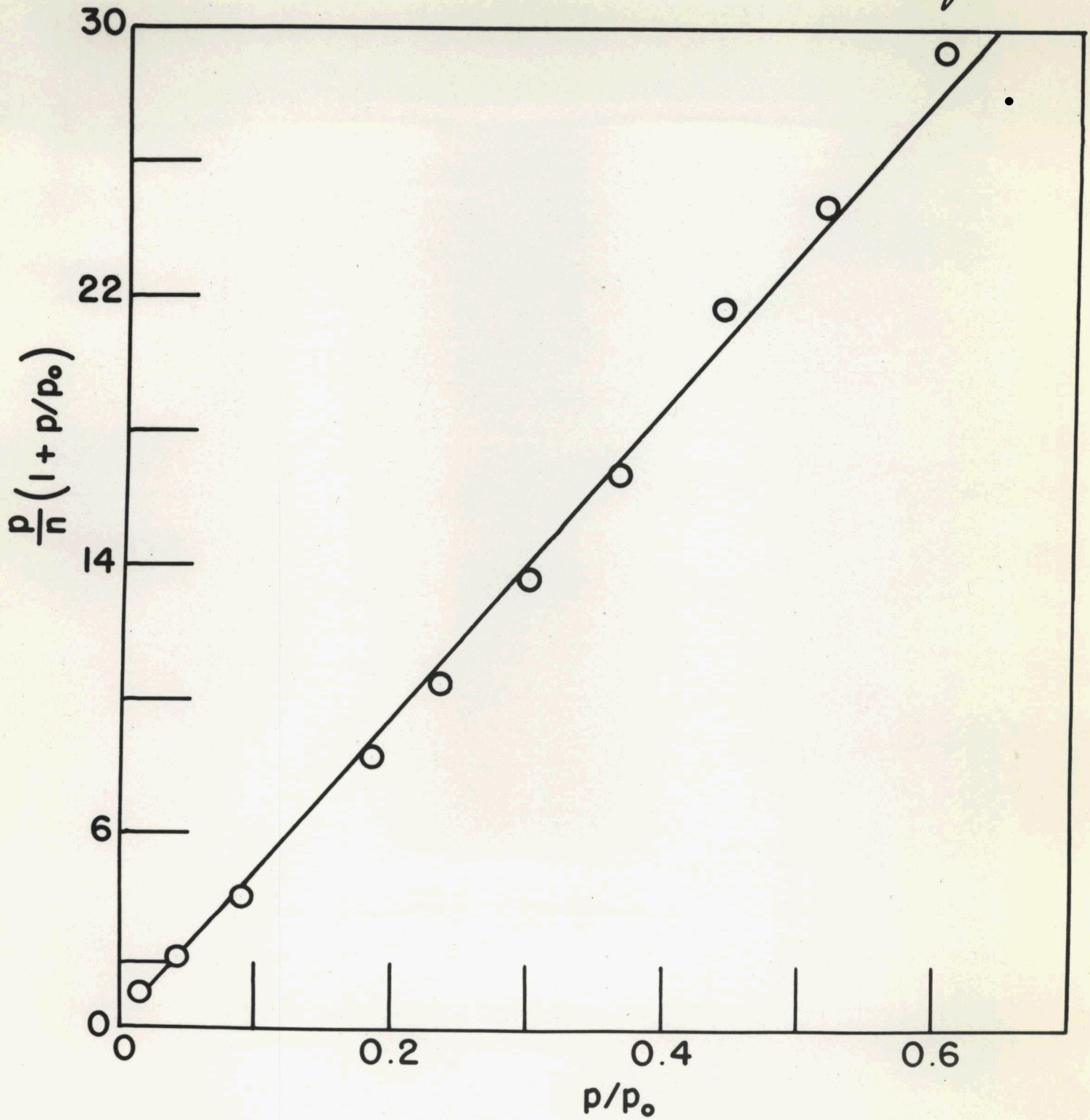


Figure 11

BET Equation for Adsorption of Ethanol on

Rutile ($TiO_2$) at 298.5°K.

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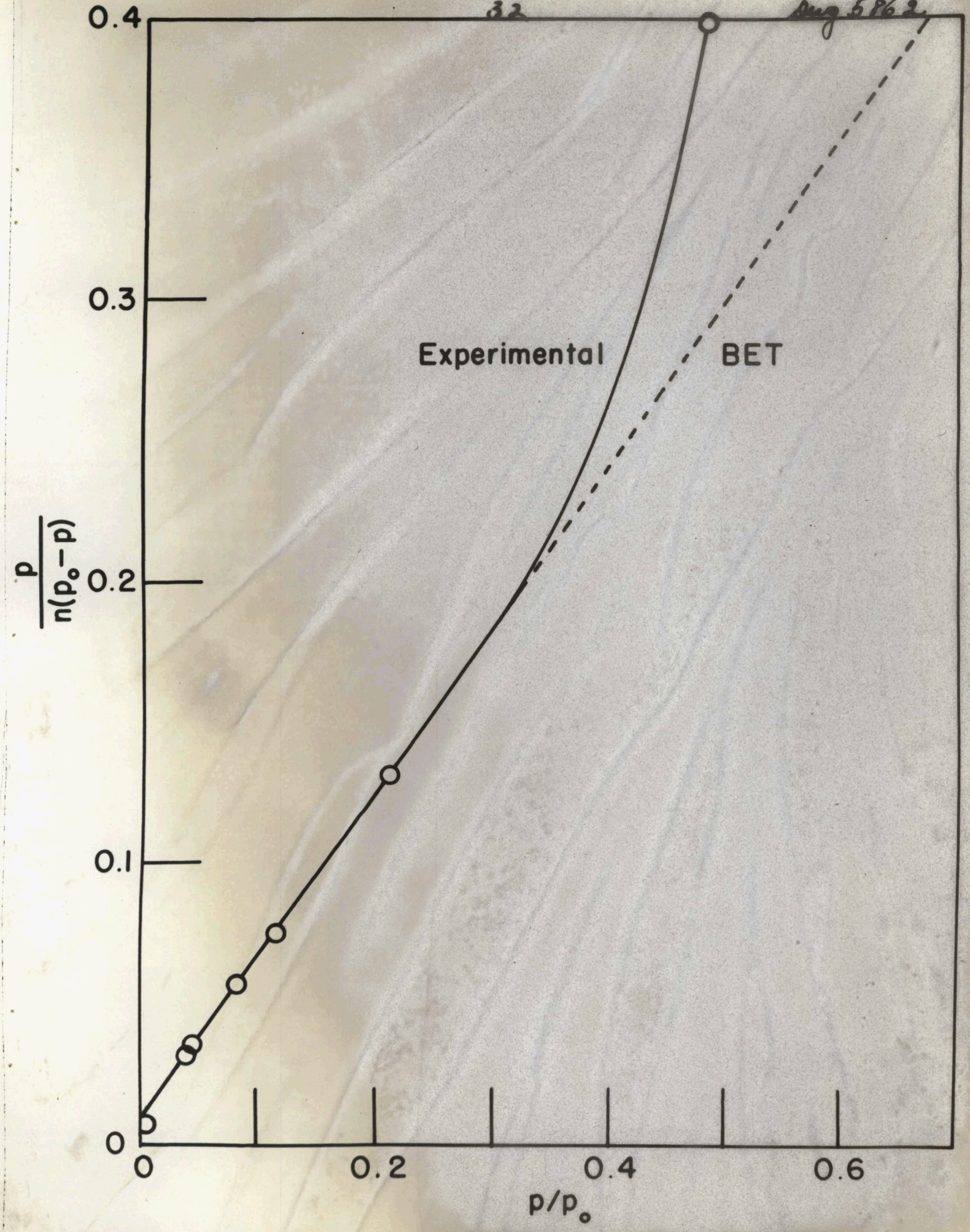


Figure 12

Hüttig's Equation for Adsorption of Ethanol on

Rutile ($TiO_2$) at 298.5°K.

Dwg. #5863

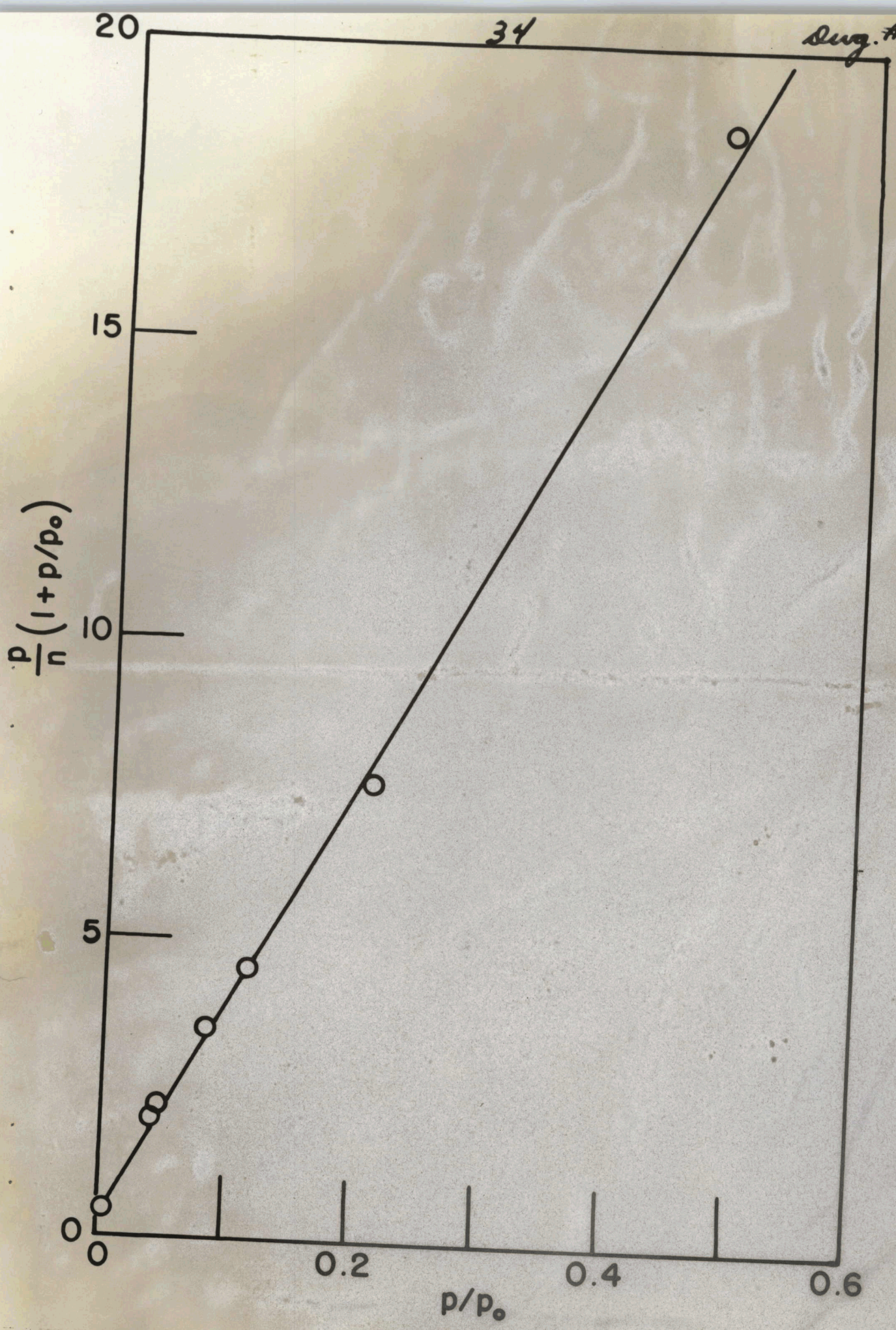
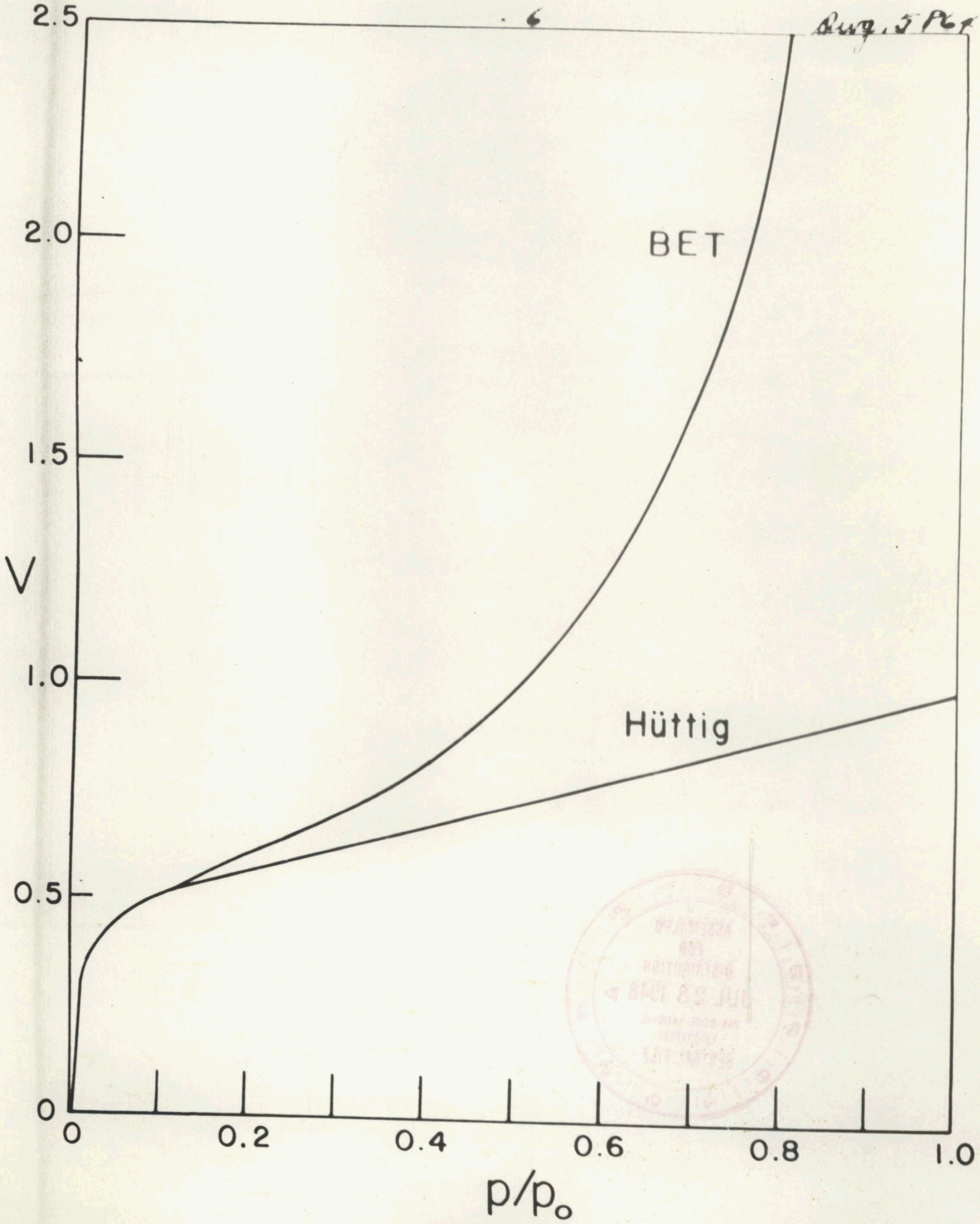


Figure 13

Comparison of the BET and Hüttig Equation for the

Same Values of C and $V_m$.

($C = 100$: $V_m = 0.5$)


2.5
2.0
1.5
1.0
0.5
0
V
BET
Hüttig
0
0.2
0.4
0.6
0.8
1.0
p/p₀