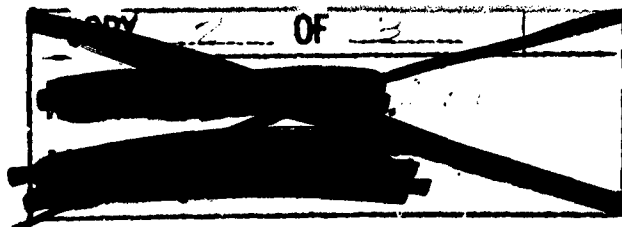


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FOURTH BIMONTHLY PROGRESS REPORT

COVERING THE PERIOD

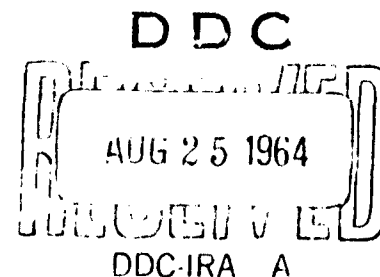
19 MAY 1964 - 18 JULY 1964

TITLE: ADSORPTION - DESORPTION PROPERTIES OF SORBENTS

PREPARED BY: A. W. LOVEN
F. J. VERMILLION

DATE: 4 AUGUST 1964

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SUMMARY

Equilibrium adsorption data is reported for activated carbons of interest as chemical agent sorbents. Measurements were made with nitrogen at low temperature and with dimethyl methylphosphonate, DMMP, at 25° and 42°C. The sorbents studied include activated carbon fibers made from Fortisan and viscose rayon, some highly activated coconut shell charcoal, and a coal-base carbon.

The nitrogen data was combined with mercury porosimeter measurements to give the total pore volume distributions from 10 to 100,000 Å radius. Striking differences are seen among the samples. Both carbon fibers show a greater proportion of volume in pores less than 10 Å than the other carbons. The effect of level of activation on pore structure is well exemplified in the coconut shell charcoals.

Isosteric heats of adsorption of DMMP on the carbon fibers and the coal-base carbon are reported. The heat data was not sensitive enough in the range of coverage measured to account for the observed differences in isotherm steepness among the various samples.

It is suggested that the hysteresis in the DMMP systems is the result of the superposition of two phenomena, one the type seen in nitrogen adsorption entailing loop closure and the other an effect extending to lower pressures. An attempt to sort these effects out by changing sample particle size was complicated by additional factors. An apparent change in the DMMP saturation capacity of the coconut shell charcoal was observed upon mechanical grinding.

The method developed for measuring rates of adsorption and desorption at constant pressure is described. Results of some desorption measurements with DMMP are discussed.

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I. STATIC ADSORPTION MEASUREMENTS

A. Measurements with Nitrogen

Nitrogen adsorption isotherms at 77.7°K were determined on the Pittsburgh Chemical Company, (PCC) 50 x 140 mesh carbon and on the two samples of Barnebey-Cheney coconut shell charcoals which were activated by Mine Safety Appliances Research to CCl_4 activities of 125.4% and 149.4%. The resulting curves are shown in Figures 1, 2, and 3. The same apparatus and procedures for sample pre-treatment and isotherm determination were used as in the nitrogen adsorption measurements reported in previous progress reports for this contract.

The application of the conventional BET method to these isotherms gives surface areas of 1198 m^2/g for the PCC 50 x 140 mesh carbon and 2038 m^2/g and 2176 m^2/g respectively for the 125.4% and 149.4% CCl_4 value coconut shell charcoals. These very high values should not be regarded as true surface areas because of the inapplicability of the BET model for these very porous materials, as discussed in previous reports. The failure is probably due to there being effectively capillary condensation in small pores even at low pressures. This leads to a greater amount adsorbed than one would expect for the true amount of surface area present and hence to a higher indicated surface area. It is seen that there is relatively little hysteresis in the nitrogen isotherms of either sample of the coconut shell charcoals, similar in this respect to the PCC carbons. Hysteresis will be discussed further in Part II.

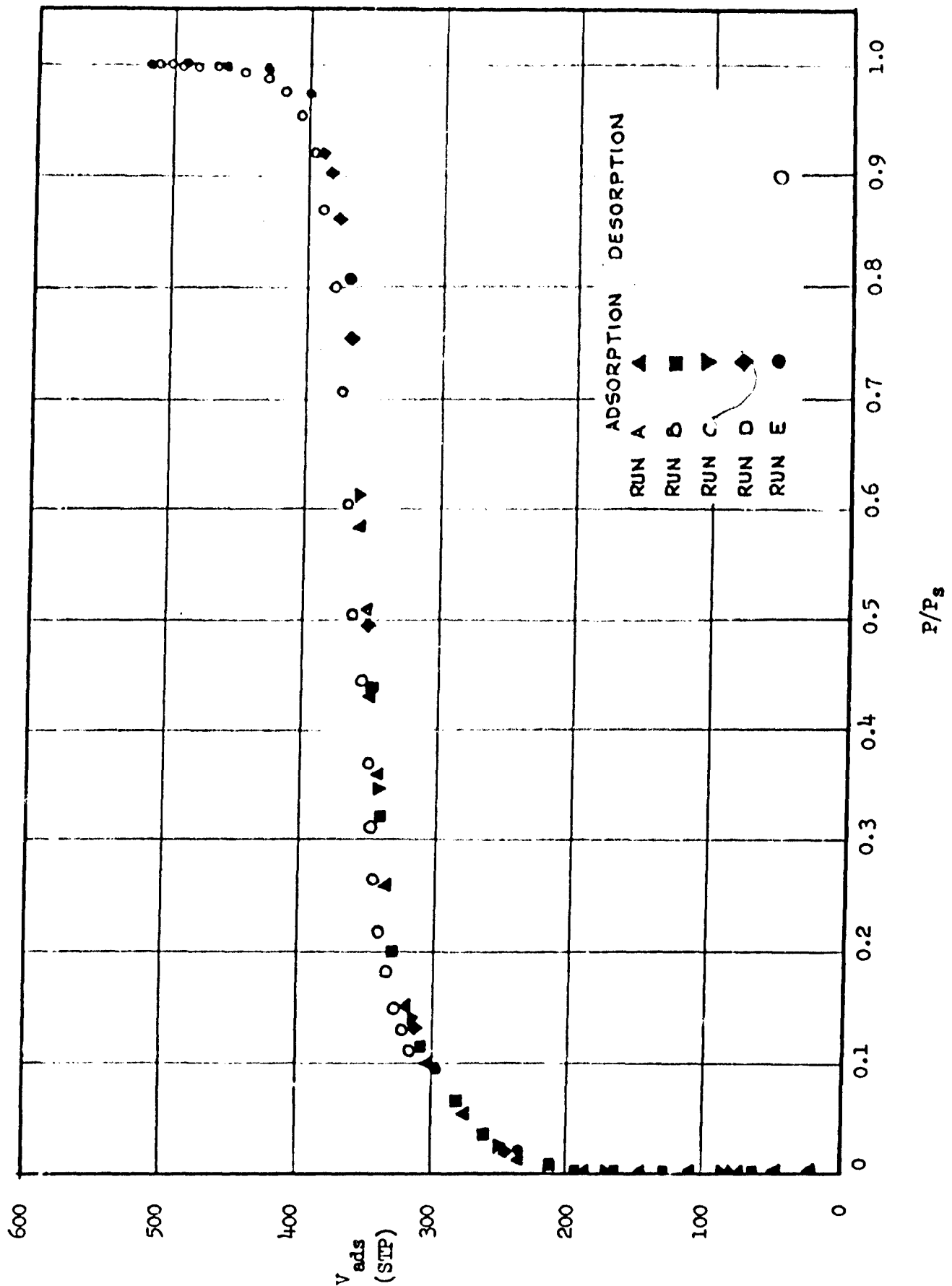
B. Measurements with Dimethyl Methylphosphonate, DMMP

The apparatus and methods described in the earlier reports were used to measure DMMP isotherms on further samples and at other temperatures. The results are shown in Figures 4 to 11. As before, sample temperature was controlled by immersing the lower end of the McBain balance case into a Dewar flask containing a copper coil through which thermostatted water was pumped. The effect of thermomolecular flow at 42°C under these circumstances is negligible.

All the isotherms were, of course, uniformly less steep at the higher temperature as required by the necessarily exothermic nature of the adsorption process. At the higher temperatures the hysteresis was seen to be less in all samples, but it should be noted that at 42°C, although the samples were adsorbed to the same DMMP pressure, the actual maximum relative pressure was less. Still, if the transition from the adsorption to the desorption isotherm is rapid, one would expect the same hysteresis

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FIGURE 1 NITROGEN ISOTHERM ON PCC 50 X 140 MESH CARBON AT 77.7°K

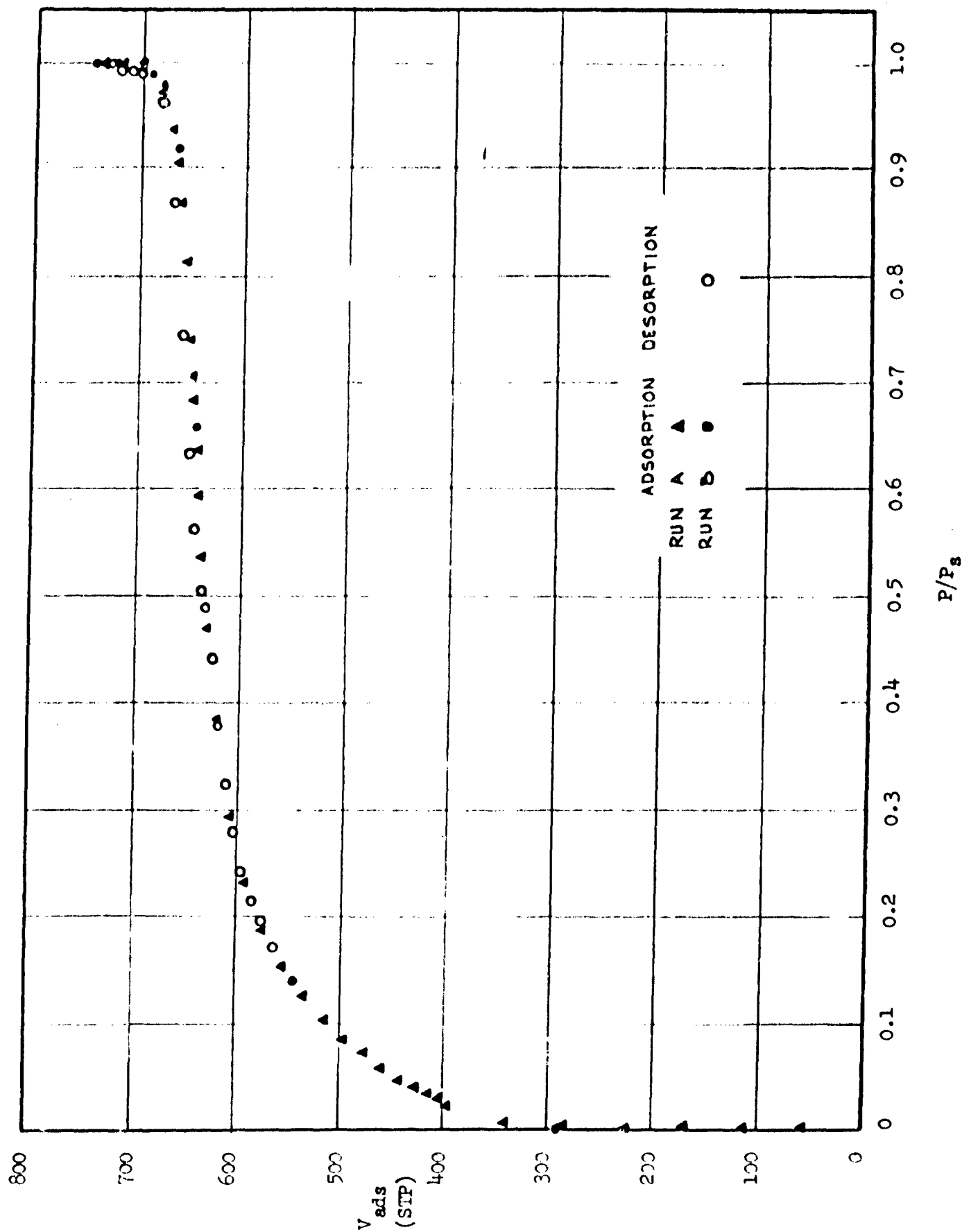


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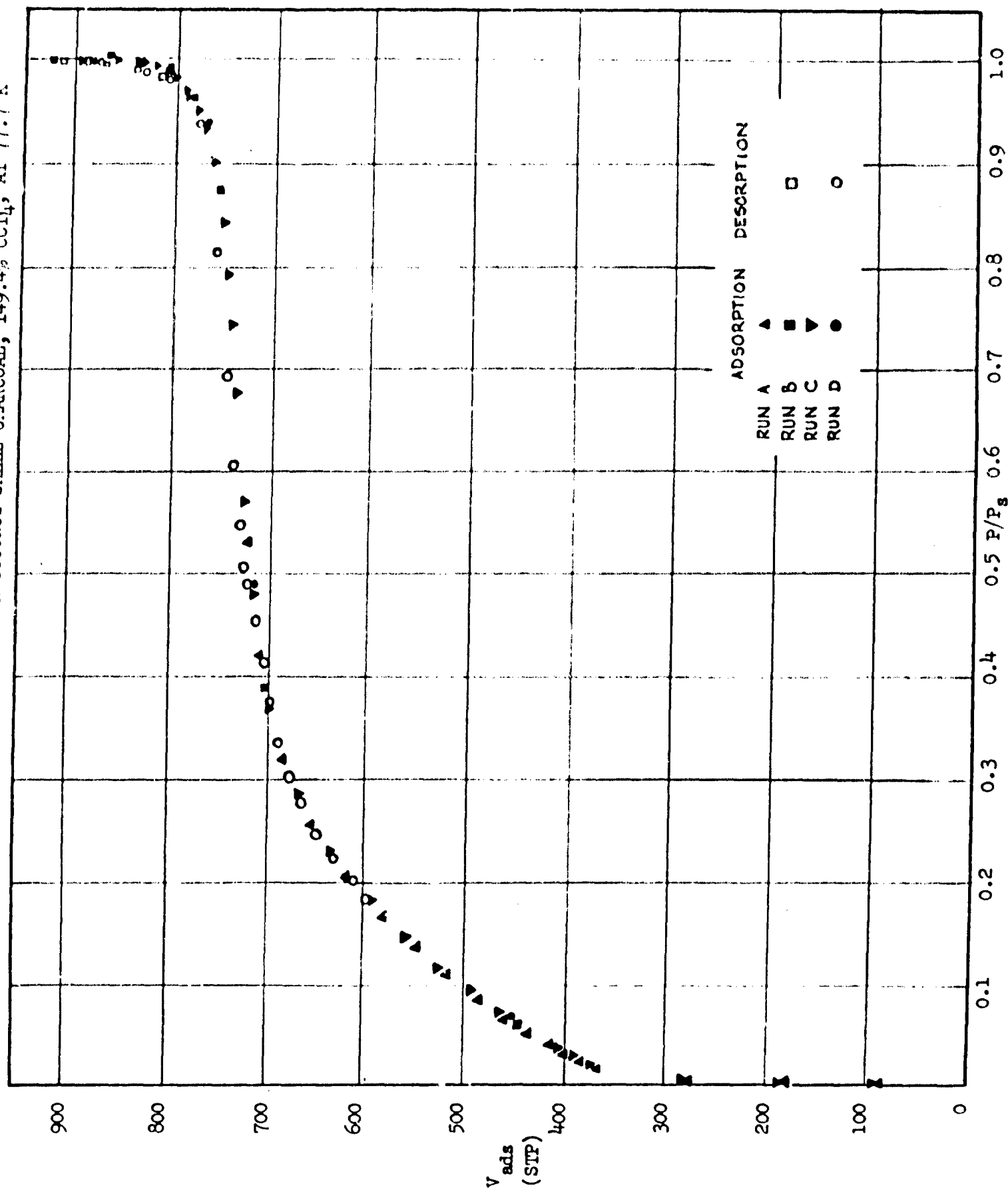
FIGURE 2 NITROGEN ISOOTHERM ON COCONUT SHELL CHARCOAL, 125.4% CCl₄, AT 77.7°K



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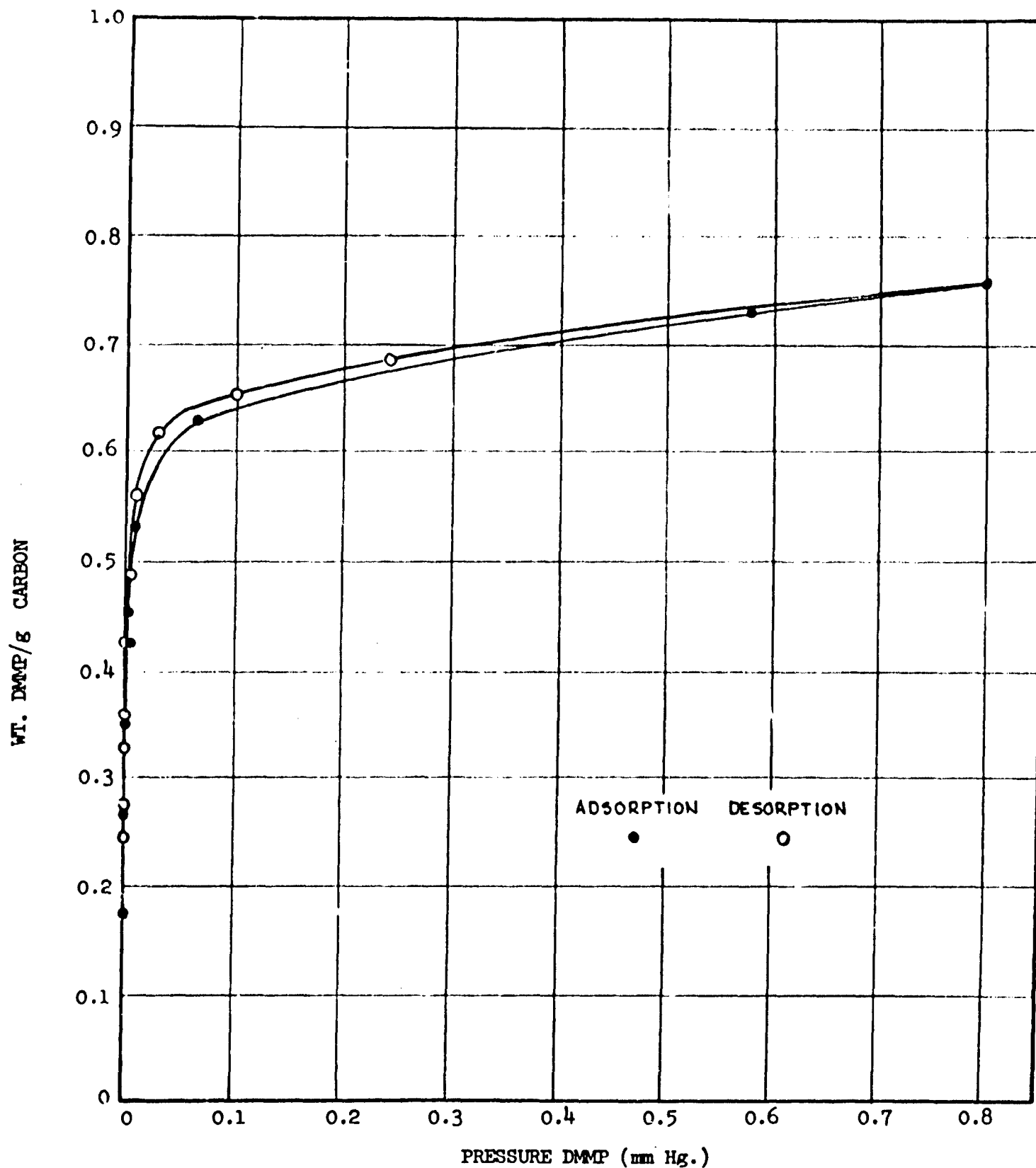
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FIGURE 3 NITROGEN ISOTHERM ON COCONUT SHELL CHARCOAL, 149.4% CCl₄, AT 77.7°K

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FIGURE 4

DMMP ISOTHERM ON NCC CARBON FIBER FELT AT 42°C



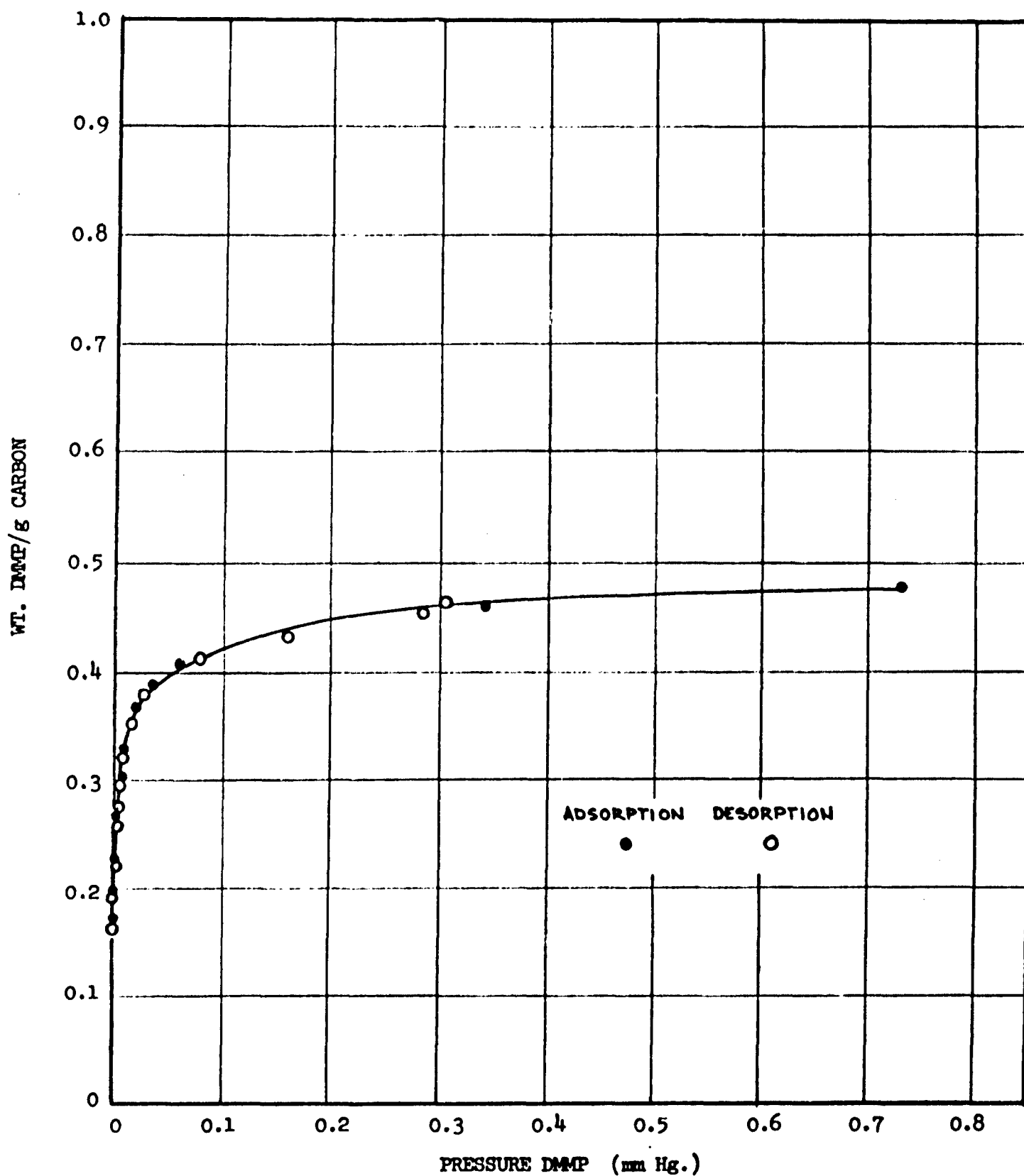
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FIGURE 5

DMP ISOTHERM ON PCC 12 x 30 MESH CARBON AT 42°C



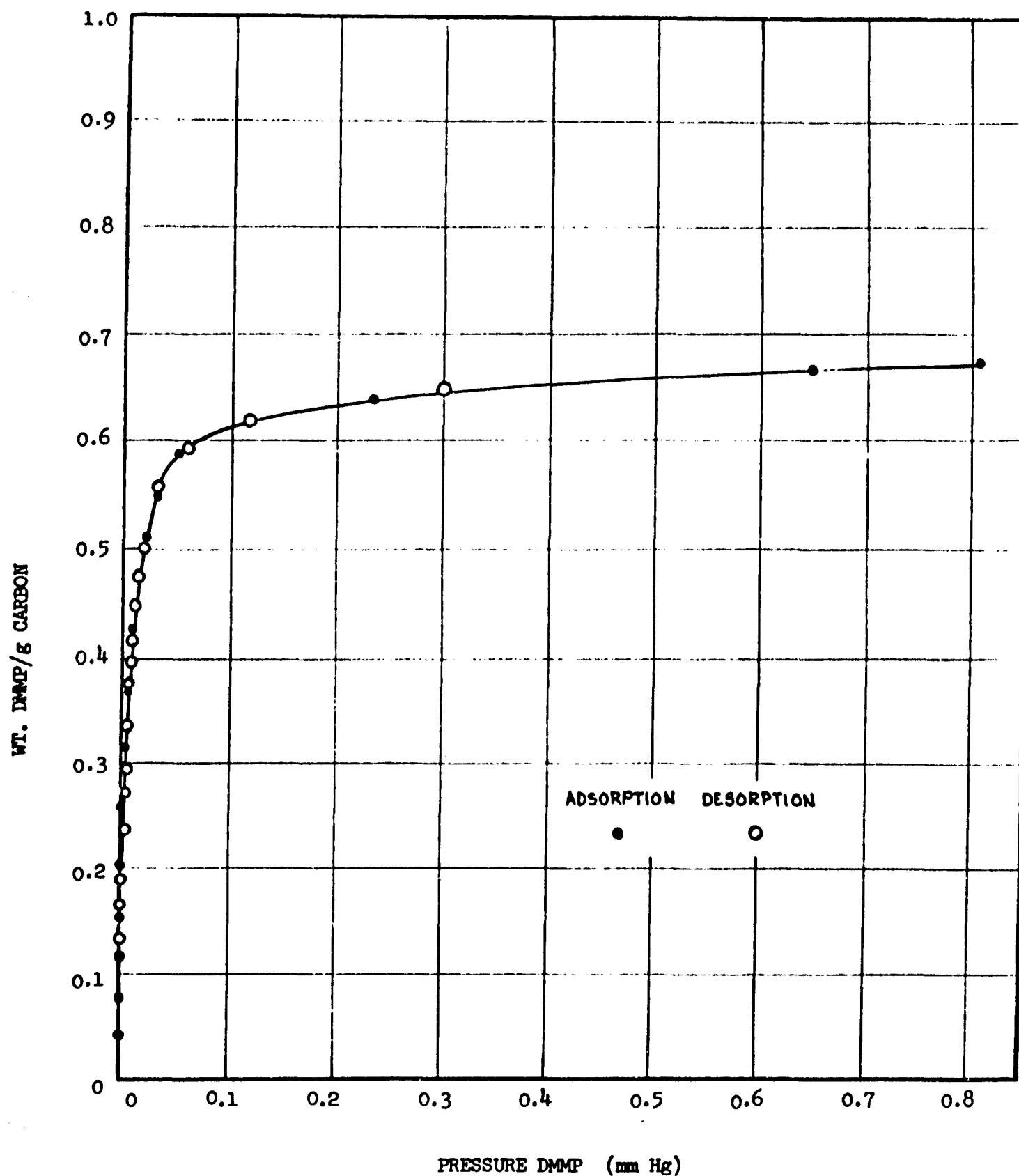
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FIGURE 6

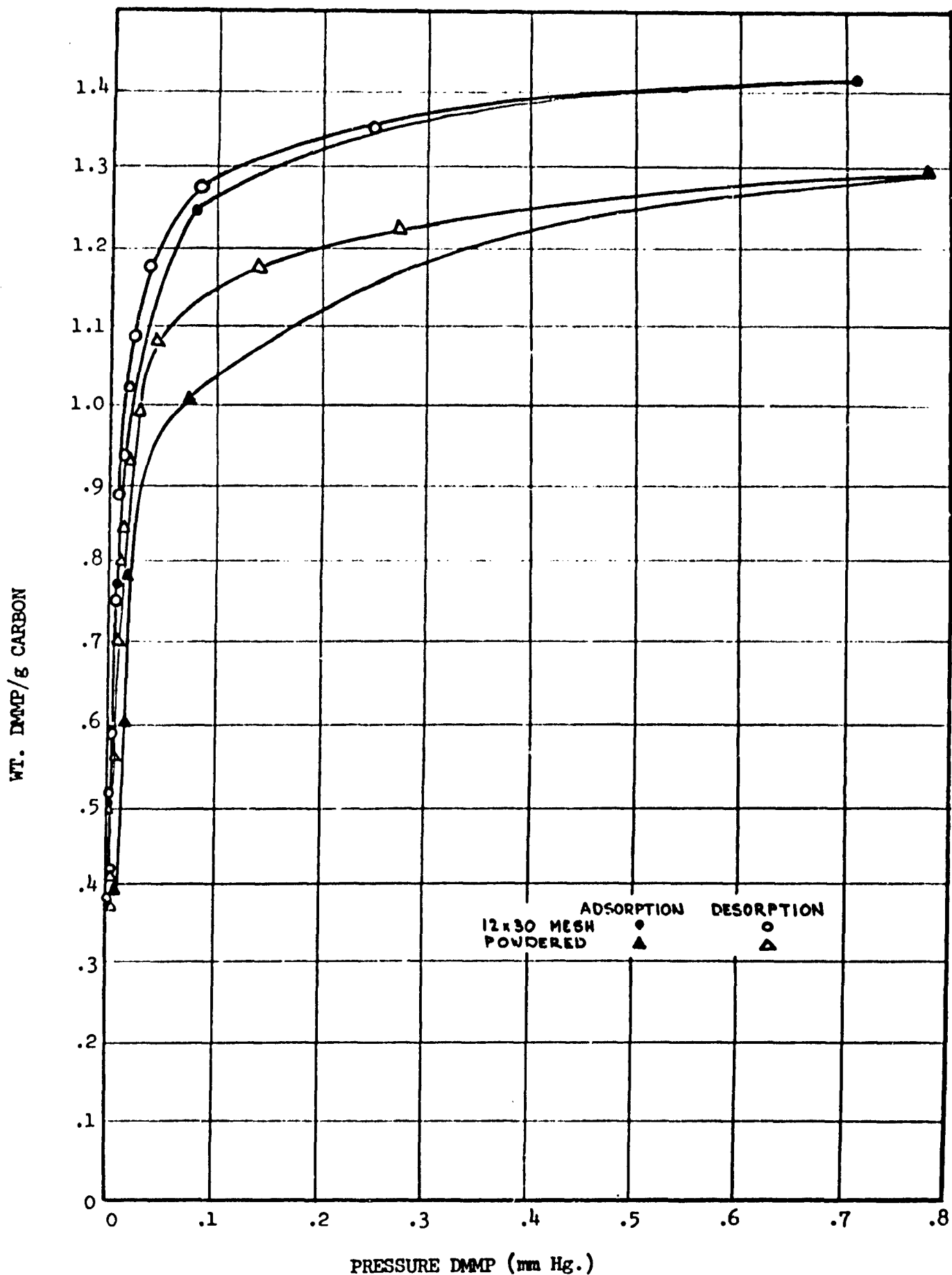
DMP ISOTHERM ON MSAR VISCOSE FELT AT 42°C



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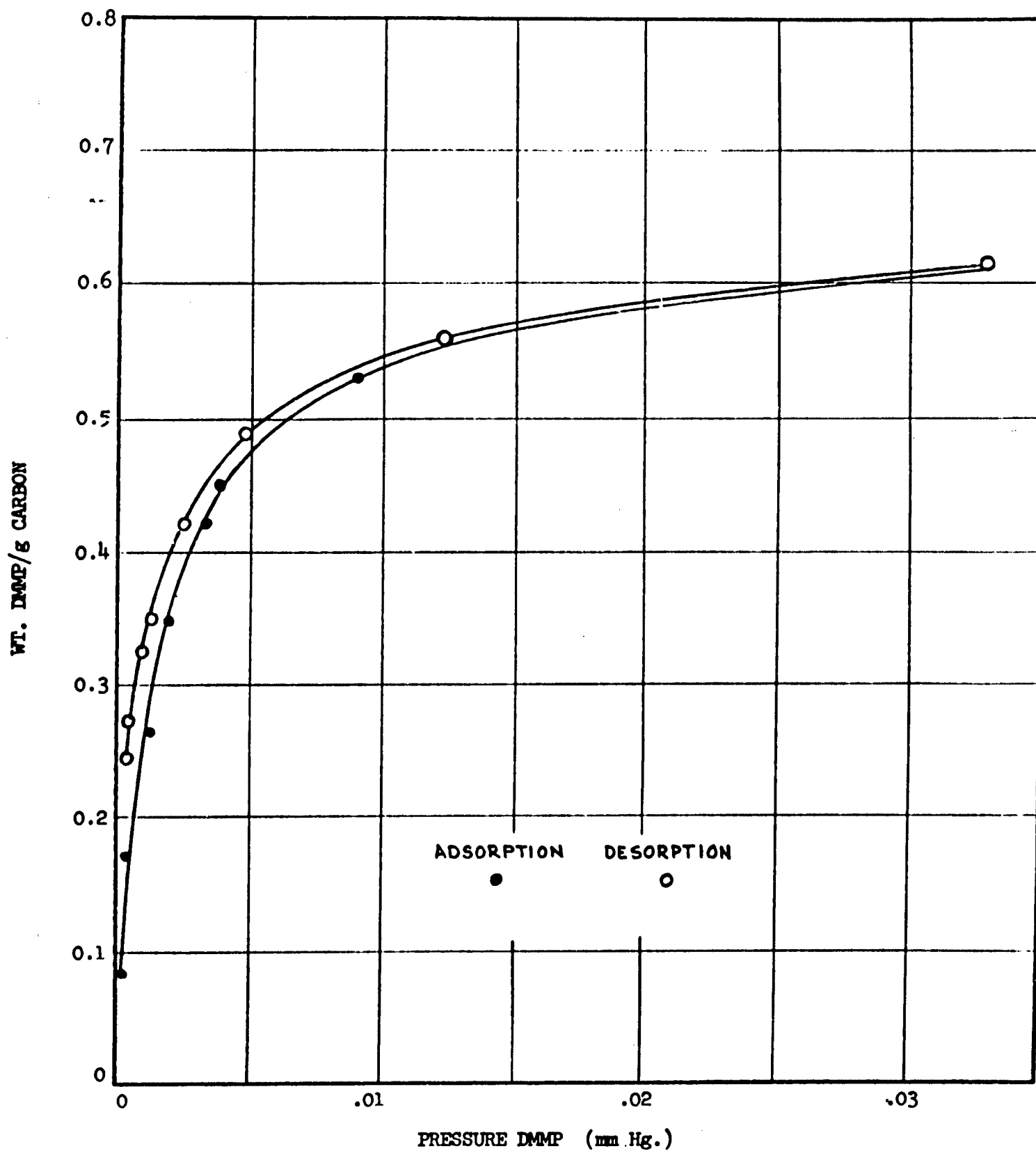
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DMP ISOTHERM ON COCONUT SHELL CHARCOAL, 149.4% CCl_4 , AT 25°C.

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FIGURE 8

DMMP ISOTHERM ON NCC CARBON FIBER AT 42°C

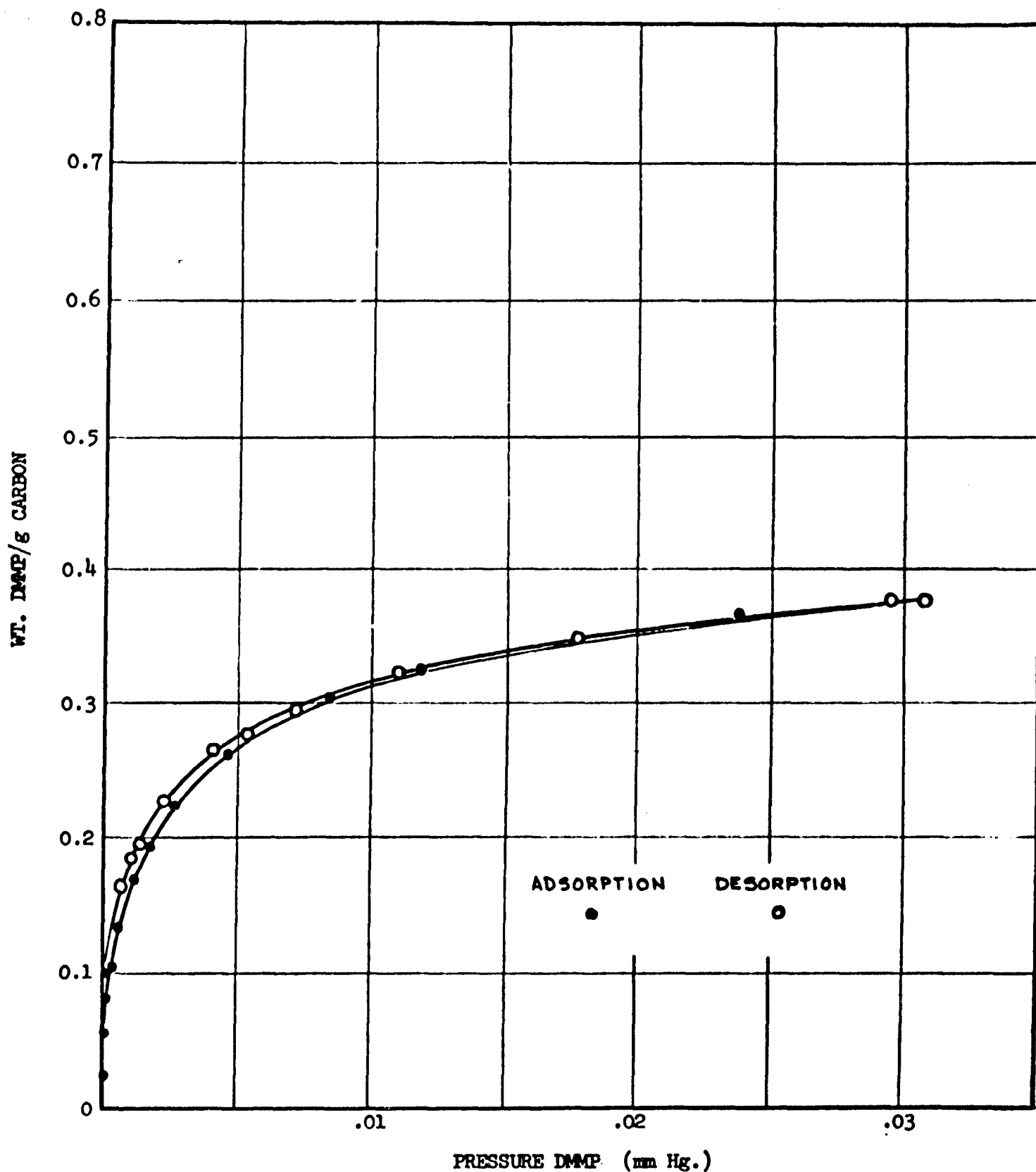


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FIGURE 9
DMP ISOTHERM ON PCC 12 x 30 MESH CARBON AT 42°C



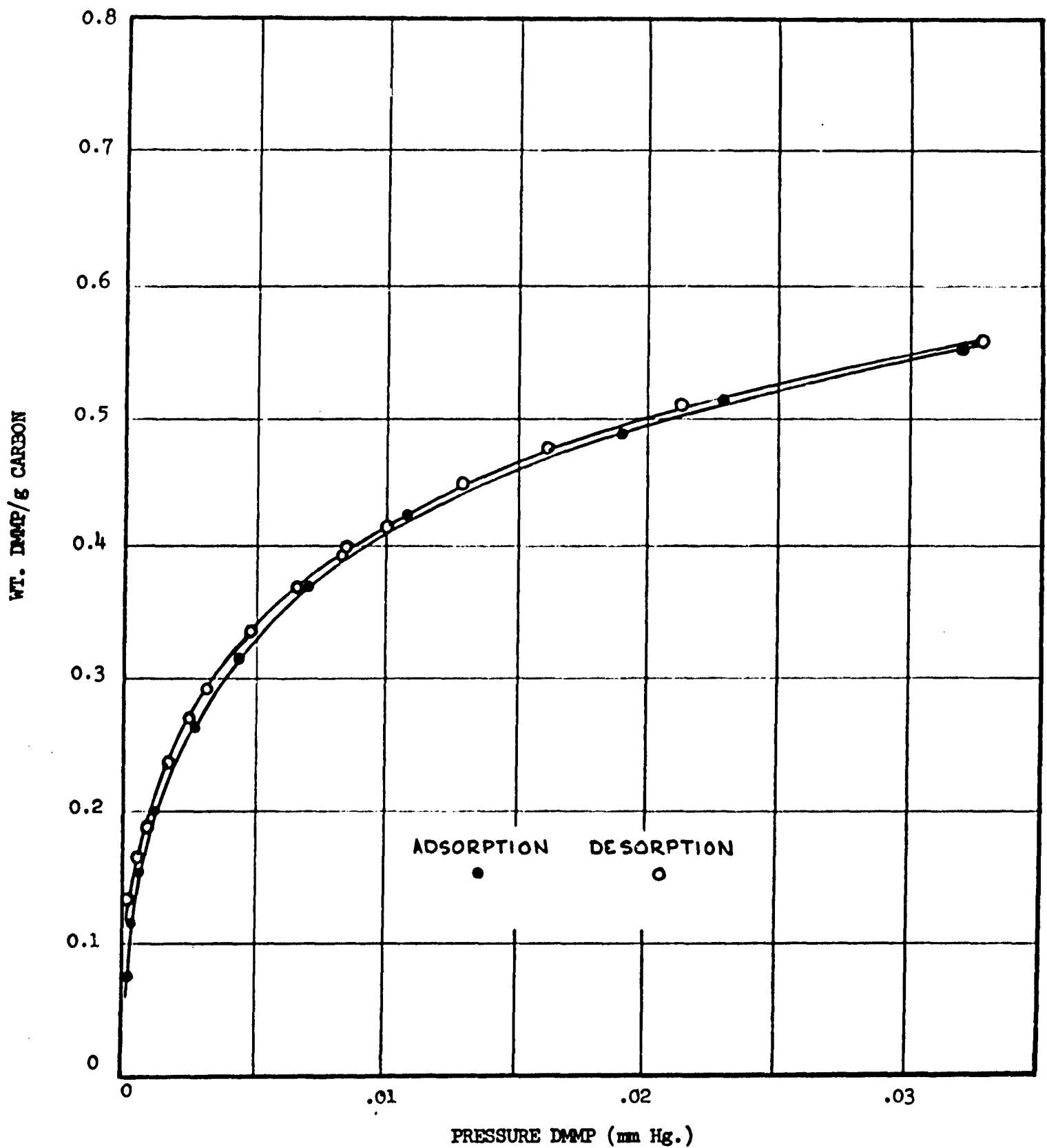
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FIGURE 10

DMP ISOTHERM ON MSAR VISCOSE FELT AT 42°C



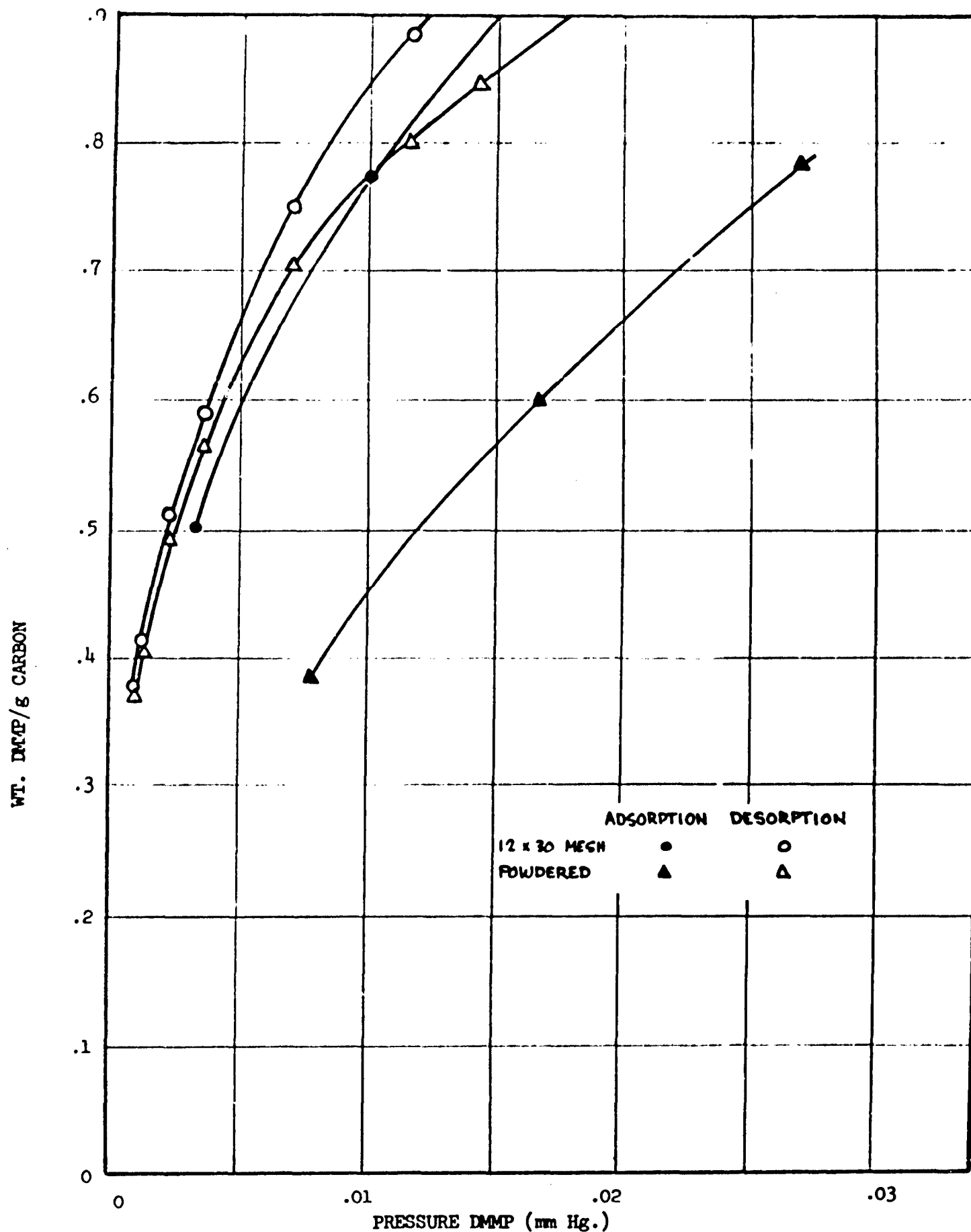
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FIGURE 11

DMP ISOTHERM ON COCONUT SIDELL CHARCOAL, 149.4%, AT 25°C



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behavior to be manifest at low pressures regardless of the exact maximum relative pressure attained.

From the nitrogen adsorption isotherm of the NCC felt it is observed that the hysteresis loop closes at a relative pressure of about 0.45. This corresponds to a radius of 18.5Å when the Kelvin equation (1) is applied, assuming a film thickness of adsorbed nitrogen on pore walls of 6.7Å. Thus it must be pores of a larger size than this which are responsible for the nitrogen hysteresis behavior. If hysteresis in the DMMP system is caused by factors inherent in the sorbent pore structure, one would expect the hysteresis loop to close when pores greater than 18.5Å are emptied. The relative pressure of DMMP to which this corresponds can be calculated from the Kelvin equation. Assuming a film thickness of 6.7Å for DMMP, for want of a better value, and using a measured surface tension of 37.8 dyne cm^{-1} , one calculates at a radius of 18.5Å a relative pressure of 0.05. When the DMMP isotherm at 25°C on the National Carbon Company (NCC) Fortisan felt is re-examined, Figure 3 of the Third Bimonthly Progress Report, it is seen that there is a hint of closure in the vicinity of a relative pressure of 0.05. The same is true of the FCC 12 x 30 mesh isotherm. It appears possible, therefore, that the hysteresis behavior is a superposition of two effects; one the same type behavior as seen in the nitrogen isotherms and the other a phenomenon connected possibly with slow diffusion into or out of the sorbent particles or perhaps a swelling phenomenon. It would be expected that the slow diffusion could be eliminated or reduced by using a smaller particle size for the measurements leaving only the nitrogen type behavior. It will be seen from Figures 7 and 11 that this was not borne out. The situation is complicated by the probably very slow inter-particle transport in the powdered material.

In the curves for the 149.4% CCl_4 coconut shell charcoal is noted the effect of grinding of the material to a fine powder on the DMMP isotherm. The powdered material was produced by grinding the 12 x 30 mesh charcoal for 3 minutes in a shaking ball grinder. It is seen that the capacity at saturation is greater for the granular material and that both its adsorption and desorption isotherms are steeper. A partial explanation for the relative steepness of the adsorption isotherms may lay in interparticle diffusion. In the powdered material where the interparticle distance is on the order of the mean free path of the gas molecules the rate of transport from the gas phase to the powder toward the bottom of the sample bucket will be slow. Thus the adsorption isotherm for the granular material is likely to correspond more nearly to an equilibrium situation and therefore, be steeper, aside from any non-diffusion-controlled hysteresis. At saturation pressure, about 0.8 mm Hg, the mean free path is shortest and furthermore the uppermost sorbent particles and sides of the sample bucket

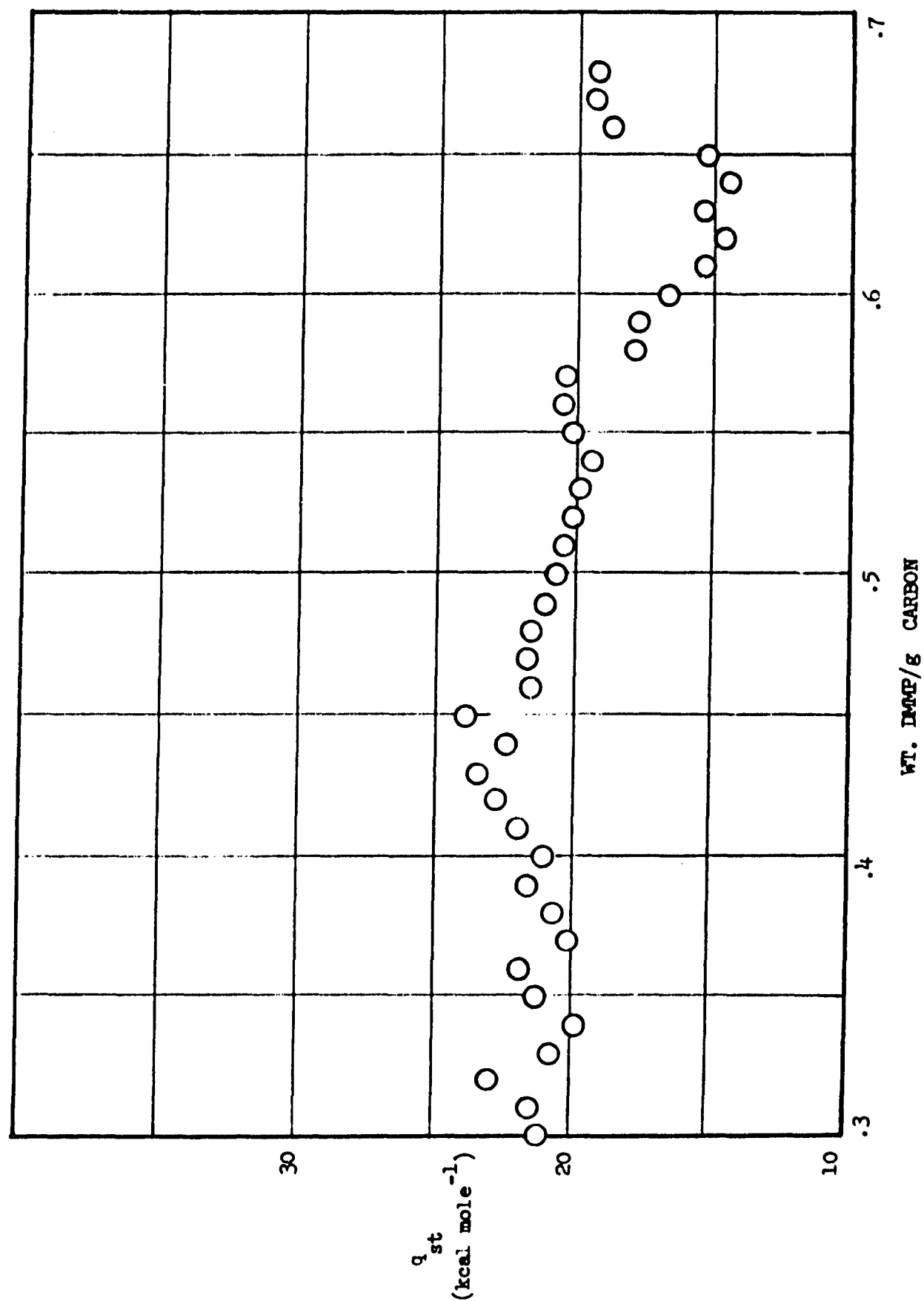
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will be covered with a mobile film of DMP allowing a rapid transport to the bottom of the sample. It would appear, therefore, that grinding of the sample has effectively destroyed some of the ~~small~~^{micropore} pore structure of the charcoal - a surprising result. During desorption it is noted that the curves for the two materials more nearly approach each other as desorption continues. This can be explained, assuming equilibrium in both cases, by the fact that adsorption at lower pressures is influenced largely by the smaller ^{micropores} pores which are less likely to be altered by mechanical grinding. Hence the total volume in small pores remains essentially the same. The powdered sample was outgassed at 300°C to constant weight after making the measurements to check for possible loss of material. No loss was detected.

From the desorption isotherms reported in this and previous progress reports isotheric heats of adsorption, q_{st} , were calculated. The heats, plotted as a function of quantity of DMP adsorbed, for the NCC felt, Mine Safety Appliances Research (MSAR) felt, and PCC carbons are shown in Figures 12, 13 and 14. It is estimated that the various errors add up an uncertainty in the heat values of about 2 kcal mole⁻¹. The justification for using desorption data for these calculations was discussed in the Third Progress Report. Due to the extreme steepness of the desorption isotherms and the attendant slowness of desorption it was not possible to get reliable heat values lower than about 35% of saturation capacity. This is because it was not possible to desorb to great extents in reasonable lengths of time. Desorption times between points in the range of coverages to which the isotherms were carried ran to 8 - 10 hours. Nevertheless the data does extend down into the significant portions of the isotherms where the variations of isotherms steepness among the samples is manifest. It is seen that there is no apparent correlation between the isosteric heats and the steepness of the isotherms. In fact the MSAR felt which shows the least steep isotherm of any of these three samples shows a somewhat higher heat of adsorption at low coverages than the NCC felt, just the reverse of what one would expect if the heat is responsible for the difference in steepness. If one assumes at, say, a coverage of 0.4 g DMP/g carbon the same Clausius-Clapeyron constant (which is related to the entropy of adsorption - see Appendix, equation (3)) for both the NCC felt and MSAR felt it is noted that a heat difference of only 1 kcal mole⁻¹ can account for the difference. The uncertainty in the data is greater than this so that it must be concluded that a decision as to whether energy term or an entropy term is responsible for the difference in isotherm steepness in these systems is unfortunately outside experimental error. Judging from the large size of the heats of adsorption compared to the heat of vaporization, 13.0 kcal mole⁻¹, all the way to saturation there is considerable influence exerted by the sorbents on molecules in even the highest layers of capillary

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FIGURE 12
ISOSTERIC HEAT OF ADSORPTION OF DMMP ON NCC FELT

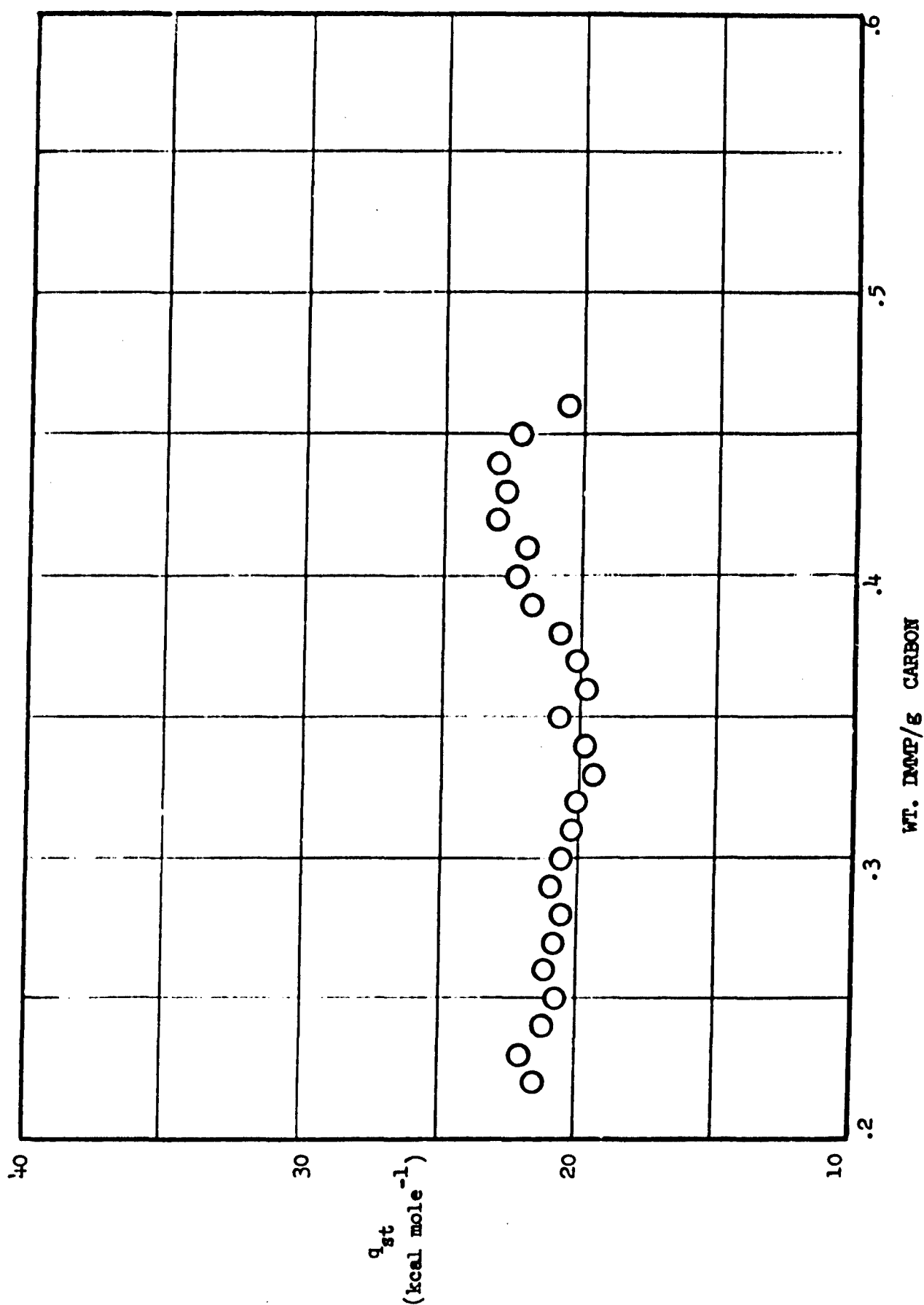


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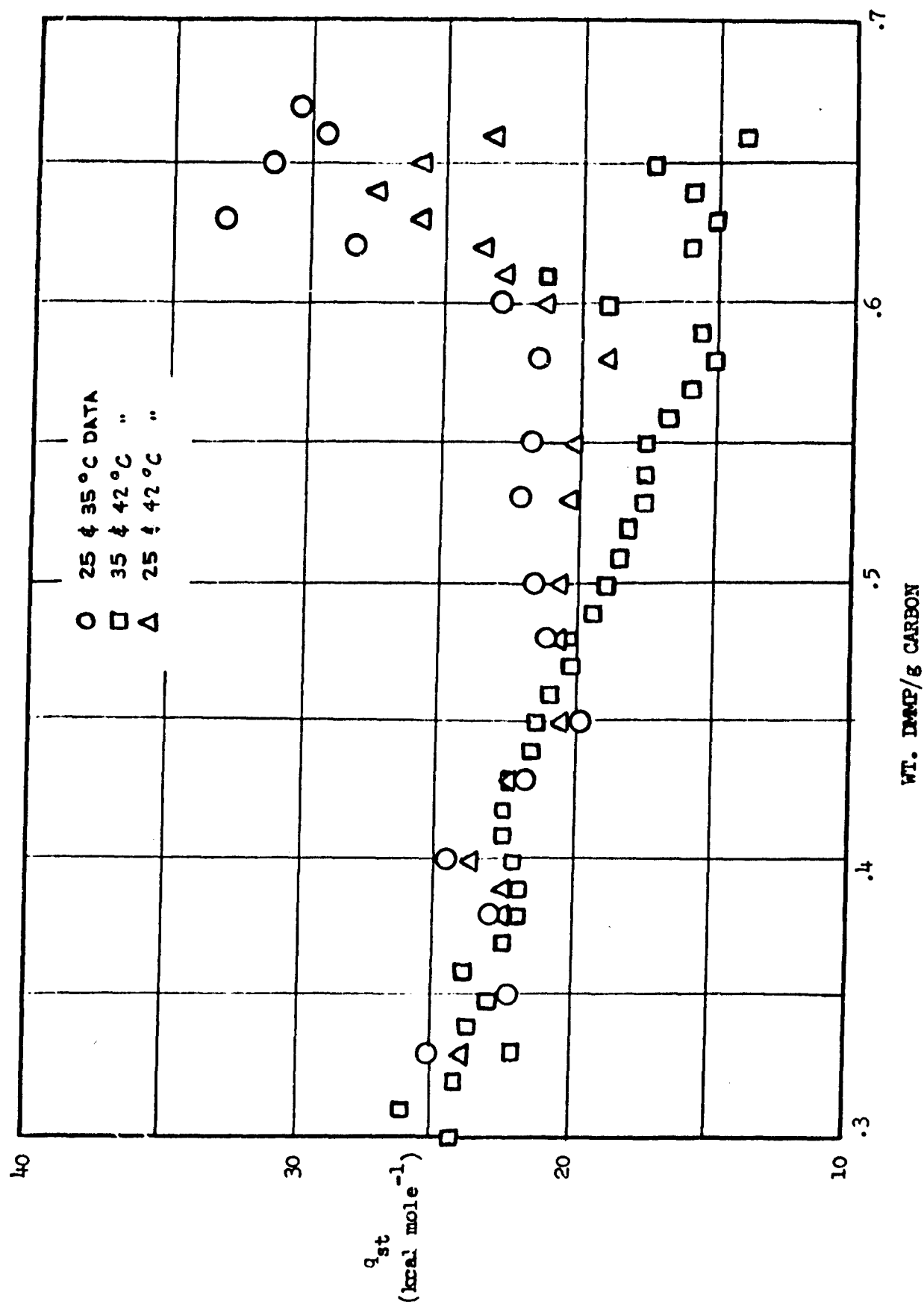
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FIGURE 13
ISOSTERIC HEAT OF ADSORPTION OF DMP ON PCC 12 X 30 MESH CARBON



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FIGURE 14
ISOSTERIC HEAT OF ADSORPTION OF DMF ON MSAR FELT



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condensed liquid.

In Figure 14 is reported values of the heat of adsorption of DMMP on the MSAR felt calculated from combinations of data at three temperatures. The great differences in heat values at large coverages calculated with the different combinations of data, or the variations with temperatures of the heat of adsorption, can be caused by a very large difference in DMMP heat capacity between the adsorbed and gas phases, perhaps involving a phase transition in the adsorbed DMMP. This should be of little consequence in adsorption at low coverages, however.

To detect possible chemical effects in the adsorption of DMMP the liquid which was accumulated in a cold trap from desorptions over a period of time from the NCC felt, PCC carbon, and MSAR felt, including even the last quantities of DMMP removed from the samples upon heating to 300°C, was analyzed by gas chromatography. As before an SE 30 silicon oil on Chromosorb W column was used. No impurities were detected indicating no catalytic break-down effected. As indicated by the weights of the samples all DMMP was removable.

II. TOTAL PORE VOLUME DISTRIBUTION

The results of our nitrogen adsorption measurements were combined with mercury porosimeter measurements to give the total pore volume distributions of the sorbents in the range of 10 to 100,000Å. The mercury porosimeter measurements were made by American Instrument Co., Silver Spring, Md. The results of these measurements are shown in Figure 15. The total pore volume at a given radius indicates the total volume in pores equal in size to or smaller than the given radius. Values of the distributions up to 1000Å were obtained from the nitrogen adsorption data while above this radius size the distribution was determined from the mercury penetration data.

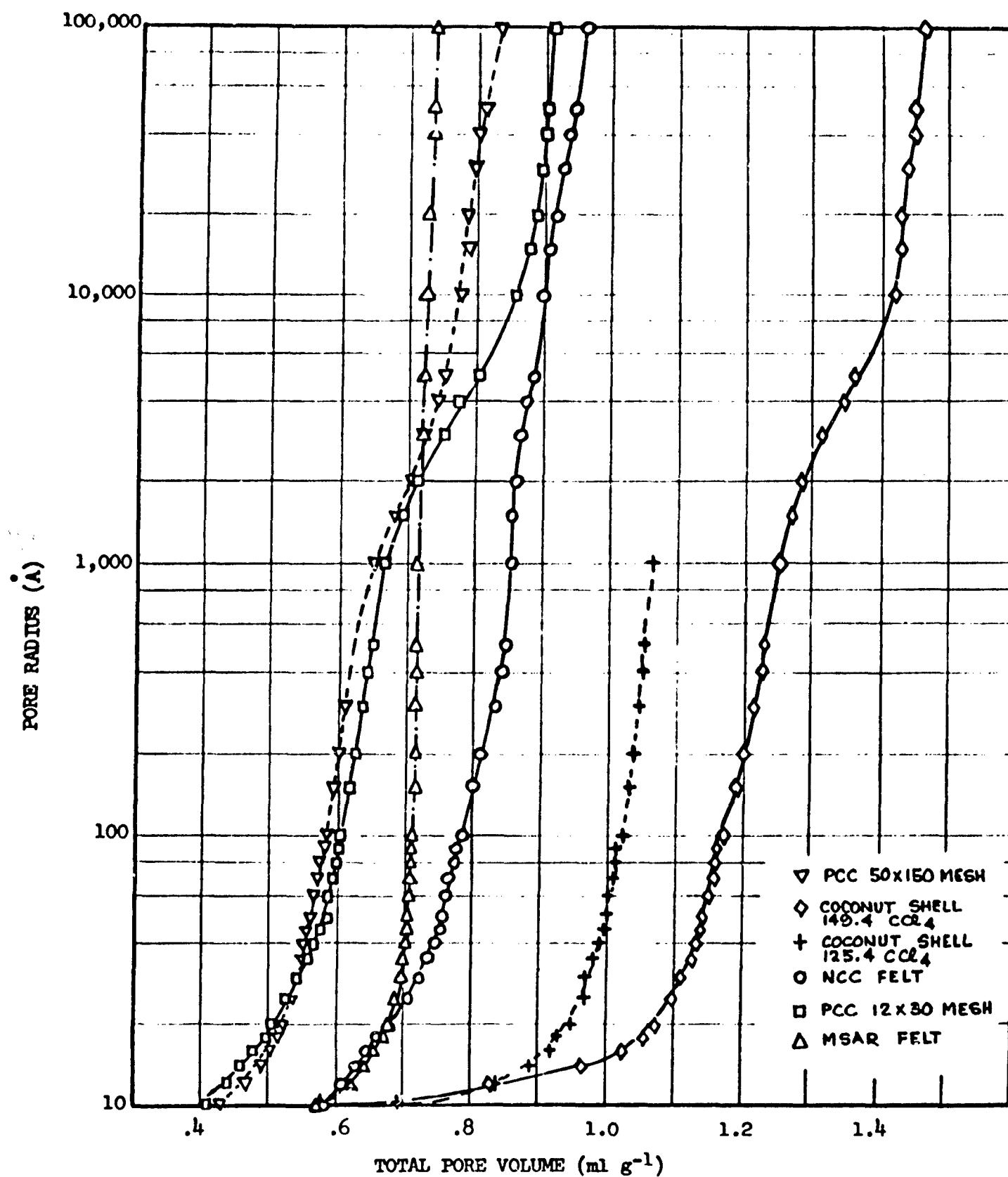
In order to calculate the total pore volume distribution from the nitrogen data first the distribution was calculated by the method of Roberts to give the volume in pores between a given size and 1000Å, as illustrated in the previous progress reports. Then from the individual isotherms the volume of nitrogen liquid adsorbed at a pressure corresponding to pores of 400Å or smaller being filled was determined. Combining these two, then, one can determine the volume in pores smaller than a given size, up to 1000Å.

The mercury porosimeter data reports the volume of mercury which can be forced into the pores of a material as a function of applied pressure. Since the pressure is correlated with the size of pores into which the mercury can enter one has measured in effect the volume in pores between a given size and a reference size, say 1000Å. Adding the value of the total pore volume in pores of 1000Å or smaller from the nitrogen adsorption measurements, to the values of pore volume in pores between 1000Å and the given size from the mercury measurements, the total pore volume distribution was extended to 100,000Å. Effectively, then, the distributions have been joined at 1000Å.

From these distributions one sees some rather large differences in pore structure among the various sorbents. Apparently the carbon fibers have little macropore volume, or volume in large pores. This is particularly true of the MSAR felt whose distribution curve rises almost vertically from 100Å. The NCC felt has more macropore volume but not quite as much as any of the granular carbons. From the curves for the two samples of coconut shell charcoal can be seen quite clearly the effect of level of activation on micropore structure. The increased pore volume of the 149.4% CCl_4 material is gained largely at the expense of pores smaller than 10Å, presumably due to an enlarging effect during the continued activation.

FIGURE 15

TOTAL PORE VOLUME DISTRIBUTION



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Since pores smaller than $10\text{\AA}$ are of primary importance in producing the steep isotherms necessary for effective agent removal and retention at low concentrations, it is expected that in this respect at least continued activation has effected no improvement. It is noted that the 149.4% CCl_4 coconut shell charcoal has approximately the same volume and distribution of volume in pores in the 20 - $1000\text{\AA}$ range as does the NCC felt. It will be remembered that hysteresis is not as great in the coconut shell carbons as in the NCC felt in either nitrogen or DMMP adsorption. This leads one to the conclusion that it is not merely quantity of pore volume in the 40 to $1000\text{\AA}$ range which is to be correlated with the hysteresis behavior but other factors as well, such as, for example, pore shape.

III. SURFACE OXYGEN STUDIES ON ACTIVATED CARBON

It will be recalled from the second progress report, p 16, that the elemental analysis of the NCC felt added up to only 95.33%, implying that there were further elements present which were not determined. To pursue this, sulfur and chlorine determinations were made on this material by Alfred Bernhardt Mikroanalytisches Laboratorium. The combined results are shown in Table 1.

Table 1. Elemental Analysis of NCC Felt

Component	Percent
Carbon	91.75
Hydrogen	0.43
Oxygen	2.05
Sulfur	2.98
Chlorine	0.77
Ash	0.99
Total	99.08

The demands on personnel for other work have prevented further progress worth reporting on this area.

IV. RATE MEASUREMENTS AT CONSTANT PRESSURE

The Cahn RG electrobalance was repaired by Cahn Instrument Company and reinstalled in the apparatus described in the Third Progress Report. The malfunction was due to a flaw in construction rather than an interaction with the DMMP vapors as first feared. The apparatus, shown in Figure 12 of the Third Progress Report, has been modified so as to incorporate a U-trap of 20 mm tubing in series between the balance case and the flexible bellows. This was done to effect more rapid removal of the DMMP vapors so as to maintain the very low pressures necessary during rates of desorption measurements.

Some rate measurements for the vacuum desorption of DMMP and PCC 12 x 30 mesh carbon and from the MSAR felt were made. To maintain constant sample temperature during desorption a heat sink consisting of a 0.8 g block of aluminum was used to support the sample on the balance pan. Sample sizes of about 4 mg were used so that the heats involved were easily supplied by the heat sink with only small changes in temperature. The procedure consisted merely of equilibrating the degassed sample to the desired DMMP pressure and recording the weight of the sample after raising a Dewar of liquid nitrogen over the U-trap.

If the rate of desorption is controlled by slow diffusion from the interior of the porous particles to the surface and the diffusion coefficient is constant, it is predicted by the laws of diffusion that the amount of DMMP desorbed plotted versus the square root of time will produce, for short times at least, a straight line (2,3). When desorption is begun near saturation for these samples it was seen that the square root curve is far from linear. This is not surprising since the first material desorbed will certainly be removed by a different process, similar to evaporation, than the more firmly held DMMP removed at longer times. In effect the diffusion coefficient is not constant due to a change in mechanism of removal with coverage. At low coverages desorption should be controlled solely by activated diffusion in the pores. If, then, one equilibrates the sample to lower pressures prior to desorption data will be obtained which is more amenable to theoretical interpretation. This was attempted but considerable difficulty was encountered in controlling initial pressure due to the outgassing of previously adsorbed DMMP vapors from the balance mechanism. It requires only a small change in quantity of DMMP present in the vapor phase to make a large change in relative pressure.

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In view of the outgassing behavior the question also arises as to whether during the actual desorption measurements the pressure is maintained sufficiently near zero. Even if the pressure is indicated zero in one part of apparatus there could be present sizable gradients in relative pressure in the vicinity of the balance mechanism. These difficulties can be circumvented by working with a more volatile adsorbate. A given change in the quantity of material in the vapor phase in this case has less effect on the relative pressure so that the adsorption effects on the balance mechanism will be of little consequence. Rate measurements with ethyl chloride, b.p. 12°C, are to be made.

V. APPARATUS FOR FLOW ADSORPTION MEASUREMENTS

The E-2 canister tester has been received from CRDL, installed, and its flow meters calibrated. An activated charcoal adsorption unit has been installed in series in the air supply line to remove any contaminating vapors.

The gas chromatograph, and F & M Model 700, to be used for effluent gas analysis, has been installed and checked out.

VI. PLANS FOR NEXT REPORT PERIOD

DMMP adsorption measurements will be continued on the coconut shell charcoals and heats of adsorption calculated.

Further insight into the nature of these hysteresis phenomena will be sought. Hysteresis loop "scanning" experiments will be made, i.e. desorption begun well before saturation.

Water adsorption measurements will be made on the sorbents of interest.

Ethyl chloride adsorption measurements will be started. It is anticipated that studies with this adsorbate will allow the determination of accurate thermodynamic quantities to low coverages.

Rates of adsorption and desorption of ethyl chloride at constant pressure will be made on the samples of interest.

The flow adsorption apparatus will be calibrated for DMMP and measurements begun.

Special samples of activated carbon will be prepared having a wide variety of type and quantity of surface oxygen complexes.

VII. REFERENCES

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2. Dacey, J. R. and D. G. Thomas, Trans. Faraday Soc., 50, 740 (1954)
3. J. Crank, The Mathematics of Diffusion, Oxford University Press, London, 1957.

VIII. APPENDIX. CALCULATION OF THE ISOSTERIC HEAT OF ADSORPTION

At the suggestion of our Project Officer this appendix has been added. It gives a brief discussion of the form and origin of the equations used for the calculation of the isosteric heat of adsorption.

The adsorption of a gas on a solid may be treated as a two phase equilibrium in which adsorbate molecules are free to distribute themselves between the gas phase and the adsorbed phase according to the laws of thermodynamics. At constant and uniform pressure and temperature, the thermodynamic equilibrium conditions require that

$$-\bar{S}_s dT + \bar{V}_s dP = -\bar{S}_g dT + \bar{V}_g dP$$

where $\bar{V}_s$ and $\bar{V}_g$ are the partial molar volumes of the adsorbate in the surface and gas phases respectively. In the gas phase $\bar{V}_g$ is merely the molar volume. $\bar{S}_s$ and $\bar{S}_g$ are the partial molar entropies for the surface and gas phases respectively. $\bar{S}_g$ is merely the molar entropy. P and T signify the pressure and temperature respectively.

Assuming $\bar{V}_g$ to be much greater than $\bar{V}_s$ and that the gas phase behaves ideally, i.e. $P = RT/\bar{V}_g$, the equation above can be rearranged to give

$$\left(\frac{d \ln P}{dT} \right)_{n_s} = - \frac{\bar{S}_s - \bar{S}_g}{RT} \quad (1)$$

The subscript, n_s , signifying the number of moles of adsorbate adsorbed per unit weight of sorbent, is added to the left hand side to emphasize the fact that the term is a function of surface coverage. Thus to define the equation the value of n_s must be given.

It can be shown that under the conditions $\bar{S}_s - \bar{S}_g = -q_{st}/T$, where q_{st} is defined as the isosteric heat of adsorption. The isosteric heat of adsorption is the heat involved when a mole of gas is adsorbed onto an infinitely large quantity of sorbent so as to maintain constant coverage. Substituting for $\bar{S}_s - \bar{S}_g$ equation (1) becomes

$$\left(\frac{d \ln P}{dT} \right)_{n_s} = \frac{q_{st}}{RT^2} \quad (2)$$

There will be a whole family of curves relating $\ln P$ to T , one for each value of n_g . Equation (2) relates the slopes of these curves to the isosteric heat of adsorption. In general the slope, and therefore q_{st} , will vary with n_g .

If q_{st} is constant with temperature, equation (2) can be integrated to give

$$\ln P = -\frac{q_{st}}{RT} + C \quad (3)$$

C is a constant. This is identical in form to the common equation describing liquid-vapor equilibrium.

Since it requires only two points to define well the slope at a point of a smooth curve, values of q_{st} as a function of n_g can be calculated from adsorption isotherms at two temperatures. A convenient form of the equations above to use for this is

$$q_{st} = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{P_2}{P_1}$$

Here P_1 and P_2 are the equilibrium pressures taken from the two isotherms at equal coverages and T_1 and T_2 are the corresponding isotherm temperatures.