

AEDC-TR-69-270

copy 1

**ARCHIVE COPY
DO NOT LOAN**



**SORPTION PUMPING OF HYDROGEN
BY CRYODEPOSITS—PREDICTION
OF SORPTION CAPACITY**

**K. E. Tempelmeyer
ARO, Inc.**

February 1970

This document has been approved for public release and
sale: its distribution is unlimited.

**AEROSPACE ENVIRONMENTAL FACILITY
ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
ARNOLD AIR FORCE STATION, TENNESSEE**

AEDC TECHNICAL LIBRARY



5 0720 00032 7702

PROPERTY OF U. S. AIR FORCE
AEDC LIBRARY
F40600 - 69 - C - 0001

NOTICES

When U. S. Government drawings specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified users may obtain copies of this report from the Defense Documentation Center.

References to named commercial products in this report are not to be considered in any sense as an endorsement of the product by the United States Air Force or the Government.

**SORPTION PUMPING OF HYDROGEN
BY CRYODEPOSITS—PREDICTION
OF SORPTION CAPACITY**

**K.E. Tempelmeyer
ARO, Inc.**

This document has been approved for public release and sale; its distribution is unlimited.

FOREWORD

The research presented in this report was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 64719F.

The results reported herein were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC, AFSC, under Contract F40600-69-C-0001. The research was conducted from April 1969 through September 1969, under ARO Project No. SW3003, and the manuscript was submitted for publication on November 11, 1969.

This technical report has been reviewed and approved.

Michael G. Buja
1st Lt, USAF
Research Division
Directorate of Plans
and Technology

Harry L. Maynard
Colonel, USAF
Director of Plans
and Technology

ABSTRACT

The applicability of several existing adsorption theories for predicting the equilibrium isotherms for the sorption of hydrogen (H_2) by carbon dioxide (CO_2) cryodeposits has been examined in the pressure range from 10^{-8} to 10^{-3} torr. It is demonstrated that the H_2 sorption capacity of CO_2 frost cryosorbents at temperatures between 12 and $20^\circ K$ may be accurately predicted by an equilibrium isotherm equation proposed by Dubinin and Radushkevich. This equation is then used to calculate families of sorption isotherms for CO_2 frosts formed at various conditions and consequently having different structures. These results may be used to estimate the H_2 capacity of cryosorption pumping systems which would employ CO_2 frost as a cryosorbent.

CONTENTS

	<u>Page</u>
ABSTRACT	iii
NOMENCLATURE	vi
I. INTRODUCTION	1
II. AVAILABLE SORPTION CAPACITY DATA	1
III. DISCUSSION	
3.1 Henry's Law and the Freundlich Equation	2
3.2 The Langmuir Theory	3
3.3 The BET Theory	5
3.4 The Potential Theory and the Dubinin-Radushkevich Isotherm Equation	7
3.5 Prediction of Hydrogen Sorption by Carbon Dioxide Frost	9
IV. CONCLUSIONS	10
REFERENCES	10

APPENDIX ILLUSTRATIONS

Figure

1. Sorption Isotherms for Hydrogen on Carbon Dioxide for Frost Formed at Various Conditions (Ref. 6)	15
2. Comparison of Isotherms for Hydrogen on Carbon Dioxide Frost at Various Temperatures with Those of Other Investigations	16
3. Sorption Isotherms in Log-Log Coordinates for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr	17
4. Sorption Isotherms for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr Plotted in Langmuir Coordinates	18
5. Brunauer's Classification of Adsorption Isotherms	19
6. Sorption Isotherms for Carbon Dioxide Frost Plotted in BET Coordinates	20
7. Sorption Isotherm Data for Carbon Dioxide Frosts Formed at a Chamber Pressure of 2×10^{-5} torr Plotted in Dubinin-Radushkevich Coordinates	21
8. Sorption Isotherms for Carbon Dioxide Frost Formed at Various Chamber Pressure Levels Plotted in Dubinin-Radushkevich Coordinates	22
9. Sorption Isotherms for Carbon Dioxide Frost from Ref. 15 Plotted in Dubinin-Radushkevich Coordinates	23
10. Experimentally Determined Values of C°	24
11. Comparison of Calculated Isotherms from the Dubinin-Radushkevich Equation for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr	25
12. Comparison of Calculated Isotherms for the Dubinin-Radushkevich Equation for Carbon Dioxide Frost Formed at Various Pressure Levels	26

NOMENCLATURE

SYMBOLS

A	Constant in Eq. (16) equal to Φk^2
a	Solubility constant in Henry's Law
b	Adsorption coefficient in Langmuir's equation, defined by Eq. (5b)
C	Dimensionless sorption capacity, ratio of the number of molecules sorbed to the number of molecules predeposited in the frost sorbent
C_m	Maximum sorption capacity
C°	Sorption capacity constant of Eq. (16)
E_a	Energy of sorption
E_L	Energy of vaporization
K	Boltzmann factor in BET theory defined by Eq. (8)
k	Boltzmann's constant
k_o	Desorption coefficient
m	Mass of a molecule
P	Pressure
P_o	Vapor pressure of the bulk liquid
P_{form}	Pressure at which frost is formed
T	Temperature
T_f	Temperature of frost
T_{form}	Temperature at which frost is formed
V_a	Volume of sorbed gas
V_{ads}	Volume of adsorbed gas
V_L	Liquid volume occupied by sorbed gas

V_o	Sorbent volume available for sorbate
a_o	Condensation coefficient
ϵ	Energy of gas-surface interaction
ρ_g	Gas density
ρ_L	Liquid density
Φ	Parameter in Eq. (15) describing sorbent porosity

SUBSCRIPTS

T	Temperature
T_f	Temperature of frost

SECTION I INTRODUCTION

Various types of cryodeposits formed on surfaces at temperatures between about 10 and 25°K have been shown to be effective sorbing media for hydrogen (H₂) (Refs. 1 to 5). In particular, carbon dioxide (CO₂) frost exhibits a high pumping speed and possesses the greatest H₂ sorption capacity of any frost thus far investigated. Consequently, the present author has investigated the H₂ sorption properties of CO₂ cryodeposits in some detail (Ref. 6) and has demonstrated that the sorption capacity of frosts depends upon the conditions at which the frost is formed. A number of experimental equilibrium isotherms for the sorption of H₂ by CO₂ frosts formed in various ways are also presented in Ref. 6. To avoid the measurement of frost isotherms for every case of interest, the ability to predict them is obviously worth seeking.

Physical sorption is fundamentally very complex. Although it has been studied intensely over the past fifty years, it is still not well understood; and no single theory can accurately describe the phenomenon. The purpose of most adsorption theories is to allow a prediction of the isotherm for a given sorbent-sorbate combination. Because of the unknown nature of the surface and the complex interaction between the surface and the sorbate molecules, such a general prediction is not possible at the present time. Consequently, the simpler problem of (1) predicting isotherms for any gas on a particular sorbent, given a single isotherm for one gas on that sorbent, or (2) predicting the isotherms at various temperatures from an isotherm obtained at one temperature, has attracted considerable attention.

The purpose of this report is to describe the usefulness of existing adsorption theories for correlating and predicting the measured H₂ sorption characteristics of CO₂ frost. The goal is to determine if the sorption capacity of CO₂ frost is predictable when the frosts are formed over a wide range of conditions and, as a consequence, have different structures.

SECTION II AVAILABLE SORPTION CAPACITY DATA

The sorption capacity of various kinds of sorbents is usually summarized in terms of equilibrium isotherm plots which have the simple functional dependence shown by Eq. (1).

$$C = f(P)_T \quad (1)$$

This type of presentation is widely used to correlate gas adsorption data for various gas-surface combinations, and it is also adequate to describe the sorption of gases by charcoal, silica gel, molecular sieves, and other porous sorbents.

The situation with frost sorbents is more complicated. The amount of gas sorbed by a frost may be conveniently expressed in terms of a dimensionless capacity,

$$C = \frac{\text{Number of molecules sorbed}}{\text{Number of molecules deposited to form the frost}}$$

This capacity parameter has the advantage of expressing the quantity of gas sorbed in a manner which makes it independent of the volume or thickness of the frost sorbent. A set of equilibrium isotherms for H₂ sorbed by CO₂ frosts formed in different ways is contained in Ref. 6 and reproduced here in Fig. 1 (Appendix). Some of these data are also compared with similar measurements by other investigators in Fig. 2. It is seen that these results do not all agree. The reasons for the disagreement are discussed in detail in Ref. 6, where it is shown that the cryosorption capacity of CO₂ frosts is strongly influenced by

1. the strike rate and/or chamber pressure level at which the frost was formed,
2. the cryosurface temperature at which the frost was formed,
3. the temperature history of the frost (also pointed out in Ref. 7)

Thus, frost cryosorbents are much more complex than molecular sieves, charcoal, silica gel, or other such porous sorbents. Consequently, the isotherms for frost sorbents depend on many more factors and have the functional form of

$$C = f[P, P_{form}, T_{form}, T_f(t)]_{T_f} \quad (2)$$

Because information about the various factors which govern the frost capacity are not given in Refs. 1 through 5, those data are of little practical value for the design of frost cryosorption pumping systems. Isotherm data given in Fig. 1 (Ref. 6) were obtained for frosts formed at (1) the pressure levels stated in the figure, (2) the same temperature at which cryosorption took place (12.4, 16.5, or 21.5°K), and (3) the frost temperature, which did not vary with time. These isotherms are quite repeatable, if one forms the frost at the conditions specified. They are used here to test the applicability of several of the prominent adsorption theories.

SECTION III DISCUSSION

3.1 HENRY'S LAW AND THE FREUNDLICH EQUATION

For very small concentrations, gases usually dissolve in solids according to Henry's law (Ref. 8):

$$C = aP^m \quad (3)$$

where $m = 1$ for nonmetals such as cryodeposits. It is a simple sorption isotherm equation and can be derived theoretically on the assumption that the gas in the solid is sufficiently dilute to obey the perfect gas law (see Ref. 8, page 105). It is quite useful in treating the problem of gas permeation through solids. Shupe (Ref. 9) has presented a rather complete survey of permeation phenomenon, and the role of Henry's law.

Brunauer (Ref. 10) states that Henry's law should hold for sorption at low pressures, but a more modern view is that this law is the expected limit of every isotherm as $P \rightarrow 0$ (see discussion by Hobson, Ref. 11). If Eq. (3) is obeyed, the measured

isotherms of frost sorbents should provide a straight line with unity slope on plots of $\log C$ versus $\log P$. Some of the sorption isotherms from Ref. 6 and given here in Fig. 1 are replotted in Fig. 3 in terms of $\log C$ and $\log P$ coordinates to check their agreement with Eq. (3). It is apparent that the pressure levels employed in this study are not low enough for the sorption of H_2 by CO_2 frost to follow Henry's law. However, as the pressure decreased, the slopes of the isotherms given in Fig. 3 increase and, for a frost temperature of $21.5^\circ K$, appear to approach the expected limit of 1. Thus, these trends suggest that cryosorption by frosts may obey Henry's law but only in the ultrahigh vacuum range. Similar trends exist for low-pressure isotherm data for nitrogen (N_2) sorbed by porous glass and charcoal (Ref. 11).

The empirical Freundlich equation,

$$C = a_1 P^{1/n} \quad (4)$$

one of the oldest isotherm equations, is similar to Henry's law and may be easily tested in the same way. The factors a_1 and n are defined to fit the experimental data. Although Eq. (4) is empirical, it is widely used, particularly by those desiring to provide "engineering estimates". It has been used successfully, for example, for correlating the sorption characteristics of various gases in charcoal (Ref. 10). Equation (4) also produces straight lines on $\log C$ versus $\log P$ plots but with various slopes which depend upon the value of $1/n$. Figure 3 also illustrates that the Freundlich equation would only provide a gross approximation to the isotherms of cryodeposits, and would not be particularly useful in correlating their isotherms.

3.2 THE LANGMUIR THEORY

The Langmuir equation resulted from one of the first theoretical treatments of surface adsorption and occupies a central position in the field of adsorption. Its derivation is given in detail by Brunauer (Ref. 10). Langmuir assumed that molecules which strike a bare surface have a certain probability of being adsorbed on the surface, but those which strike a site already occupied by an adsorbed molecule would be immediately reevaporated. Thus, adsorption, as specified by the Langmuir model, is limited to monolayer coverage. The Langmuir adsorption model is often applied to porous media such as frost, but a hypothetical effective adsorption area is used. This area, which is experimentally found to be orders of magnitude greater than the geometric surface area, corresponds to the interior surface areas of the pores, cracks, crevices, etc.

Using the notation employed here, Langmuir's equation takes the form,

$$C = \frac{C_m b P}{1 + b P} \quad (5a)$$

C_m and b are not empirical constants but have well-defined physical significance. C_m represents the monolayer sorption capacity of the frost at saturation; b is given by

$$b = \frac{\alpha_0 e^{E_a/kT}}{k_0 (2\pi m k T)^{3/2}} \quad (5b)$$

and is a coefficient of adsorption (see Ref. 10 for additional details). In practice, both C_m and b are determined from experimental isotherm data; however, they must have reasonable values which are consistent with their physical meaning.

Equation (5) can be readily put into the following two forms:

$$\frac{P}{C} = \frac{P}{C_m} + \frac{1}{b C_m} \quad (6a)$$

and

$$\frac{1}{C} = \frac{1}{C_m} + \frac{1}{b P C_m} \quad (6b)$$

Consequently, a plot of Eq. (6a) in P/C and P coordinates would provide a straight line with an intercept of $1/bC_m$ and a slope of $1/C_m$. Alternatively, a plot of $1/C$ against $1/P$ will also give a straight line (Eq. (6b)). Such plots, but in particular the former, are commonly used to determine if experimental isotherm data follow Langmuir's equation. Young and Crowell (Ref. 8) do not recommend use of the latter method because they state it places too much emphasis on the low-pressure part of the isotherm. Inasmuch as the low-pressure end of the isotherm is of paramount interest here, this latter method should provide the better test of Eq. (5).

Isotherm data from Fig. 1 are replotted in Fig. 4 in terms of $1/P$ and $1/C$ coordinates. Because the plot is highly nonlinear, the experimental frost isotherms obviously do not follow Langmuir's equation. Consequently, the sorption mechanism must be more complicated than simple monolayer coverage, and the Langmuir theory does not appear to be applicable to frost cryosorption at low pressures. This conclusion is in accord with the findings of Hobson (Ref. 11), who has investigated the sorption of H_2 by porous glass and charcoal at low pressure, and with the conclusion of Danner (Ref. 12), who has studied sorption by cold molecular sieves. However, in much earlier investigations, Schmidlin, et al. (Ref. 13), and Haygood (Ref. 14) concluded that the Langmuir model is valid for low-pressure cryotrapping of H_2 by water (H_2O). The test results given in Refs. 13 and 14 are quite limited; and, as Hobson points out, the sorption process with continuous deposition of the sorbent may lead to quite different results. In any case, Langmuir's equation clearly will not predict the isotherms for predeposited frost sorbents or mechanical sorbents at low pressures.

It is of interest to note that, when the usual P/C and P coordinates were used, the frost isotherm data of Fig. 1 produced slightly concave but relatively linear lines. However, it is repeatedly emphasized in the literature that obtaining a straight line is a necessary but not a sufficient condition for guaranteeing that the data in question obey Langmuir's equation. Values obtained for C_m and b from P/C versus P plots of the Fig. 1 data were not at all reasonable and, when used together with Eq. (5), did not produce isotherms which even approximated the measured ones. Thus, with very low-pressure isotherm data, the coordinates suggested by Eq. (6b) are recommended as a more straightforward test of the applicability of Langmuir's model.

3.3 THE BET THEORY

Brunauer (Ref. 10) has classified experimentally measured isotherms into the five basic shapes sketched in Fig. 5. The Type I isotherm is characteristic of monolayer adsorption and is the shape predicted by Langmuir's equation (which has already been shown to be inappropriate for frost sorbents). Types II to V represent multilayer or multimolecular adsorption. Microporous sorbents such as charcoal (Refs. 10 and 15), porous glass (Ref. 15), silica gel (Refs. 10 and 15), and others generally exhibit Type IV or V isotherms with adsorption-desorption hysteresis (the equilibrium desorption isotherm is displaced to lower pressures than the adsorption isotherm). It is generally agreed that this behavior, which usually occurs at higher pressures than of interest here, is associated with condensation in small capillaries or in narrow-necked micropores. Inasmuch as no sorption-desorption hysteresis is observed with frost sorbents (see Figs. 1 and 2), the capillary condensation theory (Ref. 10) is probably not applicable in predicting equilibrium isotherms for cryofrosts.

A more general adsorption theory by Brunauer, Emmett, and Teller (see Ref. 10, page 149), commonly called the BET theory, extends Langmuir's approach to the case of multilayer adsorption. The basic assumption of the BET theory is that molecules in the first layer can serve as adsorption sites for molecules in the second layer and so on. Moreover, there is a balancing of condensation and evaporation rates of molecules between layers. It is further assumed that the first layer will have some value for the heat of adsorption, E_a ; but for all succeeding layers, the adsorption energy is assumed equal to the heat of vaporization of the sorbate, E_L . The resulting isotherm equation may be expressed as

$$C = \frac{C_m K P}{(P_o - P) \left\{ 1 + (K - 1) \frac{P}{P_o} \right\}} \quad (7)$$

for multimolecular adsorption on a free surface. P_o is the vapor pressure of the sorbate, and K is defined below.

$$K = \exp (E_a - E_L) / kT \quad (8)$$

If multilayer adsorption does not occur on a free surface but is limited to n layers because of space limitation imposed by opposing walls of a crack or pore, Eq. (7) is replaced by

$$C = \frac{C_m K P / P_o}{(1 - P / P_o)} \left[\frac{1 - (n + 1) (P / P_o)^n + n (P / P_o)^{n-1}}{1 + (K - 1) (P / P_o) - K (P / P_o)^{n+1}} \right] \quad (9)$$

Equations (7) and (9) can reproduce all five isotherm slopes given in Fig. 5 with appropriate values for C_m , K , and n . Consequently, the BET theory has rather widespread application.

Because the experimental tests clearly indicate that the frosts are porous (Ref. 6), one would expect that Eq. (9) would more likely apply. However, at the very low pressures at which cryosorption takes place, $P/P_o \ll 1$, and hence,

$$(P/P_o)^{n+1} < (P/P_o)^n \ll P/P_o \ll 1$$

for all values of n greater than 1. Consequently, one may neglect the $(P/P_o)^{n+1}$ and $(P/P_o)^n$ terms in Eq. (9), in which case it reduces to Eq. (7). This conclusion is also borne out by the calculated BET isotherms for various values of n given in Refs. 8 and 16. For the case of $n = 1$, Eq. (9) reduces to the form of Eq. (5) which has already been shown to be inappropriate for the prediction of the isotherms for frosts. Thus, at very low pressures, the simpler form of Eq. (7) represents limited-multilayer adsorption.

Equation (7) may be transformed into

$$\frac{P}{C(P_o - P)} = \frac{1}{C_m K} + \left(\frac{K-1}{K}\right) \frac{1}{C_m} \frac{P}{P_o} \quad (10)$$

which shows that the BET equation is a straight line for a $P/[C(P_o - P)]$ and P/P_o coordinate system and has intercept of $1/(C_m K)$ and a slope of $[(K-1)/K][1/C_m]$. Some of the isotherm data from Fig. 1 are replotted in these coordinates in Fig. 6 and produce curves which are slightly concave but approximately linear. These curves are quite similar in shape to those which resulted when the isotherm data were plotted in terms of the usual Langmuir coordinates suggested by Eq. (6a). In this case the linear approximation to the 12.4°K isotherm data curve in Fig. 6 yields a slope and intercept of

$$\left(\frac{K-1}{K}\right) \frac{1}{C_m} = 4.25$$

$$\frac{1}{C_m K} = 6.0 \times 10^{-8}$$

which in turn lead to values of

$$K = 0.71 \times 10^8 \text{ and } C_m = 0.234$$

These values, however, are highly unreasonable. First, C_m represents the maximum sorption capacity, and the value obtained from Fig. 6 is less than actual measured values. Secondly, the heat of adsorption for H_2 on CO_2 frost has been shown to be about 1200 cal/mole (see Refs. 2 or 6). Since the heat of vaporization of H_2 is 216 cal/mole, Eq. (9) indicates that K for a 12.4°K frost must be approximately

$$K = e^{(1200-216)/(1.98)(12.4)} \approx 3 \times 10^{17}$$

rather than the value required to fit the data.

Inasmuch as reasonable values for these physical parameters were not obtained, the necessary criteria required for the applicability of the BET theory cannot be satisfied. Consequently, it cannot accurately predict isotherms for frost cryosorption at pressures below 10^{-4} torr.

3.4 THE POTENTIAL THEORY AND THE DUBININ-RADUSHKEVICH ISOTHERM EQUATION

The potential theory originally developed by Polanyi provides another approach to multilayer adsorption (see Refs. 8 or 10 for complete discussions). It considers that an interaction potential field exists near the surface of the sorbent; and, because of it, the sorbate molecules are bound to the sorbent like an atmosphere is bound to a planet. The adsorbed layers are treated as being more compressed at the surface of the sorbent and decrease in density outward. The potential theory offers no explicit isotherm equation. Rather, one can imagine a number of equipotential surfaces, ϵ , above the sorbent surface; and each adjacent pair of these surfaces encloses some volume, V , of adsorbed gas. There is a definite relationship between the gas-surface interaction potential and the adsorbed gas volume, $\epsilon = f(V)$, which is called the characteristic equation. Since ϵ and V can, in principle, be expressed in terms of pressure and temperature (see Ref. 10), the characteristic equation is equivalent to an isotherm equation.

When the sorbent temperature is less than the critical temperature of the sorbate, it is further assumed that the adsorbed film may be treated as an incompressible liquid. Then, the energy required to compress a vapor from some pressure P to the vapor pressure of the bulk liquid at the temperature of the sorbent, P_o , is given by

$$\epsilon = -kT \ln \frac{P}{P_o} \quad (11)$$

Also, the volume filled in the sorption space or equivalently the volume of the condensed sorbate would be given by

$$\text{Mass of condensed sorbate in liquid phase} = \text{Mass of sorbed gas}$$

or

$$V_L \rho_L = V_a \rho_g \quad (12)$$

Calculation of an isotherm by means of the potential theory is a complex process. Consequently, Dubinin and his coworkers have simplified matters by developing an isotherm equation within the general framework of the Polanyi potential theory¹. Dubinin writes the characteristic equation as

$$V_L = f(\epsilon) \quad (13)$$

and his experiments have shown that Eq. (13) has the form

$$V_L = V_o e^{-\phi \epsilon^2} \quad (14)$$

¹References 11, 12, 17, and 18 contain discussions of Dubinin's work. His original papers were not available to the present author.

where for porous solids V_o is taken to be the pore volume and ϕ reflects a distribution of the pore volume according to size. Equation (14) is semi-empirical and was first used to describe the sorption of gases by charcoal at much higher pressures than those of this investigation. It has been subsequently shown to be valid for molecular sieves at low temperatures (Ref. 12) and other porous media (Ref. 11). Also, Ross and Olivier (Ref. 19) use functions of this type for the development of other isotherm equations. They reasoned that a random distribution of adsorption energies, like Eq. (14), would be appropriate for a solid which has a random distribution of cracks, pores, and other defects. The present author knows of no further theoretical justification for Eq. (14); yet the fact remains that it describes a wealth of experimental data.

Combining Eqs. (11) through (14) results in the expression for the Dubinin-Radushkevich isotherm equation (hereafter referred to as the D-R isotherm equation),

$$\log V_a = \log \frac{V_o \rho_L}{\rho_s} - \phi k^2 T^2 \left[\log \frac{P}{P_o} \right]^2 \quad (15)$$

In the notation employed herein, Eq. (15) may be rewritten as

$$\log C = \log C^o - AT^2 \left[\log \frac{P}{P_o} \right]^2 \quad (16)$$

where for a given sorbate, C^o and A reflect the porosity characteristics of the frost. If the experimental isotherm data are represented by Eq. (16), they would produce a straight line when plotted with $\log C$ and $(\log P/P_o)^2$ coordinates with an intercept equal to $\log C^o$ and a slope AT^2 .

Hobson, in a series of papers (Refs. 18, 20, and 21), has shown that the D-R equation accurately represents the adsorption of N_2 on Pyrex[®] and charcoal at temperatures below 90°K and at pressures down to 10^{-9} torr. Consequently, the frost isotherms of Fig. 1 were plotted in terms of $\log C$ and $(\log P/P_o)^2$ coordinates as shown in Figs. 7 and 8.

It is observed that the isotherm data for CO_2 frost formed at a pressure level of 2×10^{-5} torr are reasonably well approximated by straight lines (Fig. 7). Moreover, the slopes of all three curves result in the same value of A ($A = 3.42 \times 10^{-5} 1/^\circ K^2$). Consequently, the D-R isotherm equation properly predicts the dependence of the experimental isotherms on frost temperature, which itself is a notable achievement. In addition, the C^o intercepts, which are an index of the total available sorption volume (in terms of the dimensionless capacity parameter), are a little larger than the maximum measured values and hence reasonable.

Isotherms for frosts formed at higher pressures are replotted in D-R coordinates in Fig. 8. As might be expected, the intercepts change significantly because frosts formed at different pressure levels have different structures. However, at a constant frost temperature, the slopes of the isotherms formed at different pressures are essentially constant. This indicates that the structure of the frost has only a weak effect on A .

The only other set of isotherm data for H_2 sorbed by CO_2 frost (obtained by Yuferov and Busol, Ref. 2) were also tested to see if they followed the D-R isotherm equation; the results are shown in Fig. 9. Again, straight line isotherms were obtained at all temperatures with the D-R coordinates. Yuferov and Busol formed the CO_2 frost at an unknown pressure and at $20.4^\circ K$. They then cooled it to lower temperatures. Consequently, values of A or C° obtained from Fig. 9 have no common basis for comparison with corresponding values from Figs. 7 and 8.

Figures 7 through 9 demonstrate that the D-R isotherm equation (Eq. (15) or (16)) is useful in predicting the equilibrium sorption characteristics of cryodeposits, even though its foundation is, in part, empirical. It can clearly account for the temperature dependence of the isotherm for H_2 on CO_2 frost. A value of $A = 3.4 \times 10^{-5}$ per $^\circ K^2$ characterizes CO_2 frosts formed over a wide range of pressures and temperatures. Values of C° , which are indices of the maximum sorption capacity, are specified by the intercepts on the ordinates in Figs. 7 and 8 and are summarized in Fig. 10 for CO_2 frosts formed in various ways. They may be used in Eq. (16), together with the previously determined value of A , to estimate the sorption capacity of CO_2 frosts over ranges of temperature and chamber pressure. Thus, application of the D-R isotherm equation requires that an isotherm be measured at one temperature to determine A and that single sorption data points be obtained at one or more different frost temperatures to define $C^\circ(T_f)$. With this information, a complete family of isotherms at various chamber pressures and sorbent temperatures may be estimated. The results of such a series of calculations are described in the following section.

3.5 PREDICTION OF H_2 SORPTION BY CO_2 FROST

Taking $A = 3.4 \times 10^{-5}$ per $^\circ K^2$ and values of C° from Fig. 10 for frosts formed at a pressure level of 2×10^{-5} torr, a series of isotherms were calculated from Eq. (16) for a wide range of chamber pressures and for frost temperatures from 8 to $24^\circ K$. The results of these calculations are shown by the solid lines in Fig. 11. They represent isotherm predictions for frosts formed at a pressure of 2×10^{-5} torr and at the same temperature at which cryosorption takes place. Measured isotherms (from Ref. 6) for frost formed at the same conditions are also given in the figure. They are observed to agree quite well with the calculations. The agreement exhibited in Fig. 11 is not unexpected because the $21.5^\circ K$ isotherm and single points on the other two isotherms were, in effect, used to define A and C° , respectively. It should also be noted that varying shapes of the isotherms exhibited in Fig. 1 for frosts at different temperatures are, in general, also predicted by the D-R equation.

A complete set of equilibrium isotherms of CO_2 frosts formed at various strike rates have been predicted using Eq. (16). In all cases, the value of A was taken as 3.4×10^{-5} , and C° values were obtained from Fig. 10. Computations were made for frost temperatures from 6 to $26^\circ K$ and chamber pressures from 10^{-9} to 10^{-2} torr. These predictions are given in Fig. 12.

Subsequent to the calculations, additional isotherm data were obtained at a temperature of $16.5^\circ K$ and for a frost formed at a pressure of 1×10^{-3} torr. They are

plotted together with the calculated isotherms in Fig. (12d). The calculated isotherms are completely independent of these data. It is apparent that this isotherm was accurately predicted by the D-R isotherm equation. The accuracy of Eq. (16), outside of the frost temperature range of 12 to 21°K and, in particular, at lower temperatures, is not known. It would be of some practical interest to pursue sorption capacity measurements for frosts at temperatures below 12°K to determine the accuracy of the D-R equation in this range.

SECTION IV CONCLUSIONS

The applicability of several adsorption theories has been examined to determine whether they are useful in predicting the H₂ cryosorption capacities of CO₂ frost. Cryosorption isotherm data from Ref. 6 were used to test the usefulness of various existing theories. This study has led to the following conclusions:

1. Although H₂ cryosorption pumping by frost has been carried out at pressures below 10⁻⁷ torr, the pressures were apparently not low enough for the H₂ sorbed by a CO₂ frost to follow Henry's law.
2. The classical Langmuir and BET theories for monolayer and multilayer adsorption will not accurately predict the sorption of H₂ by CO₂ frost at low pressures.
3. The cryosorption capacity with frost sorbents at various temperatures and pressures may be predicted by application of the Dubinin-Radushkevich isotherm equation with reasonable accuracy. This equation also predicts the temperature dependence of the isotherm quite well.
4. Sufficient information is given herein to allow accurate prediction of the H₂ sorption capacity of CO₂ frost at temperatures down to 12°K. A series of calculations was carried out, and equilibrium isotherm predictions are presented in graphical form for CO₂ frosts formed at various conditions.

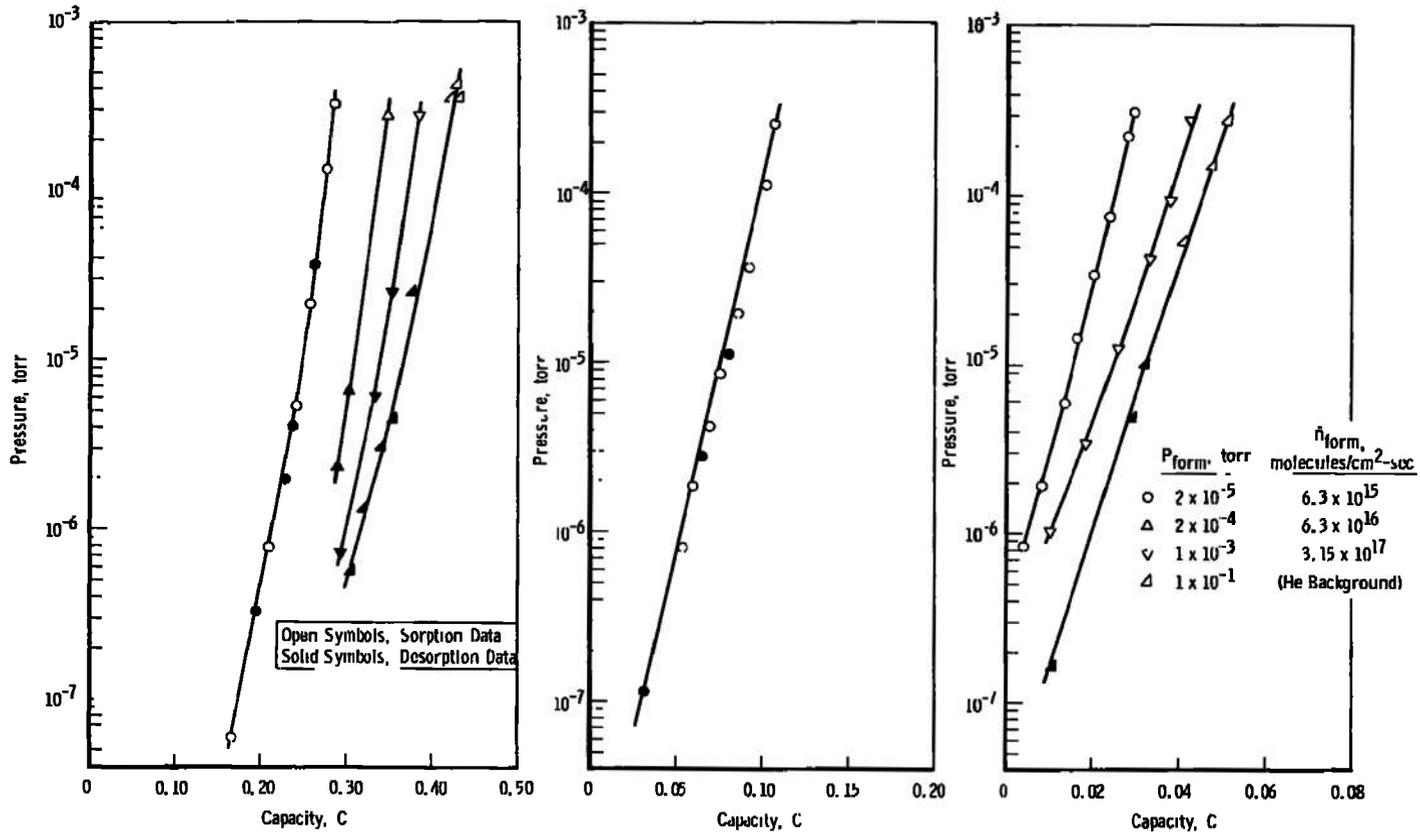
REFERENCES

1. Dawbarn, R. "Cryosorption of Hydrogen by 12-20°K Carbon Dioxide Cryodeposits." AEDC-TR-67-125 (AD655067), July 1967.
2. Yuferov, V.B. and Busol, F.E. "Sorption of Hydrogen and Neon by Layers of Solids Formed by Vapor Condensation." Soviet Physics—Technical Physics, Vol. 11, No. 11, May 1967, pp. 1518-1524.
3. Müller, E. "Adsorption Isotherms on Solid Carbon Dioxide." Cryogenics, Vol. 6, No. 4, August 1966, pp. 242-243.

4. Hunt, A.L., Taylor, C.E., and Omohundro, J.E. "Adsorption of Hydrogen on Solidified-Gas Films." Advances in Cryogenic Engineering, Vol. 8, 1963, pp. 100-109.
5. Southerlan, R.E. "10–22°K Cryosorption of Helium on Molecular Sieve 5A and Hydrogen on Condensed Vapors." AEDC-TR-65-49 (AD463339), May 1965.
6. Tempelmeyer, K.E. "Sorption Pumping of Hydrogen by Cryodeposits—Sorption Capacity Measurements." AEDC-TR-69-266, February 1970.
7. Hengevoss, J. "Influence of the Temperature History of Condensed Argon on its Hydrogen Adsorptivity at Low Temperatures." Journal of Vacuum Science and Technology, Vol. 6, No. 1, January/February 1969, pp. 58-62.
8. Young, D.M. and Crowell, A.D. Physical Adsorption of Gases. Butterworth, London, 1962.
9. Shupe, Dean S. "Theoretical Analysis of the Effect of Surface Processes on the Permeation of Gases through Metals." Ph. D. Dissertation, Massachusetts Institute of Technology, February 1969.
10. Brunauer, S. The Adsorption of Gases and Vapors: Volume I, Physical Adsorption, Princeton University Press, 1963.
11. Hobson, J.P. "Physical Adsorption at Extremely Low Pressure." Chapter 14 in The Solid-Gas Interface, (Flood, E.A., Editor) Marcel Dekker, Inc., New York, 1967.
12. Danner, R.P. "The Adsorption of Binary Gas Molecules on Molecular Sieves." Ph. D. Dissertation, Lehigh University, 1966.
13. Schmidlin, F.W., Heflinger, L.O., and Garwin, E.L. "Some Investigations of Cryotrapping." Transactions of the Ninth National Vacuum Symposium, Part II, Section I, pp. 197-204, The Macmillan Co., New York, 1962.
14. Haygood, J.D. "Steady-State Sorption of Gases during Vapor Deposition." Journal of Physical Chemistry, Vol. 67, No. 10, October, 1963, pp. 2061-2064.
15. Barrer, R.M. "Surface and Volume Flow in Porous Media." The Gas-Surface Interaction, Vol. 2, Chapter 19, Marcel Dekker, Inc., New York, 1967.
16. Adamson, Arthur W. Physical Chemistry of Surfaces (Second Edition). Interscience Publishers, New York, 1960.
17. Veguilla-Berdecia, L.A. "Some Theoretical Aspects of Cryosorption." "Final Report of the Goddard Summer Workshop Program in Measurement and Simulation of the Space Environments," June 15 to September 15, 1964, NASA TM X-55168, pp. B-7-B-20.

18. Hobson, J.P. "A New Method for Finding Heterogeneous Energy Distributions from Physical Adsorption Isotherms." Canadian Journal of Physics, Vol. 43, No. 11, November 1965, pp. 1934-1940.
19. Ross, Sydney and Olivier, James P. On Physical Adsorption. Interscience Publishers, New York, 1964.
20. Hobson, J.P. "Analysis of Physical Adsorption Isotherms on Heterogeneous Surfaces at Very Low Pressures." Canadian Journal of Physics, Vol. 43, No. 11, November 1965, pp. 1941-1950.
21. Hobson, J.P. "Theoretical Isotherms for Physical Adsorption at Pressures below 10^{-10} torr." Journal of Vacuum Science and Technology, Vol. 3, No. 5, September/October 1966, pp. 281-284.

**APPENDIX
ILLUSTRATIONS**



a. 12.4°K Equilibrium Isotherms b. 16.5°K Equilibrium Isotherms c. 21.5°K Equilibrium Isotherms

Fig. 1 Sorption Isotherms for Hydrogen on Carbon Dioxide for Frost Formed at Various Conditions (Ref. 6)

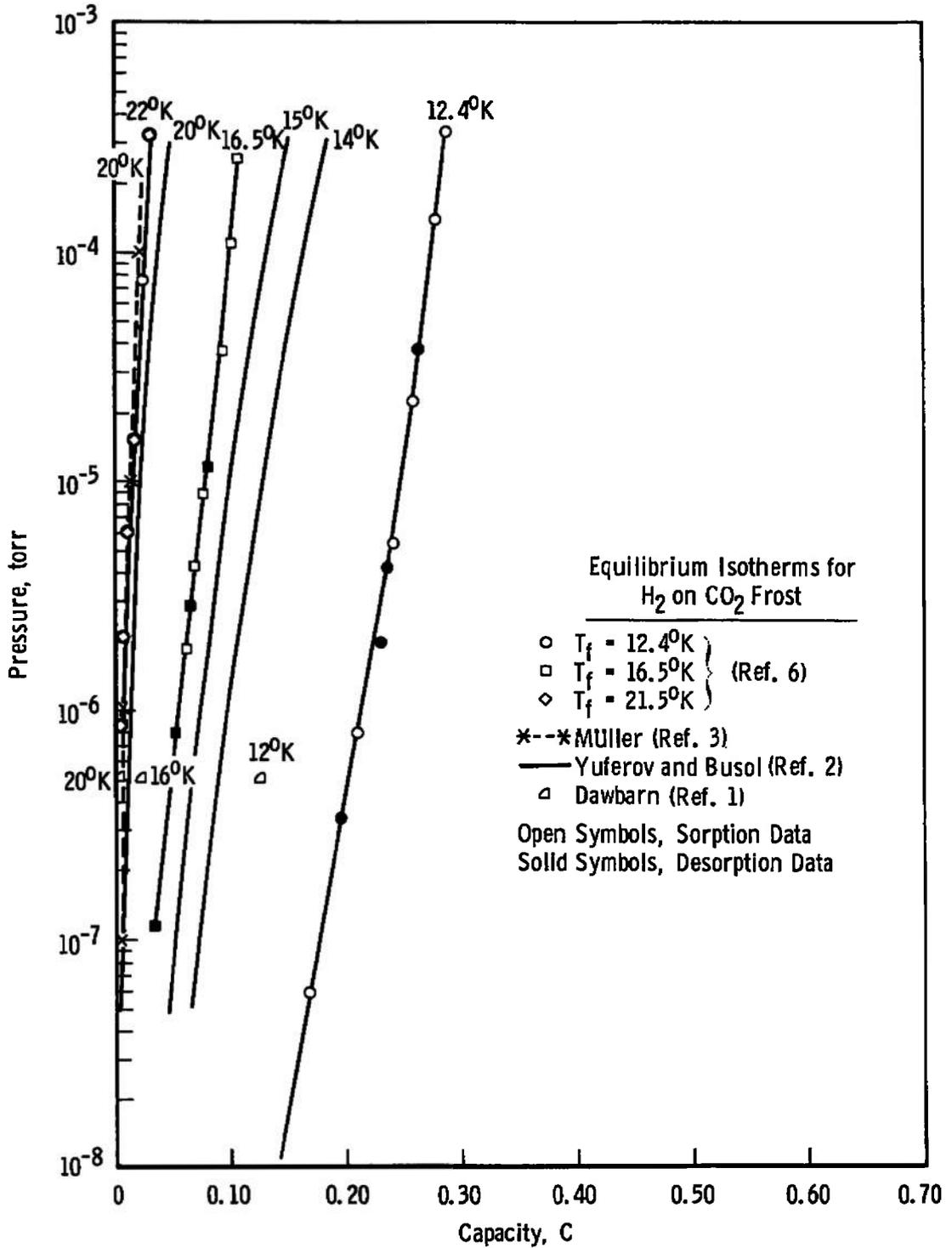


Fig. 2 Comparison of Isotherms for Hydrogen on Carbon Dioxide Frost at Various Temperatures with Those of Other Investigations

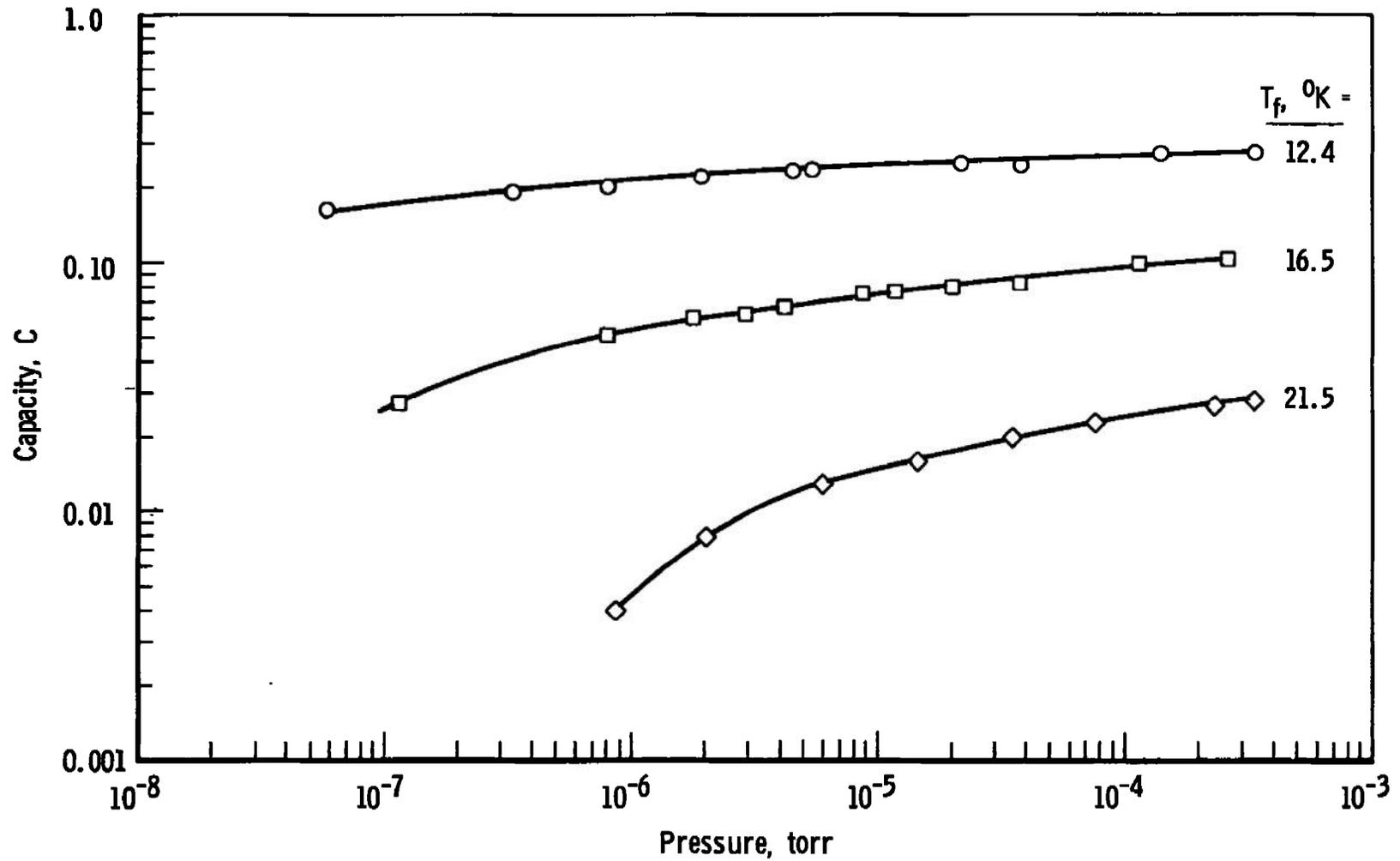


Fig. 3 Sorption Isotherms in Log-Log Coordinates for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr

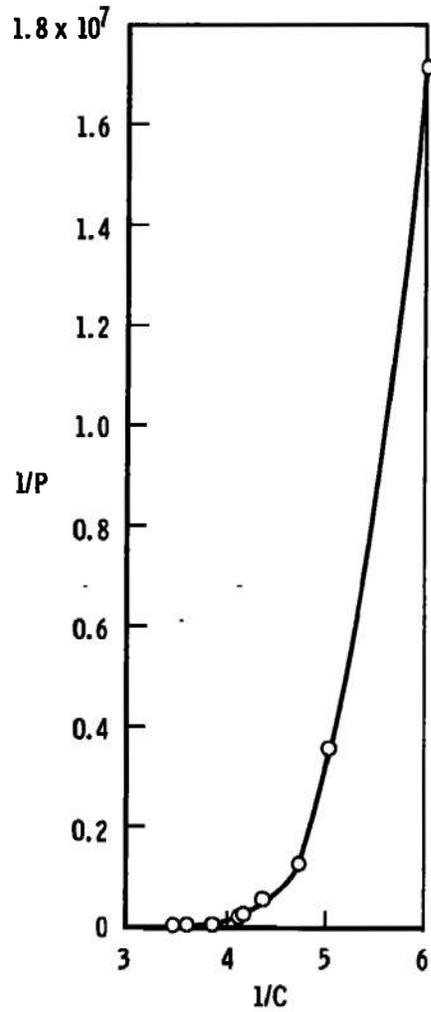
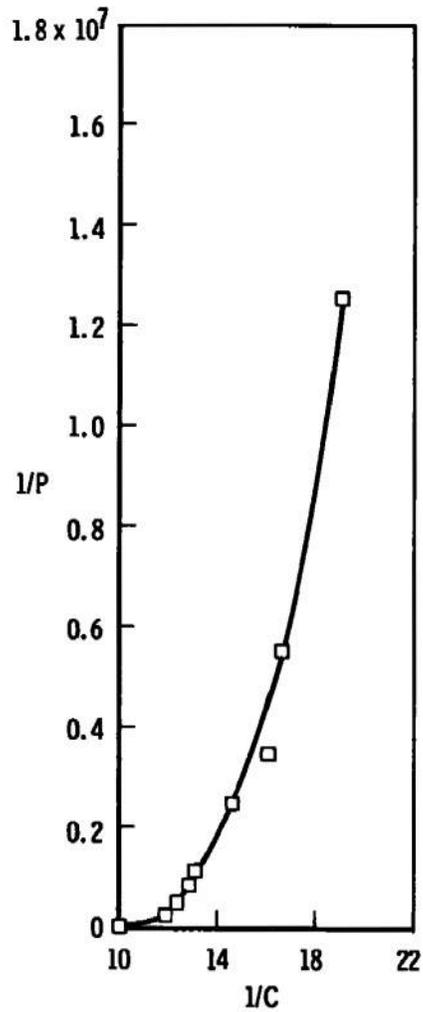
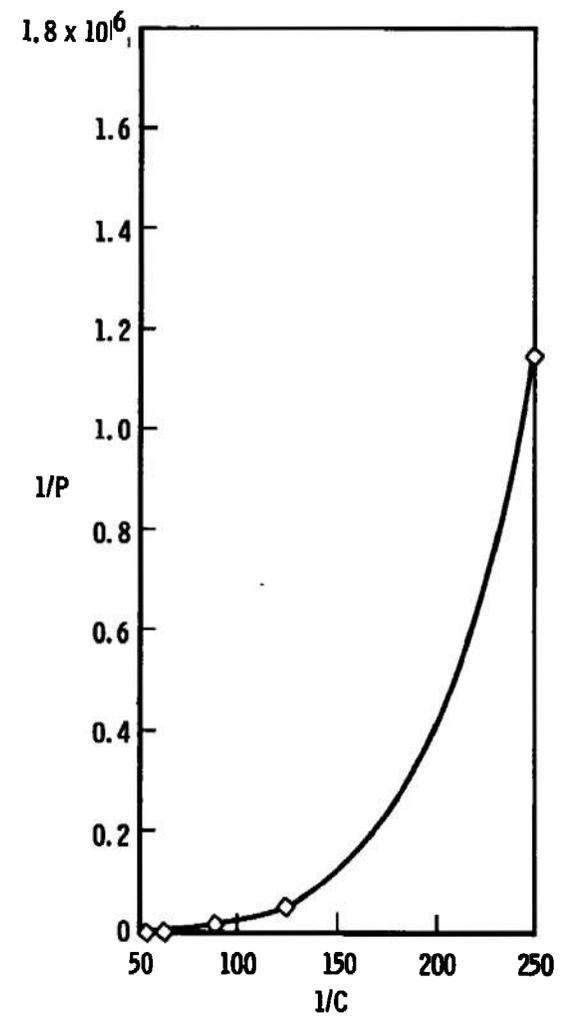
a. $T_f = 12.4^\circ\text{K}$ b. $T_f = 16.5^\circ\text{K}$ c. $R_f = 21.5^\circ\text{K}$

Fig. 4 Sorption Isotherms for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr Plotted in Langmuir Coordinates

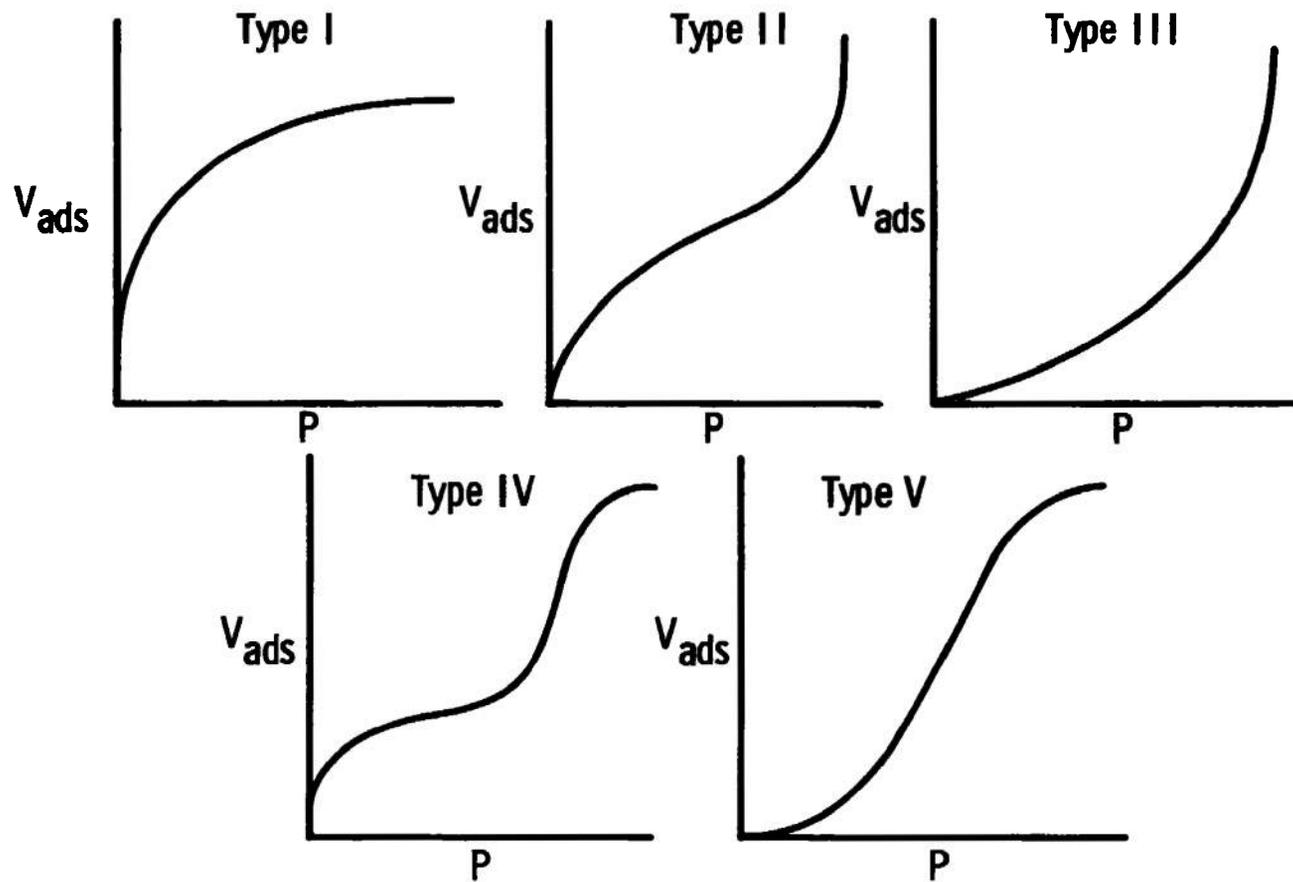


Fig. 5 Brunauer's Classification of Adsorption Isotherms

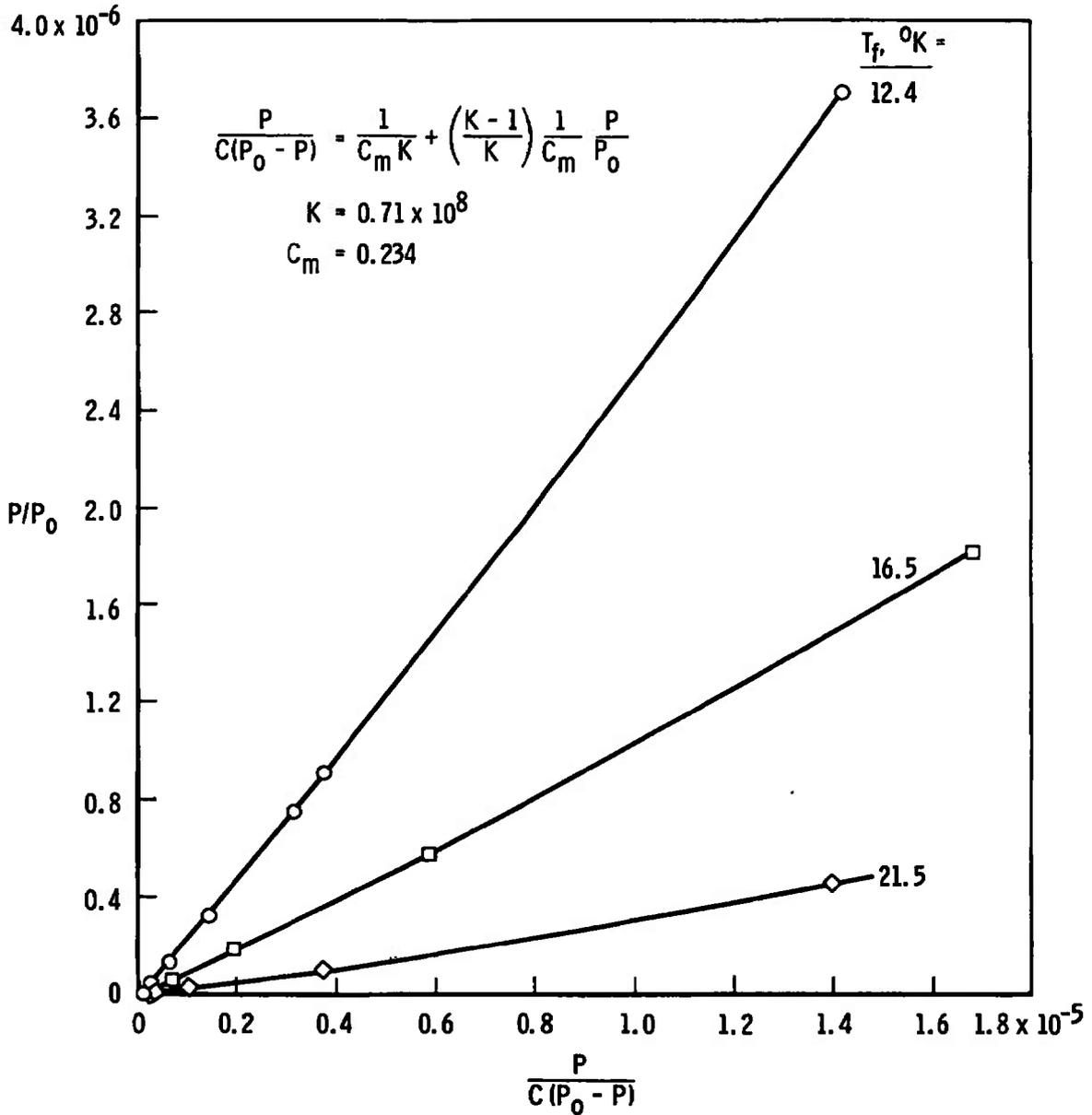


Fig. 6 Sorption Isotherms for Carbon Dioxide Frost Plotted in BET Coordinates

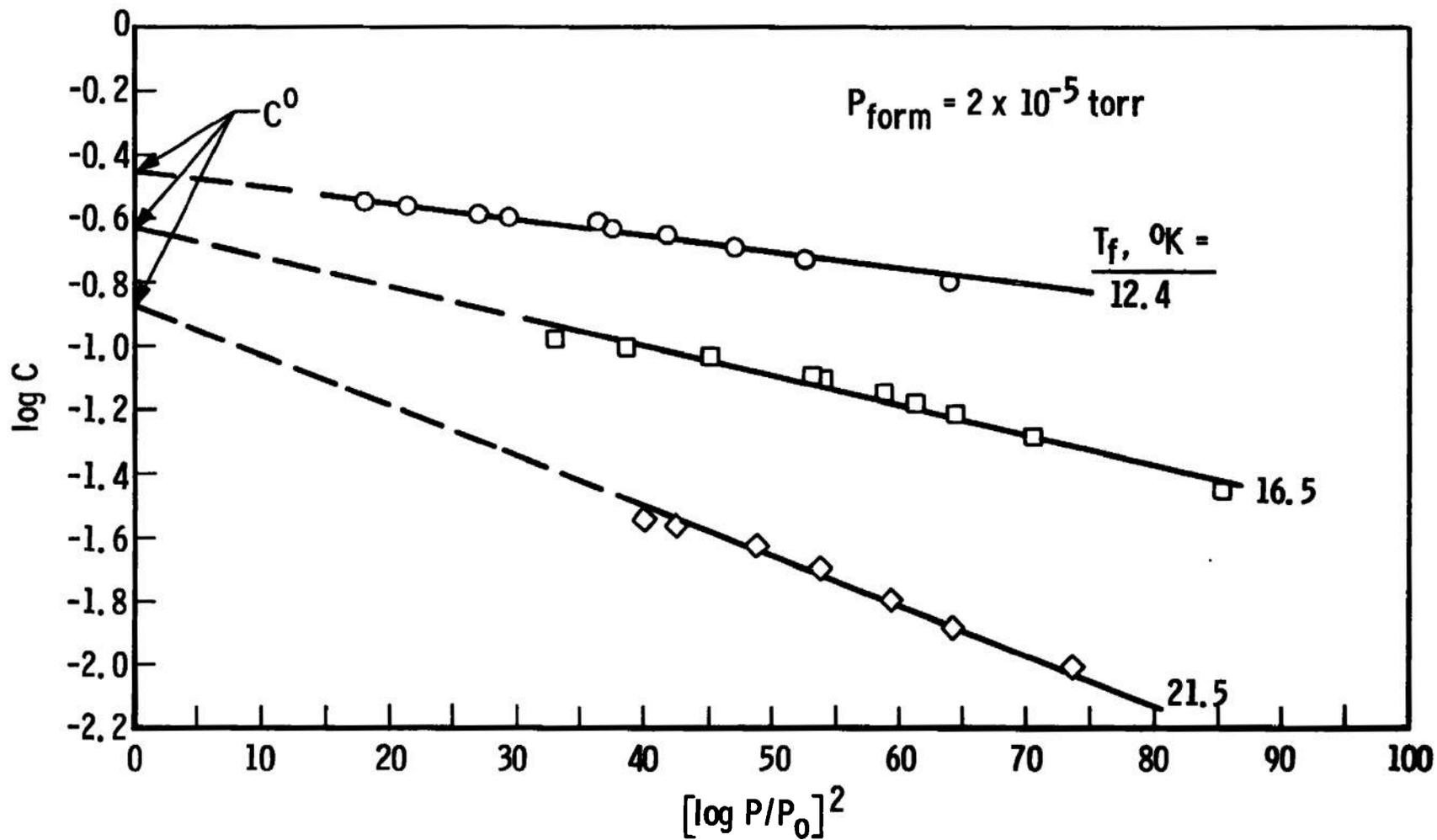


Fig. 7 Sorption Isotherm Data for Carbon Dioxide Frosts Formed at a Chamber Pressure of 2×10^{-5} torr Plotted in Dubinin-Radushkevich Coordinates

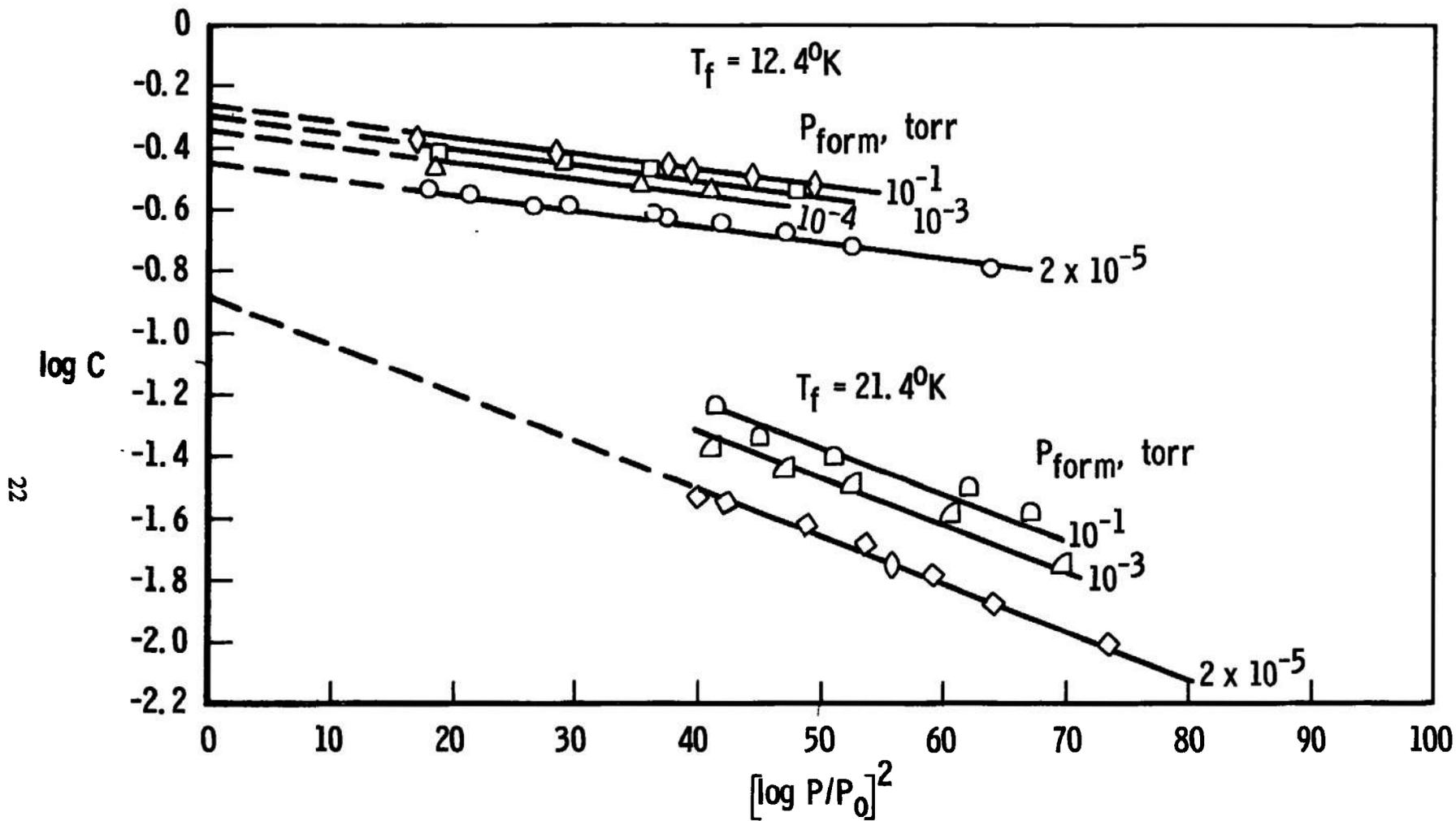


Fig. 8 Sorption Isotherms for Carbon Dioxide Frost Formed at Various Chamber Pressure Levels Plotted in Dubinin-Radushkevich Coordinate.

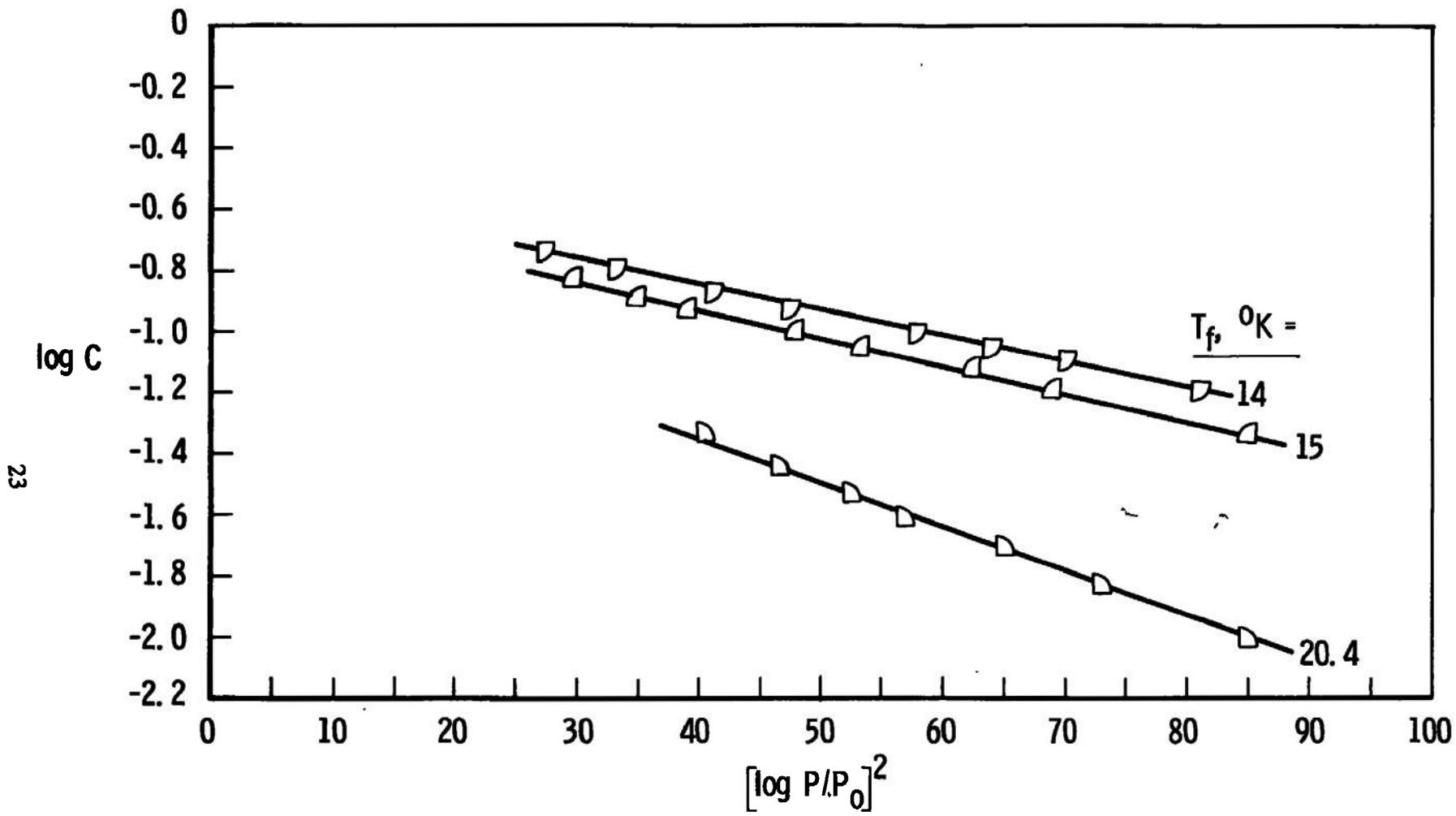


Fig. 9 Sorption Isotherms for Carbon Dioxide Frost from Ref. 2 Plotted in Dubinin-Radushkevich Coordinates

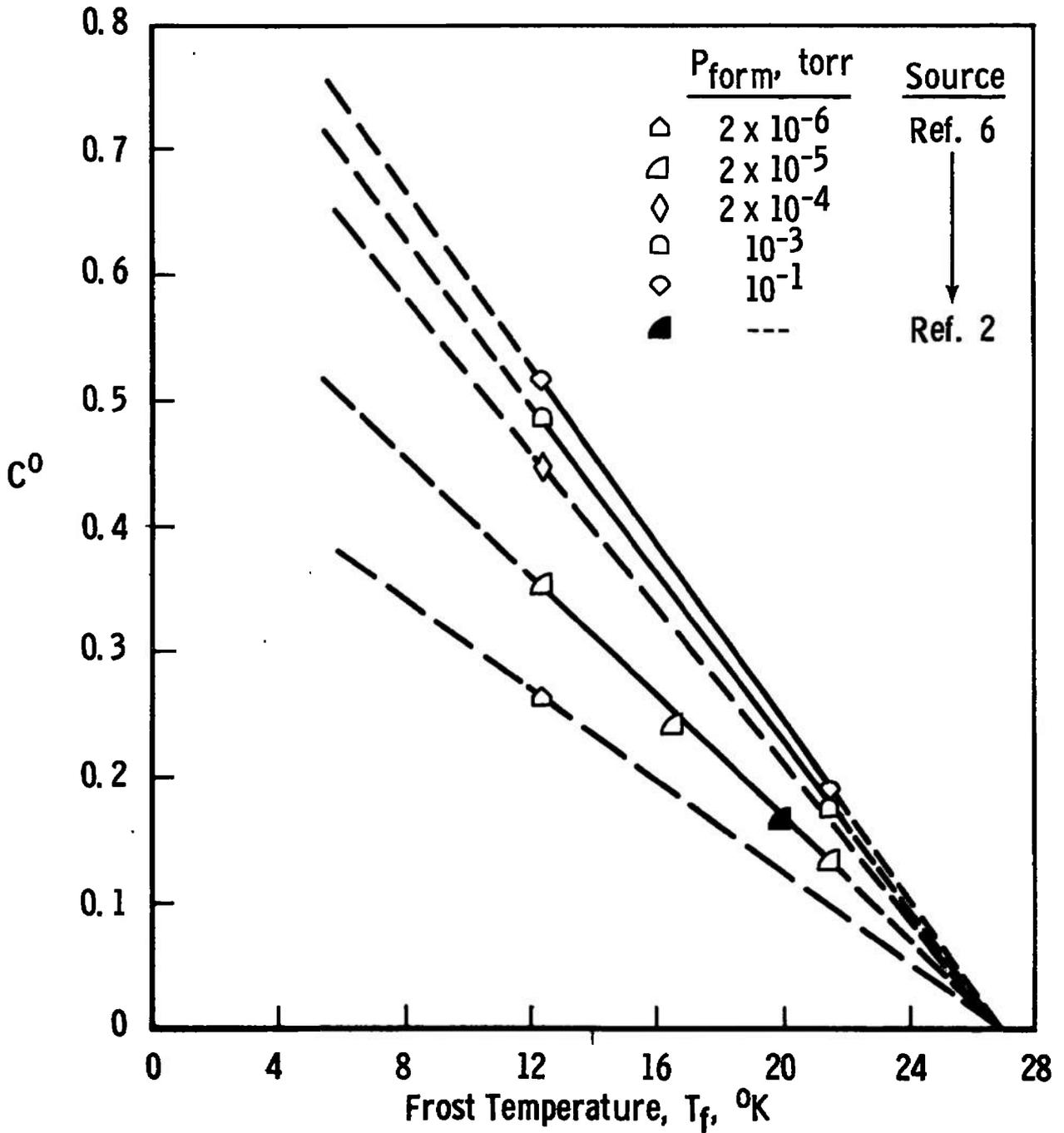


Fig. 10 Experimentally Determined Values of C°

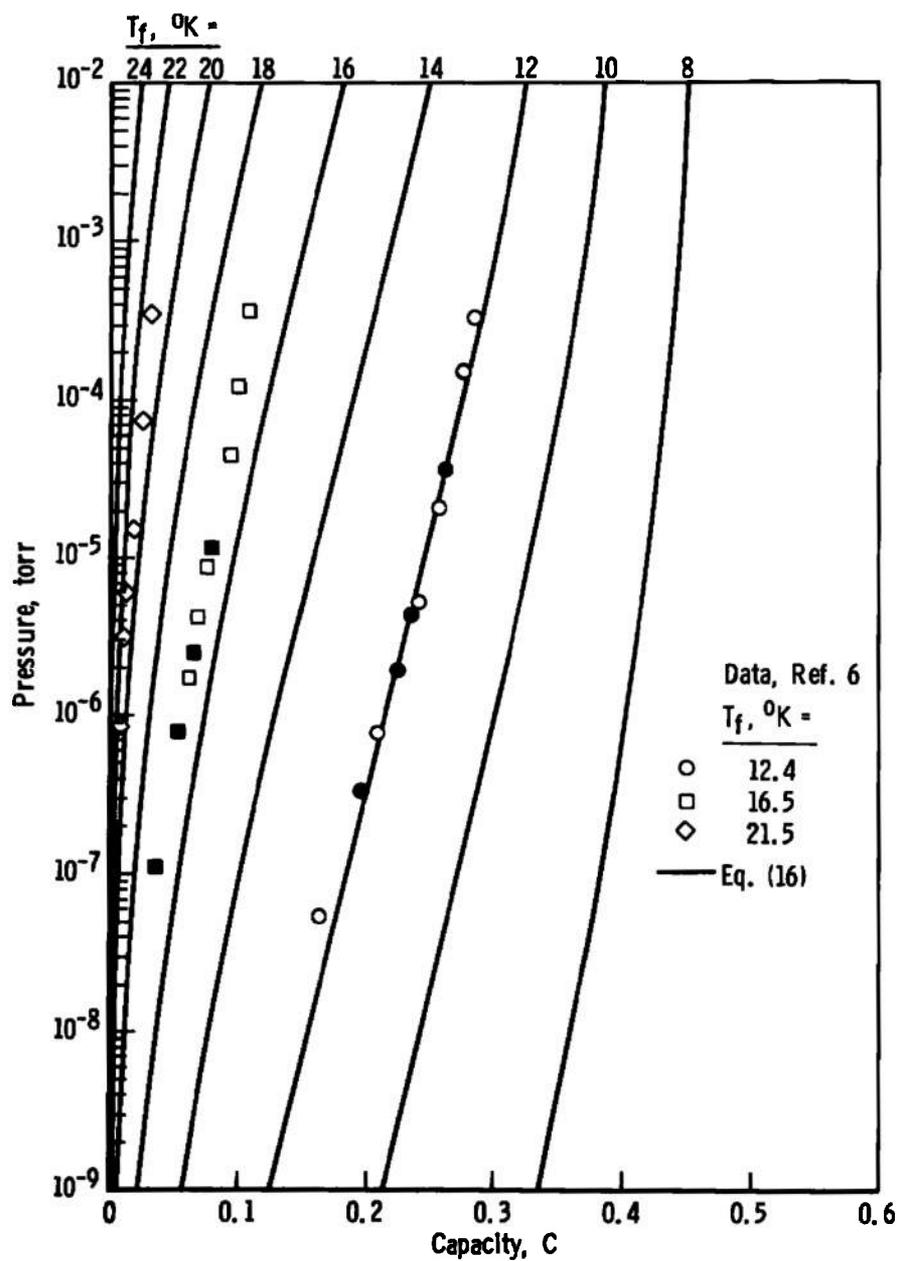
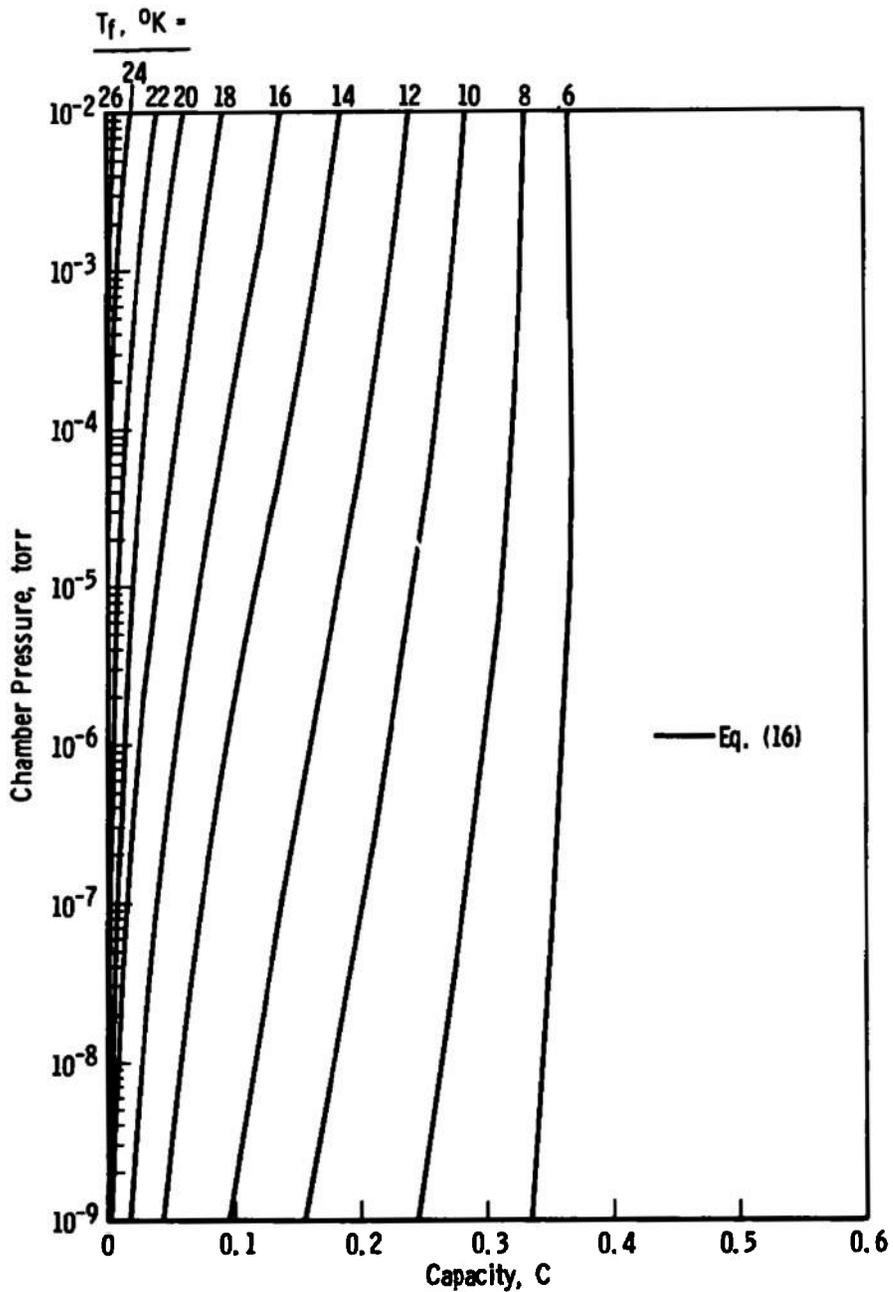
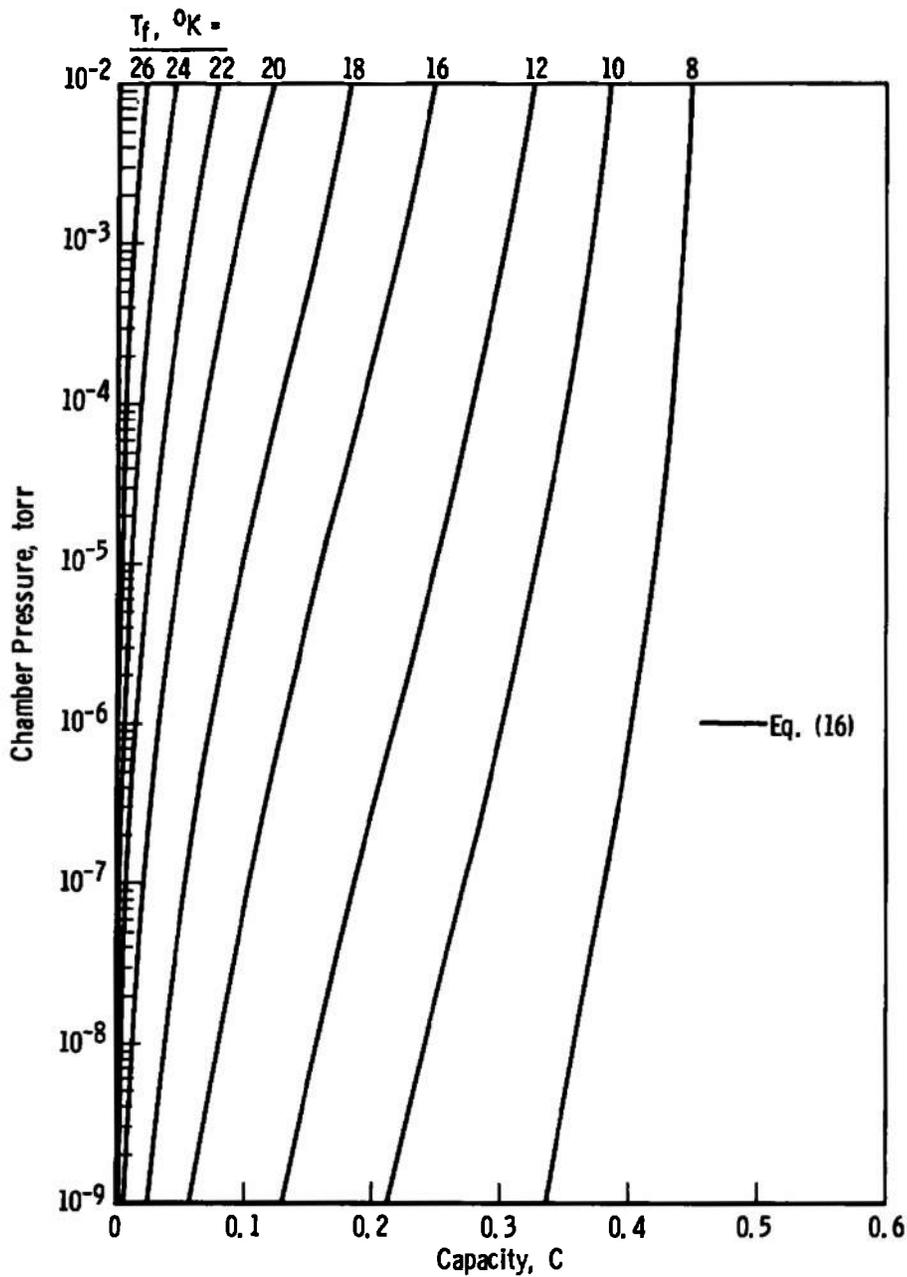


Fig. 11 Comparison of Calculated Isotherms from the Dubinin-Radushkevich Equation for Carbon Dioxide Frost Formed at a Pressure Level of 2×10^{-5} torr



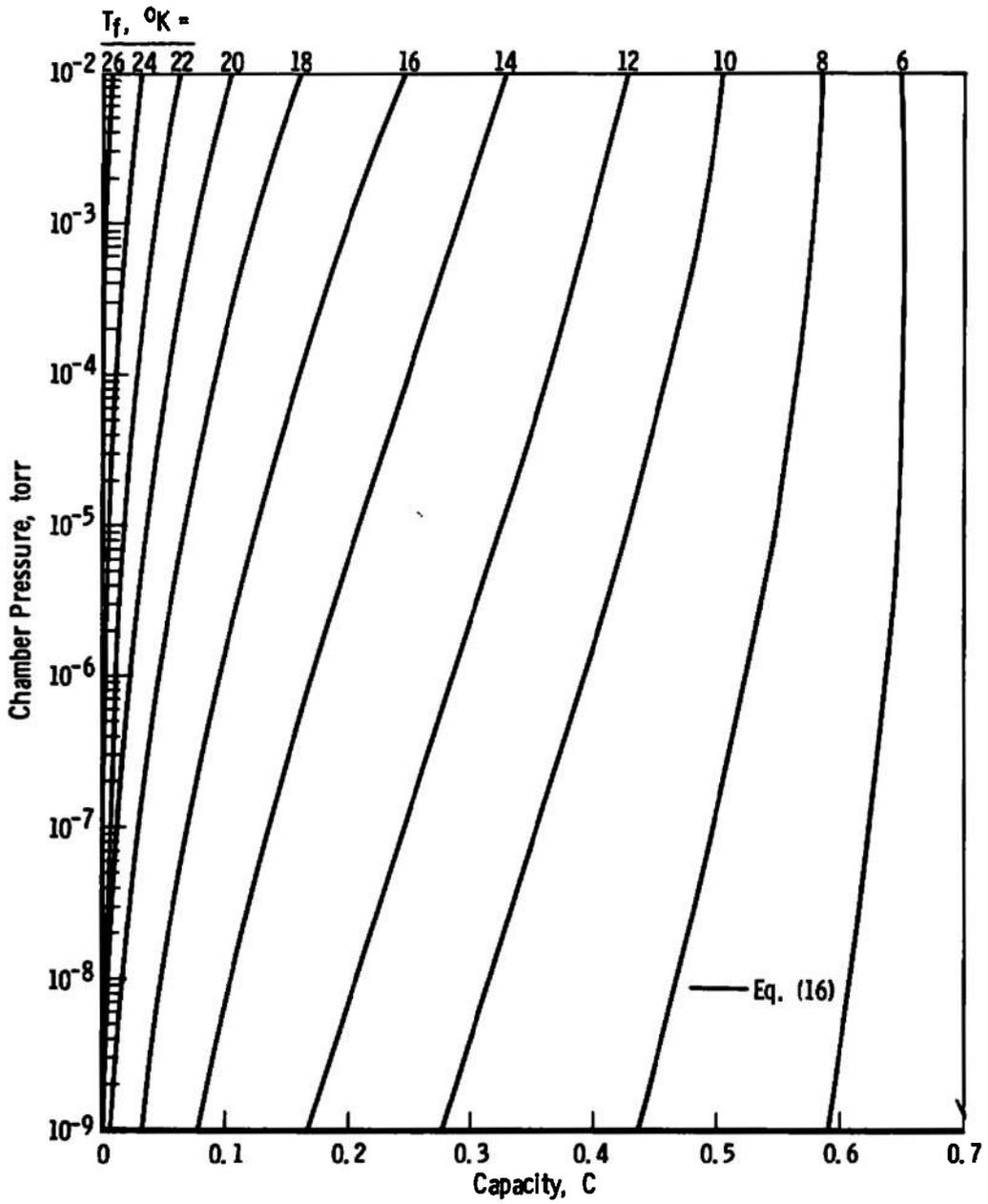
a. $P_{form} = 2 \times 10^{-6}$ torr

Fig. 12 Comparison of Calculated Isotherms for Dubinin-Radushkevich Equation for Carbon Dioxide Frost Formed at Various Pressure Levels



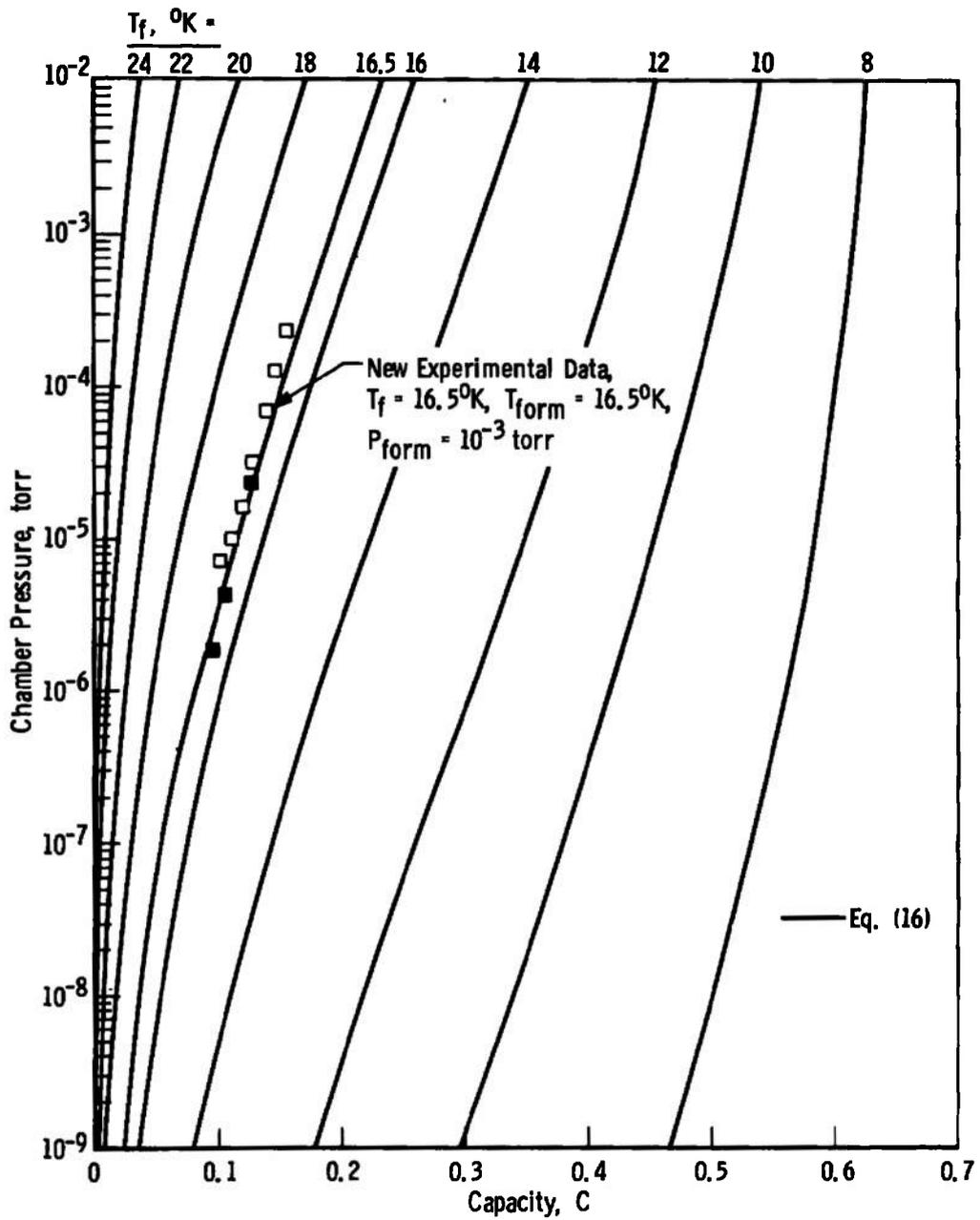
b. $P_{\text{form}} = 2 \times 10^{-5}$ torr

Fig. 12 Continued



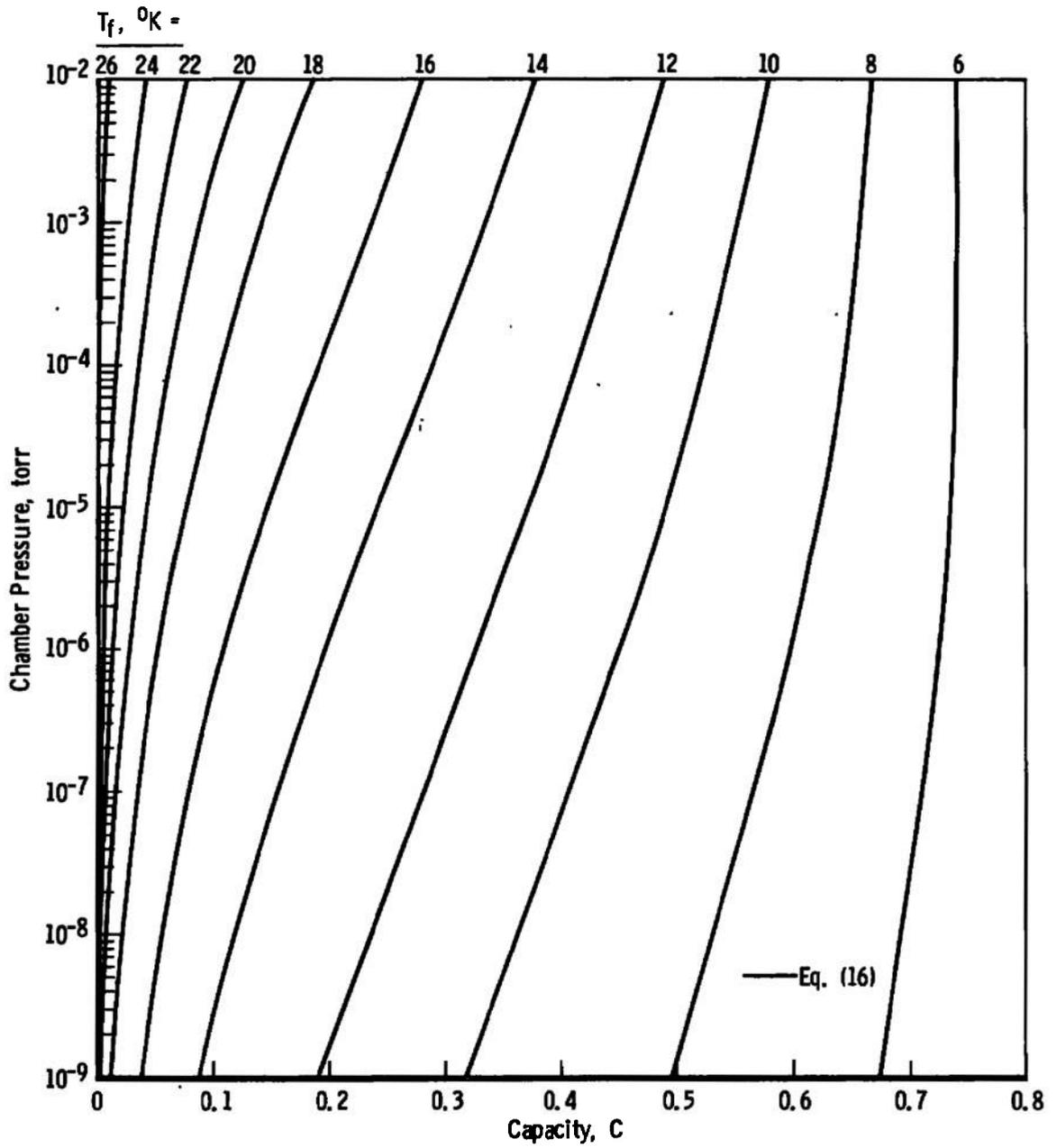
c. $P_{\text{form}} = 2 \times 10^{-4}$ torr

Fig. 12 Continued



d. $P_{\text{form}} = 1 \times 10^{-3}$ torr

Fig. 12 Continued



e. $P_{form} = 1 \times 10^{-1}$ torr
Fig. 12 Concluded

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Arnold Engineering Development Center ARO, Inc., Operating Contractor Arnold Air Force Station, Tennessee		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE SORPTION PUMPING OF HYDROGEN BY CRYODEPOSITS-PREDICTION OF SORPTION CAPACITY			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) April through September 1969 - Final Report			
5. AUTHOR(S) (First name, middle initial, last name) K. E. Tempelmeyer, ARO, Inc.			
6. REPORT DATE February 1970		7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 21
8a. CONTRACT OR GRANT NO. F40600-69-C-0001		8b. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-69-270	
b. PROJECT NO.			
c. Program Element 64719F		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) N/A	
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES Available in DDC		12. SPONSORING MILITARY ACTIVITY Arnold Engineering Development Center, Air Force Systems Command Arnold Air Force Station, Tenn.37389	
13. ABSTRACT The applicability of several existing adsorption theories for predicting the equilibrium isotherms for the sorption of hydrogen (H ₂) by carbon dioxide (CO ₂) cryodeposits has been examined in the pressure range from 10 ⁻⁸ to 10 ⁻³ torr. It is demonstrated that the H ₂ sorption capacity of CO ₂ frost cryosorbents at temperatures between 12 and 20°K may be accurately predicted by an equilibrium isotherm equation proposed by Dubinin and Radushkevich. This equation is then used to calculate families of sorption isotherms for CO ₂ frosts formed at various conditions and consequently having different structures. These results may be used to estimate the H ₂ capacity of cryosorption pumping systems which would employ CO ₂ frost as a cryosorbent.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
sorption pumping hydrogen capacity carbon dioxide frost						
2. Hydrogen -- Pumping						
3 Carbon dioxide						
4 Cryodeposits						
15-2						

AFSC
Arnold AFSS Test