EQUILIBRIUM PROPERTIES OF SUBMONOLAYER HE^4 FILMS

Thesis by

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ABSTRACT

Isosteres have been measured for submonolayer films of helium-four adsorbed on a sintered copper sponge precoated with each of the other noble gases. These measurements were carried out at temperatures between 3^{o}K and 4^{o}K, and at coverages between 0.5 and 1.0 monolayer; the pressures encountered were in the range from 10^{-7} Torr to 10^{-1} Torr. On the neon-coated substrate, the lower binding energy and higher lateral mobility made it feasible to take useful data at coverages as low as 0.025 monolayer. From the isosteres, information is derived about the partial molar entropy, entropy and heat capacity of the film.

It appears that the submonolayer film is a well-defined entity whose qualitative properties remain unchanged as the substrate precoating is varied. These include a transition into a highly ordered state as the coverage is increased, a total heat capacity which is not monotonic with coverage, and significant lateral mobility. The transition into the ordered state is initiated at higher coverage as the temperature is lowered, and this anomaly is discussed in terms of a model in which two dimensional crystalline patches are broken up by thermal fluctuations.

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INTRODUCTION

This research, a comparative survey of the properties of sub-monolayer films of helium-four adsorbed on various substrates, is descended from several diverse lines of prior investigation including studies of the saturated helium II film and of multilayer adsorbed helium films, the study of physical adsorption in general, and the more recent interest in adsorbed sub-monolayers as examples of two dimensional systems of matter.

The isotopes of helium--especially helium-four--have, in the bulk state, properties which render them truly unique among all known substances. It is only natural then that the properties of the adsorbed state of helium have long been the object of earnest, if somewhat uncoordinated, inquiry.

It is hoped that this and other recent studies mark the beginning of systematic exploration in an area where the experimental data sometimes seem lost in a sea of speculation.

CHAPTER I

BACKGROUND MATERIAL AND PREVIOUS RESULTS

1.1 Early studies of helium films

The saturated film of helium II, discovered by Rollin(1) in 1936, has a thickness on the order of a hundred atomic diameters and possesses the characteristic properties (excellent mass and heat transport) of superfluid helium.(2) Experiments have been performed by many investigators(3,4) to determine the effects of reducing the film thickness. These measurements of the unsaturated film were carried out using a wide variety of substrates.(5) It was generally found that the indicators of superfluidity such as the specific heat anomaly(6) and the onset of superfluid flow(7) moved to lower temperatures with decreasing film thickness, the former seeming to disappear altogether for thicknesses below a few layers.

Superfluidity has been associated with the Bose-Einstein condensation ever since this relationship was first proposed by London(8) in 1938. Since the Bose-Einstein condensation is not expected to take place (at non-zero temperatures) in two dimensions,(9) the above results may represent the gradual disappearance of this phenomenon as the properties of the film change continuously from those of a three dimensional system into those of a two dimensional system.

The question of collective behavior of any sort at submonolayer coverages does not seem to have been considered in these early studies because the film was believed to be solid. It had been predicted by Hill(10) that any film would become localized (solid) when the temperature became lower than about one-tenth of the barrier height between adsorption sites ($kT_{Loc} = Q_{barrier}/10 \simeq Q_{adsorption}/10$). This condition is generally met for adsorbed helium below 4.2°K, since adsorption energies are typically of the order of 100°K or more, as we shall see below. In the special case of adsorbed helium, there was a second reason for assuming the film to be solid at low coverages: In many of the earlier studies, for example that of Long and Meyer(11) or of Schaeffer *et al.*,(12) the data were interpreted as being representative of systems with extremely high densities of helium atoms in the first layer--densities comparable to that of solid three dimensional helium. It was well known that for bulk helium the λ-transition moves to lower temperatures as the density is increased beyond the normal liquid density, consequently attempts(13,14) were made to relate the observed data to this familiar effect.

Recent theoretical and experimental work has demonstrated that the first adsorbed layer is not anomalously dense, and that it is not necessarily immobile. This is discussed further in section 1.3 (below). The relevance of the early studies to the present work is limited by the fact that they extended down to a monolayer at best and by the fact that they were carried out with a bewildering variety of substrates(5) which seem to have been chosen primarily on the basis of surface-to-volume ratio without regard to surface uniformity.

1.2 Physical adsorption(15,16)

Whenever a gas is in contact with a surface, the concentration of the gas atoms is greater than average in the vicinity of the surface. This is the phenomenon of adsorption; it is due to the existence of attractive forces between the atoms in the surface and the atoms of the gas. Physical adsorption must be distinguished from other processes such as absorption (in which the gas penetrates into the body of the substrate) and chemisorption (in which a chemical reaction takes place between the adsorbate and the substrate). However some or all of these processes may take place simultaneously in a system and the lines of demarcation between them are not always clear.

Adsorption in general is a phenomenon which may cover a very wide range of physical parameters and chemical substances--sticking times from microseconds to centuries; pressures from microtorrs to kilobars; substrates from solid hydrogen to white hot tungsten; adsorbates from He^3 to complex hydrocarbons; etc. The more important applications of this phenomenon are in such areas as purification of chemicals with activated charcoal, dying of fabrics with complex dyes, etc. However, since our main purpose is to investigate the fundamental properties of matter we shall be concerned with the simplest possible systems of adsorbate and substrate--helium and the other noble gases.

An adsorbed system has an area A within which the atoms may exert a spreading pressure ϕ; the spreading pressure is a function of the number N of atoms adsorbed. In any case of practical importance the adsorbed system is in contact with, and hopefully in equilibrium with, a bulk system of gas having a pressure P (not to be confused with ϕ); consequently N is smaller than the total number of atoms within the combined system unless P is vanishingly small. N is frequently expressed in terms of the "monolayer capacity" N_m which will be discussed later; $N/N_m \equiv \theta$.

The study of an adsorbing system frequently begins with the measurement of P as a function of N at constant temperature. If a suitable surface is placed within a volume and evacuated, it is expected that P and N will both be zero. Subsequently if gas is admitted to the volume and the equilibrium pressure measured, it will generally be found that P increases monotonically with N. If, as is often the case, the isotherm is being carried out at a temperature below the critical temperature of the bulk adsorbate, then P will approach (or even reach) the vapor pressure P_0, of the bulk liquid (or solid) and stop rising.

From a family of adsorption isotherms (N as a function of P at constant T) one can derive isosteres (P as a function of T at constant N).

Isotherms and related measurements are used to determine parameters of the system such as the monolayer capacity and the energy of adsorption as well as to help provide insight into the nature and behavior of the adsorbed film. The atoms of a submonolayer film may have lateral mobility across the surface, or they may be localized in fairly definite adsorption sites. Even though the solid crystalline substrates with which we are concerned presumably have a periodic network of attractive sites, it does not necessarily follow that the film will be immobile. The adsorbate atoms may have enough energy at higher temperatures to surmount the potential barriers between sites, and there is the possibility of quantum mechanical tunneling through the barriers at any temperature.(17,18)

Somewhat related is the question of whether the film can be characterized analogously to a bulk system as a (two dimensional) solid, liquid, or gas; and what phase transitions are possible between these cases. One possible phase of a submonolayer film, especially at higher temperatures, would be that of a gas-like phase in which the atoms were uniformly distributed across the substrate; but it might also be possible to have the formation of liquid- or solid-like patches with higher than average density.

It has been shown(19) that crystalline solids of arbitrarily large size cannot exist in two dimensions. However the film could exist in a polycrystalline form; furthermore the regularity of the substrate might impose a regular structure on the film.(20) Liquids (or amorphous solids if there is tunneling) would not ordinarily be expected to persist down to absolute zero, but one can of course not be too sure in the case of helium. In fact the very features--low mass, large zero point energy, small mutual interactions, etc.--which make helium useful for studying the physics of adsorption may also complicate any efforts to categorize the film as a single one of these phases. In the bulk state, liquid helium has an extremely low density and it undergoes a peculiar transition characteristic of Bose gases. At lower temperatures it acquires a relatively small entropy as well as a specific heat which varies as T^3--characteristic of a Debye solid--retaining all the while the outward, macroscopic appearance of a liquid.

Phase transitions, if they occur, between these states may manifest themselves in adsorption isotherms as discontinuities. But inhomogeneities in the substrate may smear out these steps until they are no longer recognizable; this is discussed further in section 1.3.

The isotherms with which we are concerned in this discussion are of two distinct types. First there are the preliminary isotherms of the noble gases other than helium, adsorbed on bare copper; in this case we require only limited information--the monolayer capacity. Secondly we have the isotherms of helium on precoated copper; here we wish to derive as much information as possible about the system. We shall now summarize briefly some of the older, semiqualitative theories of adsorption which, although they are quite useless for discussing the detailed behavior of helium, have some value for obtaining limited information about various isotherms and for comparing the properties of adsorbing systems fabricated by different investigators.

If the coverage is very low then a possible isotherm would be: $P \propto \theta$; i.e. the pressure might rise linearly with the coverage. This simple case is not adequate for the system we are dealing with.

A more realistic model for some systems might be the following: The substrate has adsorption sites which can accommodate only one atom, the adsorption energy is the same for each site, and the adsorbate atoms do not interact with one another. From these assumptions it is possible to derive an equation called Langmuir's Isotherm:(21)

$$N = N_m \frac{bP}{1 + bP}$$

N_m is the number of atoms required to fill all of the sites, and b is related to the energy of adsorption. It should be noted that this equation breaks down near one monolayer since $P \longrightarrow \infty$ as $N \longrightarrow N_m$. Furthermore it is possible for a system to yield an isotherm which follows this form closely, even though the system does not obey the model--i.e. there are other, more complicated models which yield similar behavior.(22)

The Langmuir isotherm is useful only below one monolayer; however it is quite possible that an adsorption process might proceed to form two or more layers. This is a much more complicated process. In general if an atom is adsorbed on a site on top of a pre-existing atom, the binding energy will be less than in the first layer; however unless the difference in energy is very pronounced, the second layer may start to form before the first is completed. This difficulty is accentuated if the substrate contains sites of various adsorption strengths. Furthermore, by the time second and higher layers have started to form, the adsorbate atoms will certainly be quite close together, and assumptions about a lack of interaction become even more tenuous.

In spite of these difficulties, there exists a fairly simple "theory" of multilayer adsorption which yields the so called BET equation. The assumptions underlying the BET model are the same as those of the Langmuir with the following important exception: When a gas atom strikes a site containing a previously adsorbed atom, it is not necessarily reflected, instead it may be adsorbed, although generally with a lower adsorption energy than that of the first layer. Third, fourth, etc, atoms may also be adsorbed with this same energy, which is generally assumed to be equal to the bulk latent heat of the adsorbate. The following equation results:(23)

$$\frac{P/q}{N(1 - P/q)} = \frac{1}{N_m C} + \left[\frac{C - 1}{N_m C}\right] \cdot \left(P/q\right) .$$

This equation between P and N contains three parameters:

N_m - the monolayer capacity

C - related to the two heats of adsorption

q - frequently (but not always) identified with the bulk vapor pressure, P_0.

The general forms of the Langmuir and BET isotherms are shown in figures (1-1) and (1-2) on a linear scale.

Since the BET equation contains three adjustable parameters, it is quite flexible and can be made to fit a large variety of experimental isotherms over at least a portion of their range. This of course detracts from its usefulness as a tool for analyzing the detailed behavior of an adsorbing system, just as in the case of the Langmuir isotherm. However, it is generally used to get a rough picture of the behavior of a system and, in particular, for arriving at a numerical value for the monolayer capacity, N_m.

The monolayer capacity is a clear and unambiguous quantity only for those models which are unrealistically simple: e.g. the substrate consisting of a mathematical plane and the adsorbate consisting of non-interacting hard spheres; or the substrate consisting of a lattice of very deep and localized adsorption sites (potential wells) all having exactly the same depth. As soon as one considers, for example, the case where the adsorption sites do not all produce the same adsorption energy for an adsorbate atom, then the concept of monolayer capacity begins to lose validity, since it is quite possible to have

Figure (1-1)

General shape of an isotherm
obeying Langmuir's equation

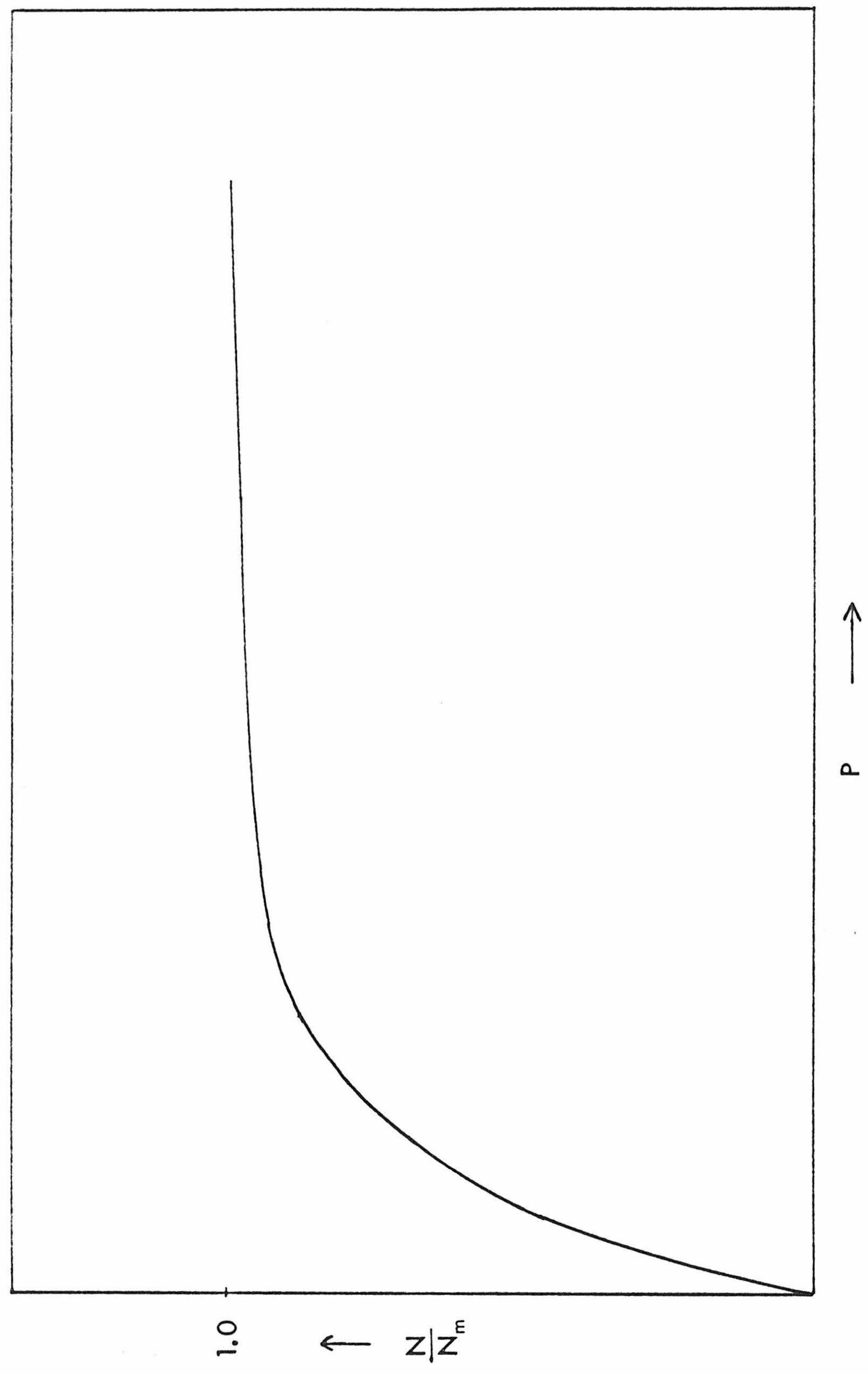
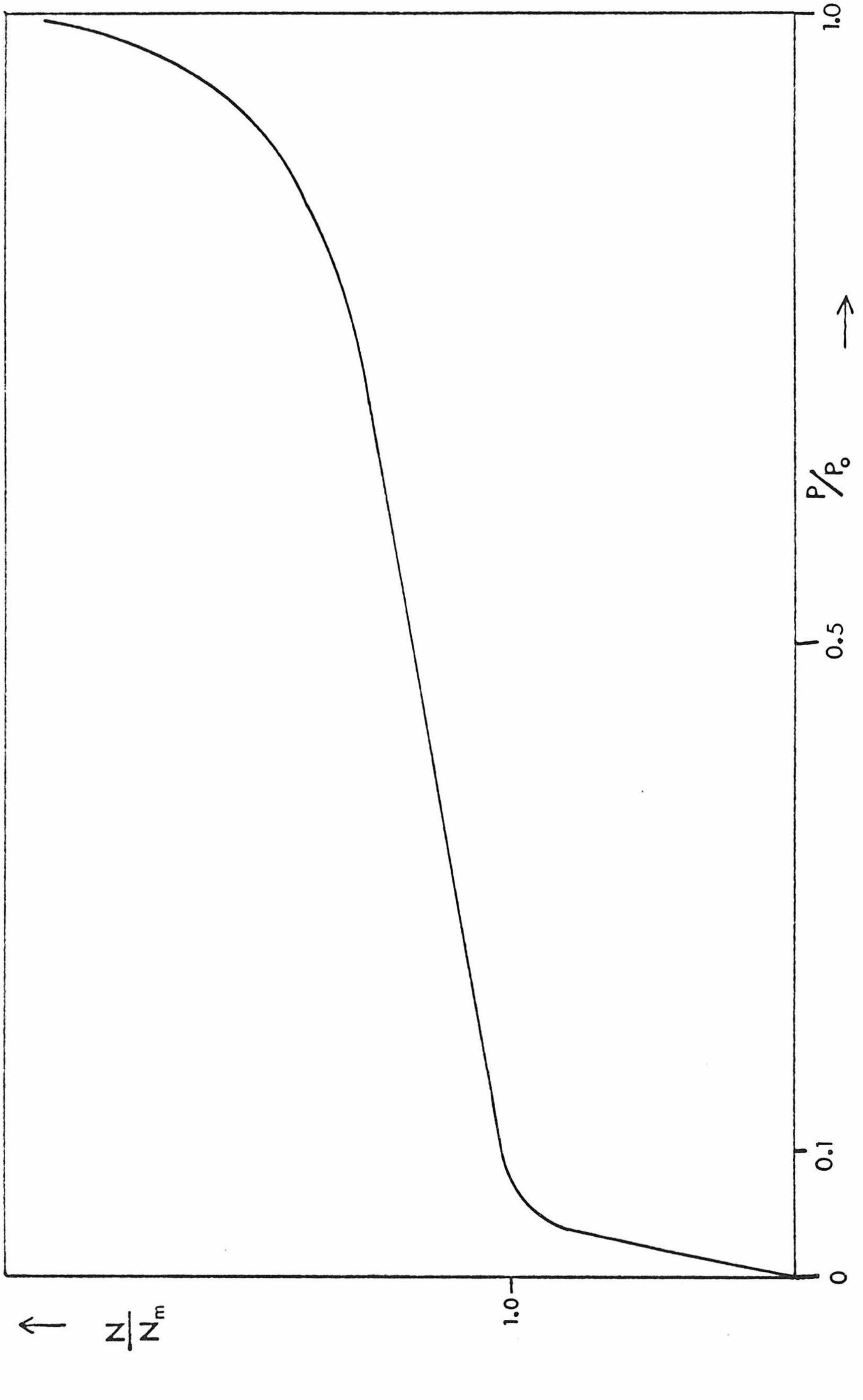

1.0
Z/Z_m ←
P →

Figure (1-2)

General shape of an isotherm
obeying the BET equation


P/P_o →
0
0.1
0.5
1.0
← Z/Z_m
1.0

two or more adsorbate atoms occupying one site, while other sites are still vacant. Furthermore, interactions between adsorbate atoms may also act to degrade the concept of a clearly defined monolayer.

Nevertheless, many of the systems which we will be concerned with in this paper do exhibit properties which can be interpreted reasonably well by assuming the existence of a monolayer capacity. It will be noted in figure (1-2) that, starting from the origin, the pressure rises very slowly as N is increased, up to a point, and then begins to rise quite rapidly in a linear fashion. Intuitively, it seems quite reasonable that this knee of the curve should occur when the atoms can no longer fall into the first layer with its large adsorption energy and must instead begin forming a second layer where they are not so tightly held to the surface. The BET equation provides a reproducible method of locating the coverage which represents one monolayer,(24) the values which it gives are generally considered to be accurate to about 10%. Frequently, $N = N_m$ when $P/P_0 \simeq 0.10$; however helium is an important exception to this rule.

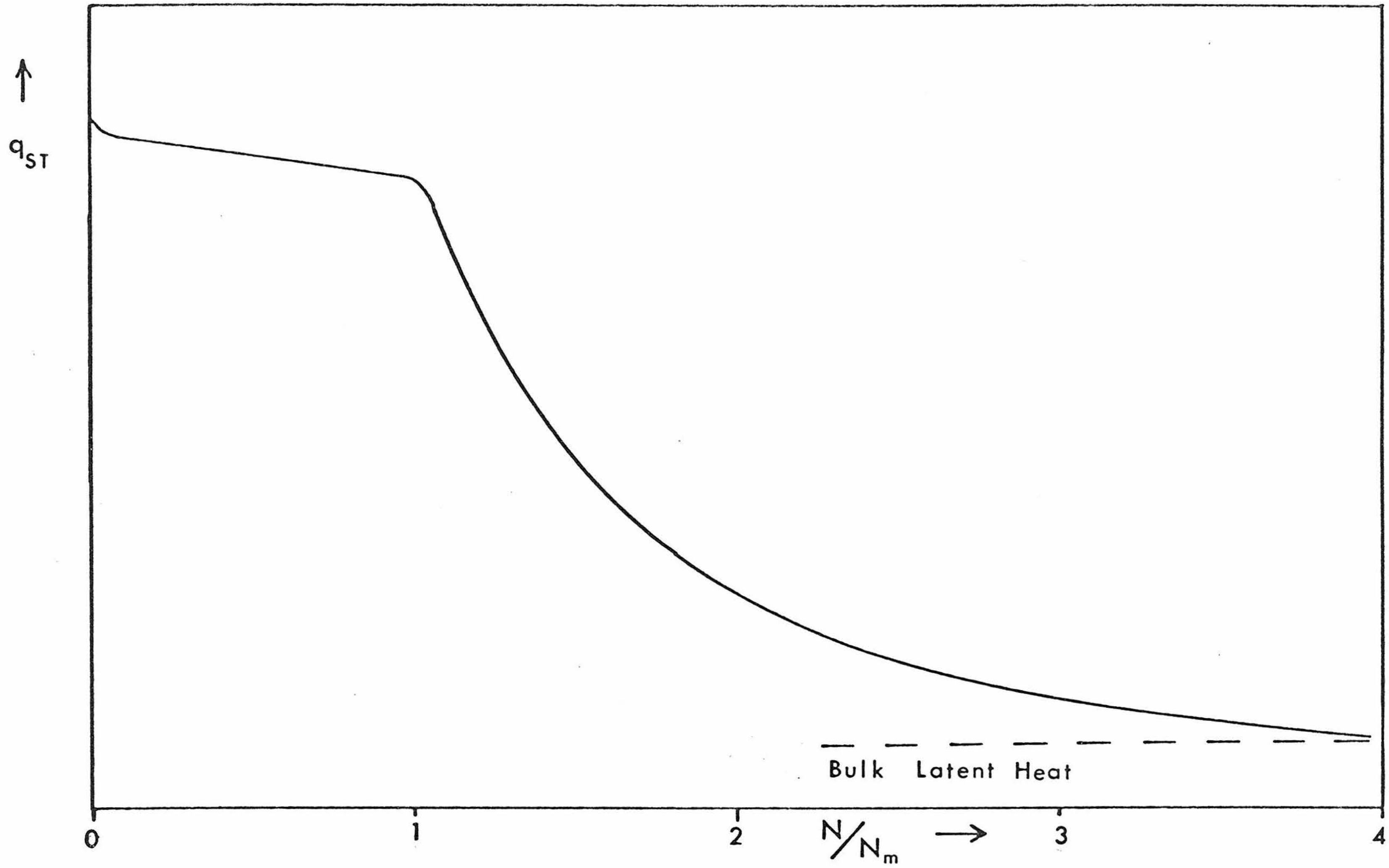
As mentioned earlier, it is also possible to measure P as a function of T at constant N; such plots are called isosteres. There are often experimental difficulties encountered in trying to measure isosteres directly, rather than inferring them from a family of isotherms, but happily these problems are minimized in the case of submonolayers of helium. Isosteres are often plotted as Ln(P) as a function of T^{-1}; in this form the slope, dLn(P)/d(1/T), of the isostere is equal to the so-called isosteric heat of adsorption q_{st}/R, (expressed in degrees Kelvin). A subsequent plot of q_{st}/R as a function of N can give another indication of N_m as shown, schematically, in figure (1-3); however such a plot is not backed up by a convenient model such as BET, and hence it is not often used to get a reproducible monolayer capacity, unless the break is exceptionally sharp.

There are other measurements which can be performed on adsorbed films with thermal techniques, including: direct calorimetric measurement of q_{st}, the rate of permeation through a porous medium, and direct measurements of the heat capacity of the adsorbed atoms.

Figure (1-3)

The behavior of the isosteric heat of adsorption as a function of coverage

(The actual systems discussed in this work do not display such a sharp transition.)


q_{ST}
Bulk Latent Heat
0
1
2
3
4
N/N_m

1.3 Recent experimental and theoretical studies of adsorbed helium films

There has been recent interest(25-29) in submomolayer films of adsorbed helium as physical models on which to test various theories of the behavior of matter in two dimensions. A collection of atoms in two dimensions may be approximated by a submonolayer adsorbed film; however it must be recognized that this is only an approximation. There are several ways in which the film fails to satisfy the requirements of mathematical two dimensionality. First of all, the adsorbed atoms are three dimensional so that no adsorbed film can ever be truly two dimensional. Secondly substrates in the form of homogeneous mathematical planes do not exist in the real world--even the face of a crystal is a grid of potential wells as seen by an adsorbate atom. Finally, in any case of practical importance, the film is always in contact with, and interchanging particles with, its three dimensional vapor.

In spite of these objections, it has been found that adsorbed films do in fact exhibit at least some of the properties which would be expected of two dimensional systems--for example there is the disappearance of the λ-transition mentioned earlier.

More recently it has been discovered(30,31) that submonolayer helium films (at least under some conditions) exhibit the specific heat temperature dependence which is characteristic of two dimensional Debye solids at low temperatures: the specific heat, $C/N \propto T^2$.

It was demonstrated by Meyer(32) and by Hobson(33) that helium monolayers are completed while the pressure of the three dimensional gas in equilibrium with them is still extremely low. This solved the question of the alleged high densities of the first layer seen by earlier investigators who were actually observing the completion of the third or fourth layer. This fact was confirmed by McCormick, et al.(30) who also measured the specific heat of submonolayer helium films and interpreted their data to imply mobility of the adsorbate atoms since their measured specific heats were neither independent of coverage nor exponential in temperature, both of which are required by an immobile, non-interacting model.

It is not clear whether this observed mobility is unique to the specific system used or whether it is a general property of adsorbed helium films caused by the tunneling mentioned earlier. There can be little doubt that quantum mechanical tunneling occurs quite generally in adsorbed systems, but the crucial question is whether or not it is a sufficiently rapid process to influence the outcome of a practical experiment. The tunneling time is extremely dependent on the size and shape of the barriers, relatively small changes can change the tunneling time by many orders of magnitude.(34) The present experiment is sensitive to the existence of mobility in the film in two qualitative ways: Non-linearity of the isotherms at exceedingly rarefied coverages may be an indication that the adsorbate atoms are interacting with one another via their lateral mobility. Secondly a mobile submonolayer may reach equilibrium faster than one which must depend on gas pressure-driven diffusion.(35)

It would seem reasonable that first-order phase transitions should make their presence known very explicitly in adsorption isotherms by a vertical step in the isotherm. Such transitions have been predicted(36,37) for films in general, and have been observed in the isotherms of many substances.(38) There is no a priori reason why such transitions should not occur in helium submonolayers and, in fact, previous results have been interpreted as indicative of such transitions.(39) It may be due only to a lack of experimental data that they have not been observed in helium isotherm data; however there is also the problem of surface non-uniformity. If the character of the substrate varies in a continuous manner, then the transition may be smeared out over a range of coverages and appear as a less noticeable feature on the isotherm. It has recently been pointed out by Stewart and Dash(31) that substrates of the type with which we are concerned--copper, plated with noble gases--may consist of two or more discrete macroscopic areas with significantly different adsorption characteristics. This makes it possible to have several phases coexisting in the system at one time. Finally it should be noted that higher order transitions are also possible in films;(40) and that even complete localization does not necessarily rule out the possibility of phase transitions since the atoms may still move from one surface location to another by way of the gas phase.(10,41,42)

Hence at the beginning of the present research the 4.2°K isotherm of helium on argon-coated copper was known down to one monolayer(30) but nothing was known experimentally about the behavior of the isotherms at lower coverages and temperatures.(43) Furthermore there had been no comparative studies (in this regime) of the effects of changing the nature of the substrate preplating. Thermal measurements in this region whether they be adsorption isotherms, heat capacities, or whatever, are fairly difficult and extremely time consuming; consequently the purpose of the present research was to survey the behavior on a consistently chosen set of substrates over the widest practical range of coverage and temperature to provide the basis for future studies on those substrates which seemed to be the most interesting. Sintered copper powder, precoated with a noble gas, has a number of properties (discussed in chapter II) which make it a desirable substrate material. For this reason argon-coated copper has been used in several recent studies.(30,31,44) The effect of the substrate upon the properties of the helium film is one of many areas in which experimental data is lacking; consequently in the present experiment each of the four common noble gases (neon, argon, krypton, and xenon) was used as a precoating. This permitted the substrate to be varied in a controlled and somewhat continuous fashion.

1.4 Thermodynamic relationships in two dimensions

In principle, the measurements which we are talking about in this research (the pressure P as a function of the coverage N and the temperature T) would be useful for deriving quite a bit of diverse quantitative information about the film if they were sufficiently accurate and detailed and if they extended (or could be extrapolated) to zero coverage. It will turn out that this is not possible at least in the present experiment, and we will often have to be satisfied with qualitative information.

We will now show how Ø as well as the total entropy and total heat capacity (S and C) and their molar couterparts can, in principle, be derived from our experimental data.(45) Since Ø and A behave analogously to P and V, we can write for the energy of the film:

$$U = U(S, V, A, N)$$

whence:

$$dU = TdS - PdV - \left.\frac{\partial U}{\partial A}\right|_{SVN} dA + \mu dN,$$

making the reasonable (in the case of helium) assumption that the interaction between substrate atoms is much stronger than that between substrate and adsorbate so that the number of sites is not a function of the amount adsorbed; i.e. that A and N are independent.

Ø is defined analogously to P:

$$P \equiv - \left.\frac{\partial U}{\partial V}\right|_{SAN} \qquad \phi \equiv - \left.\frac{\partial U}{\partial A}\right|_{SVN}$$

so that:

$$dU = TdS - PdV - \phi dA + \mu dN. \qquad (1\text{-}1)$$

It is possible to define a Gibbs Free Energy in more than one way for a film, due to the extra variables, however for our purpose it is advantageous to choose:

$$G' = G'(T,P,A,N) = U + PV - TS$$

so that

$$dG' = -SdT + VdP - \phi dA + \mu dN.$$

Since the chemical potential of the film, μ, is equal to $(\partial G'/\partial N)_{P,T,A}$ we have:

$$d\mu = - \left.\frac{\partial S}{\partial N}\right|_{PTA} dT + \left.\frac{\partial V}{\partial N}\right|_{PTA} dP - \left.\frac{\partial \phi}{\partial N}\right|_{PTA} dA + \left.\frac{\partial \mu}{\partial N}\right|_{PTA} dN .$$

For a fixed surface area, an isostere implies $dN = 0 = dA$ which reduces the expression for $d\mu$ to:

$$d\mu = - \left.\frac{\partial S}{\partial N}\right|_{PTA} dT + \left.\frac{\partial V}{\partial N}\right|_{PTA} dP . \qquad (1\text{-}2)$$

In the case of the un-adsorbed gas surrounding the film, we can write:

$$d\mu_g = -\frac{S_g}{N_g}\,dT_g + \frac{V_g}{N_g}\,dP_g.$$

If the two systems, film and gas are in thermodynamic equilibrium:

$$d\mu = d\mu_g \qquad \text{(i)}$$

$$T = T_g \qquad \text{(ii)}$$

$$P = P_g \qquad \text{(iii)}$$

$$V \ll V_g \qquad \text{(iv)}$$

$$V/N \ll V_g/N_g \qquad \text{(v)}$$

The first two of these relationships are obvious, however the others require further explanation. (iv) and (v) will be considered together:

These two inequalities are nearly always assumed to be true for adsorbed systems, however we will verify numerically that they are satisfied for the conditions of interest in the apparatus used in the present experiment.

In the present apparatus $V_g \simeq 50$ cm^3. V is harder to estimate but the area of the surface is $A \simeq 10^6$ cm^2 while the thickness of the film is $t \simeq 1$ atomic diameter (for a monolayer film) $\simeq 3$ Å(46) $= 3 \times 10^{-8}$cm. If $V = At$, we have: $V \simeq .03$ cm$^3 \ll 50$ cm^3.

Or we may consider that a full monolayer of helium contains $\simeq$ 20 STP $cm^3 \simeq .001$ mole $\simeq .004$ gm. If these atoms were in bulk liquid form they would occupy a volume $V \simeq .004\ gm/(.2\ gm/cm^3) = .02\ cm^3 \ll 50 cm^3$. Furthermore, the molar volume of the film, $V/N \simeq .03\ cm^3/.001$ mole $= 30\ cm^3$/mole; whereas the molar volume of the gas at, say $T = 4^oK$ and $P = .076$ Torr, is given by:

$$\frac{V_g}{N_g} = \frac{RT}{P} = \frac{(.0821\ \text{liter}\cdot\text{atm/mole}^oK)(4^oK)}{10^{-4}\ \text{atm}}$$

$$\frac{V_g}{N_g} \simeq 3000\ \text{liter/mole} \quad = \quad 3 \times 10^6\ cm^3/\text{mole}$$

$$\gg 30\ cm^3/\text{mole}$$

We make the assumption that the "volume" of the film for sub-monolayer coverages is proportional to the coverage.

Relation (iii) is less obvious; in fact if our system contained an additional (hypothetical) non-adsorbing component then this relationship would not even be true since the pressures referred to are total rather than partial pressures.

In fact, the functions defined in the literature(45) such as $(\partial S/\partial N)\big|_{PTA}$ must be carefully considered since, in the absence of such a non-adsorbing gas, P cannot properly be considered to be an independent variable--for a given T and A, it must vary with N. It can be shown however,(47) that the dependence of P on N and T introduces only small errors into $(\partial S/\partial N)$; multiplicative factors on the order of: $1 + 1/V_g\left[V + A(\partial \phi/\partial P)\big|_{NT} \right]$.

$V \ll V_g$ as usual, but we are left with the term $(A/V_g)(\partial \phi/\partial P)\big|_{NT}$. In the limit of very thick films, this term may not be negligible, however we are concerned here with films of monolayer thickness or less and the derivative does not lend itself to either experimental or theoretical measurement. Consequently we shall follow what seems to be the custom of previous authors(48) and assume that $\partial \phi/\partial P \simeq 0$. It does seem intuitively reasonable that the forces due to P_g should not be transmitted into the plane of the film (to affect ϕ) in films whose thickness has been assumed to be negligible.

We can now write:

$$d\mu = d\mu_g$$

$$-\left.\frac{\partial S}{\partial N}\right|_{PTA} dT + \left.\frac{\partial V}{\partial N}\right|_{PTA} dP = -\frac{S_g}{N_g}\,dT + \frac{V_g}{N_g}\,dP$$

$$\left[\frac{S_g}{N_g} - \left.\frac{\partial S}{\partial N}\right|_{PTA}\right] dT = \left[\frac{V_g}{N_g} - \left.\frac{\partial V}{\partial N}\right|_{PTA}\right] dP.$$

If, as previously assumed, the effective volume of the film is proportional to the coverage, then we have: $\partial V/\partial N = V/N \ll V_g/N$; and we can write:

$$\left.\frac{V_g}{N_g}\frac{dP}{dT}\right|_{\substack{\text{along}\\ \text{isostere}}} = \frac{S_g}{N_g} - \left.\frac{\partial S}{\partial N}\right|_{PTA}.$$

The pressures which we are considering in this experiment are so low that helium still can be considered an ideal gas even at a few degrees Kelvin; hence:

$$PV_g = N_g RT$$

or

$$\frac{V_g}{N_g} = \frac{RT}{P}$$

hence:

$$\left.\frac{d\,\mathrm{Ln}(P)}{dT}\right|_{\substack{\text{along}\\ \text{isostere}}} = \frac{\frac{S_g}{N_g} - \left.\frac{\partial S}{\partial N}\right|_{PTA}}{RT}. \qquad (1\text{-}3)$$

The entropy of a monatomic, ideal gas is given by:(49)

$$\frac{S_g}{N_g R} = -\mathrm{Ln}(P) + \frac{c_p}{R}\,\mathrm{Ln}(kT) + c_p + \frac{3}{2}\,\mathrm{Ln}\left[\frac{m}{2\ \hbar^2}\right]$$

which equals (for helium):

$$\frac{S_g}{N_g R} = 7.549 + \frac{5}{2}\,\mathrm{Ln}(T) - \mathrm{Ln}(P) \qquad (1\text{-}4)$$

where T is expressed in $^{\circ}$K and P in Torr. Thus the measurement of adsorption isosteres permits us to determine $(\partial S/\partial N)$ as a function of T. If these measurements could be carried out at a given temperature down to zero coverage, it would be a simple matter to integrate $(\partial S/\partial N)$ to obtain absolute values for the entropy of the film as a function of coverage. Two such measurements at nearby temperatures would give rise to a determination of the heat capacity or specific heat. This is of interest because there are independent experimental methods of measuring the specific heat.

Returning to the differential of the film energy:

$$dU = TdS - PdV - \phi dA + \mu dN;$$

we may apply the Euler relation to get:

$$U = TS - PV - \phi A + \mu N.$$

If we now define:

$$F' = U + PV + \phi A - TS \ (= G' + \phi A),$$

we find:

$$F' = \mu N.$$

Thus we have two differentials for F' which we may set equal:

$$\mu dN + N d\mu = dF' = -SdT + VdP + Ad\phi + \mu dN$$

whence:

$$Nd\mu = -SdT + VdP + Ad\phi.$$

If we assume once again that the film is in equilibrium with the gas, then $d\mu = d\mu_g$, and we obtain an expression for ϕ.

$$d\mu_g = d\mu$$

$$-\frac{S_g}{N_g} dT + \frac{V_g}{N_g} dP = -\frac{S}{N} dT + \frac{V}{N} dP + \frac{A}{N} d\phi$$

At fixed temperature (i.e. along an isotherm), $dT = 0$ and we have:

$$\left[\frac{V_g}{N_g} - \frac{V}{N}\right] dP = \frac{A}{N}\, d\phi$$

once again $V_g/N_g >> V/N$; and we have

$$d\phi = \frac{N}{A}\ \frac{V_g}{N_g}\ dP$$

$$= \frac{N}{A}\ \frac{RT}{P}\ dP$$

$$= \frac{NRT}{A}\ d\mathrm{Ln}(P)$$

hence:

$$\phi(P) \;=\; \underset{\text{along isotherm}}{\int_0^P} \frac{NRT}{AP}\, dP. \qquad (1\text{-}5)$$

In those theoretical models which view the adsorbed film as a two dimensional system, ϕ appears in a way which is analogous to the pressure, P, of an ordinary three dimensional system; for example the equation of state of an "ideal two dimensional gas" would be: $\phi A = NRT$.

CHAPTER II

EXPERIMENTAL GOALS, METHODS, AND APPARATUS

An ideal adsorption substrate for research purposes would satisfy many conflicting criteria. It should be easily prepared in a reproducible manner, free from cracks and pores of truly atomic dimensions. It should contain a large surface area within a relatively small volume and yet have a sufficiently open structure that the time for pressure equilibrium is reduced to reasonable levels. It should also have good thermal conductivity so that all parts of the substrate will stay at the same temperature (this is especially important for calorimetric measurements), but it should also have a small heat capacity.

Pre-plated, sintered copper sponges satisfy many of these requirements reasonably well and consequently have been used in this research. Their construction will now be reviewed:(50)

The copper powder is supplied(51) in the form of flakes whose dimensions are on the order of microns. After being cleaned with ether, the powder is pressed into a container of OFHC copper(52) at pressures on the order of a few thousand pounds per square inch. The resultant material has a density between 1/2 and 2/3 that of bulk copper. The sponge--i.e. powder and casing--is then sintered by being heated to approximately 600°C in an atmosphere of dry hydrogen (purified in activated charcoal at 77°K). The sponge is then permitted to cool slowly over a period of five to ten hours. When the surface area of such a sponge is measured in the manner to be described subsequently, it generally turns out to be on the order of 4 m^2 per cm^3 of sponge.

The basic measurements in the present research were made with helium adsorbed on the copper sponge which had been pre-coated with another noble gas. There are several important reasons for adsorbing the helium on a noble gas layer rather than on bare copper: First of all the pressure corresponding to a given coverage and temperature is considerably higher at submonolayer coverages than if bare copper were used. Secondly it is assumed that the preplating will help to smooth out any irregularities which may be present in the bare copper. And finally the nature of the substrate can be varied in a controlled manner without changing its basic geometry. A more detailed description of the particular sponge used in this research, as well as the rest of the experimental apparatus will appear later in this chapter.

Four noble gases were used as substrates in this work--neon, argon, krypton, and xenon. The first step, however, was to determine the monolayer capacity of the bare sponge for nitrogen at $77^{\circ}K$; this number has no direct use in the rest of the experiment, but it does serve to compare the properties of the sponge with those of sponges used by other researchers since a nitrogen isotherm of $77^{\circ}K$ has become a sort of a standard way of determining a relative value for the surface area of a sponge. Gross departures from the expected value may indicate poor sintering, or some other concealed fault. Next, an isotherm was taken on bare copper for each of the four gases, and was fitted to the BET equation to determine a monolayer capacity. It will become apparent after the apparatus and experimental method has been more fully described that the experimenter is not free to do such isotherms at any arbitrary temperature if the most accurate results are to be obtained; consequently each isotherm was taken at the temperature which represented the best compromise between accuracy and practicality. In the case of argon, a series of isotherms was taken, in order to determine the isosteric heat of adsorption of argon on copper as a function of coverage.

Finally, the information gained above was used to determine the amount of gas to be used in the preplating--generally 1.0 to 1.5 monolayers-- and the isotherms and isosteres of helium were carried out. As will be seen, the experimental apparatus was designed to permit the making of heat capacity measurements. This might have been desirable had some particularly interesting feature appeared in the isotherm data, which could have required heat capacities to be measured on the same sponge.

As mentioned earlier, these systems at submonolayer coverages were totally unexplored at the beginning of the present research; and it was not known whether certain regions would turn out to have special interest. Consequently it was necessary to design the apparatus in as general a fashion as possible. This necessitated certain compromises in the design of the equipment which may be observed in the subsequent description. For example: It now appears that to adequately describe the $4.2^{o}K$ isotherm of helium on argon between, say, 0.05 and 2.0 layers would require pressure measurements over the range: 10^{-8} Torr $\lesssim P \lesssim 10^{+2}$ Torr. Clearly it is impossible for any single setup to perform optimally over such a range, and further more refined studies might require a separate apparatus for each region of interest. This is discussed further in appendix I.

The experimental apparatus is shown in figure (2-1), with further detail in figures (2-2) - (2-5). The sponge was fabricated as described above, then a large hole was bored into the sintered powder so that the resulting mass has the shape of a thin cylindrical shell. The purpose of this was to minimize the distance through which gas must travel in the sponge to achieve a uniform distribution. Unfortunately, this action greatly increases the dead volume, severely reducing the accuracy of any measurements which may be attempted at low temperature and "high" pressure. At $3^{o}K$, for example, this dead volume of approximately 50 cm^3 has the same effect as a room temperature volume of 50(300/3) = 5000 cm^3; and contains (at $P \simeq 3$ Torr) as much gas as a typical completed monolayer. A copper cap is soft soldered to the top of the casing; this

Figure (2-1)

The experimental apparatus, especially the gas-handling and measuring systems.

The abbreviations and symbols used in this figure are:

T.P. - Toepler pump (see figure 2-3)

C.T. - liquid nitrogen cold trap

G.S. - gas storage bulb

⊗ - stopcock

Ⓜ - metal, bellows-sealed vacuum valve

Ⓘ - special glass-indium valve (see figure 2-9)

Ⓥ - bakeable vacuum gauge set

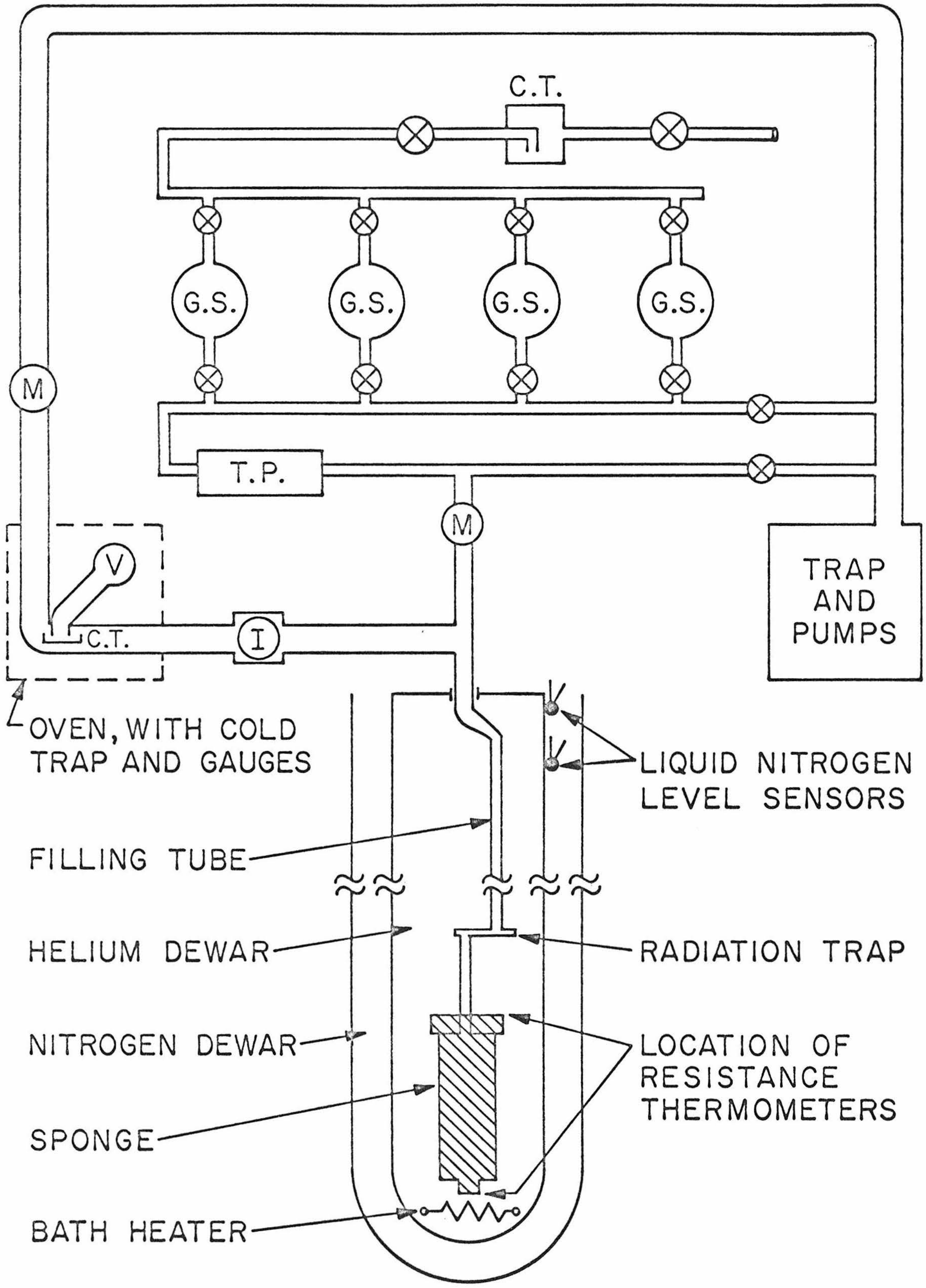

C.T.
G.S.
G.S.
G.S.
G.S.
M
T.P.
M
V
C.T.
I
TRAP AND PUMPS
OVEN, WITH COLD TRAP AND GAUGES
LIQUID NITROGEN LEVEL SENSORS
FILLING TUBE
HELIUM DEWAR
RADIATION TRAP
NITROGEN DEWAR
LOCATION OF RESISTANCE THERMOMETERS
SPONGE
BATH HEATER

Figure (2-2)

Detail of copper sponge

The specifications of the sponge used in this experiment are as follows:

Dead volume of sponge = 50 cm^3 ± 5%.

Mass of powder after machining = 146 gm.

Density of powder/density of bulk copper = 0.57.

BET nitrogen monolayer 77°K = 21.5 STP cm^3 ± 5%.

Surface area derived from above = 94 m^2.
(see equation 3-1)

Volume occupied by powder after machining= 30 cm^3.

Surface to volume ratio $\simeq$ 3 m^2/cm^3.

Thickness of powder after machining $\simeq$ 0.125 in.

I.D. of filling tube = 1.55 mm.

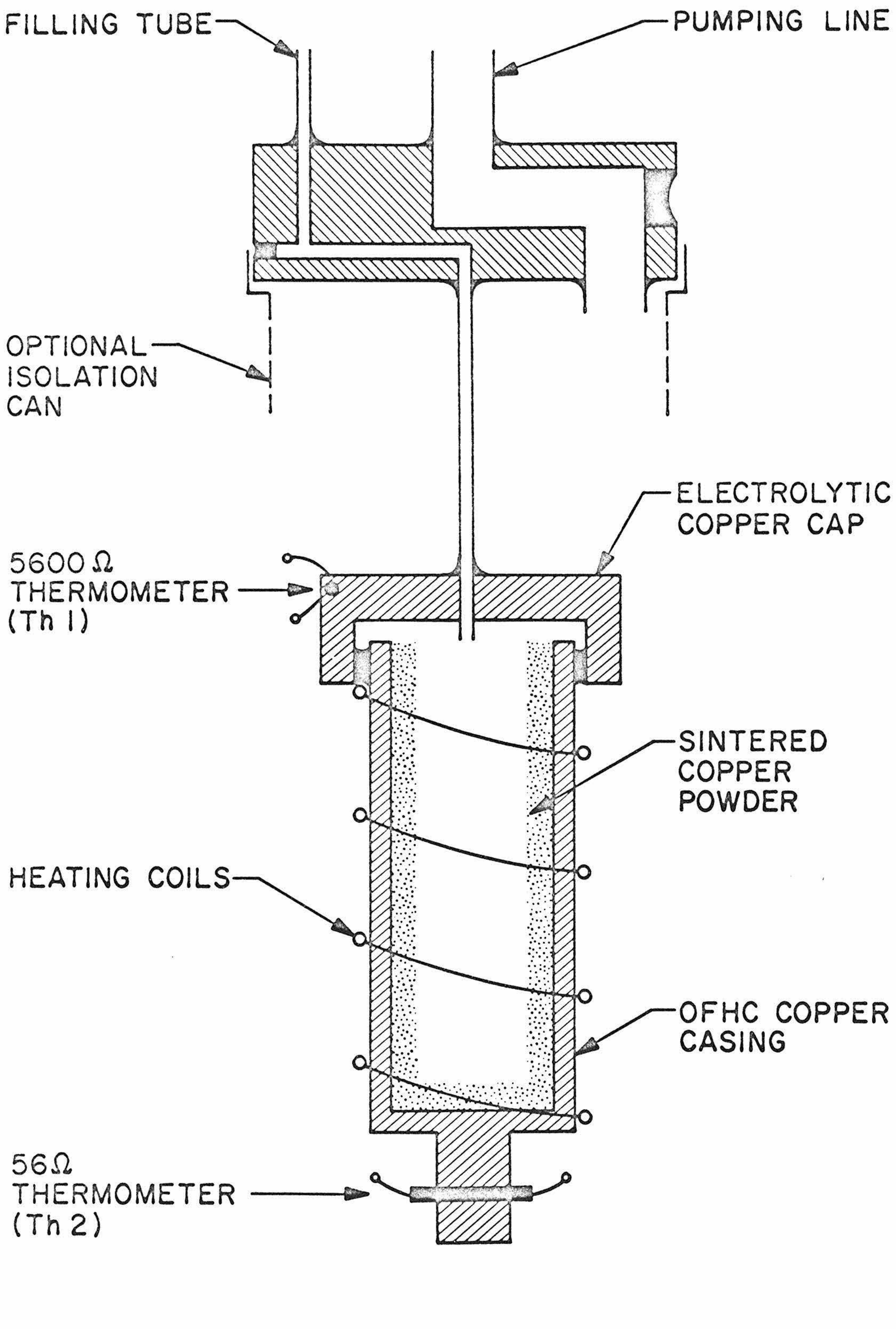

FILLING TUBE
PUMPING LINE
OPTIONAL ISOLATION CAN
ELECTROLYTIC COPPER CAP
5600 Ω THERMOMETER (Th 1)
SINTERED COPPER POWDER
HEATING COILS
OFHC COPPER CASING
56 Ω THERMOMETER (Th 2)

Figure (2-3)

Detail of mercury-filled Toepler pump

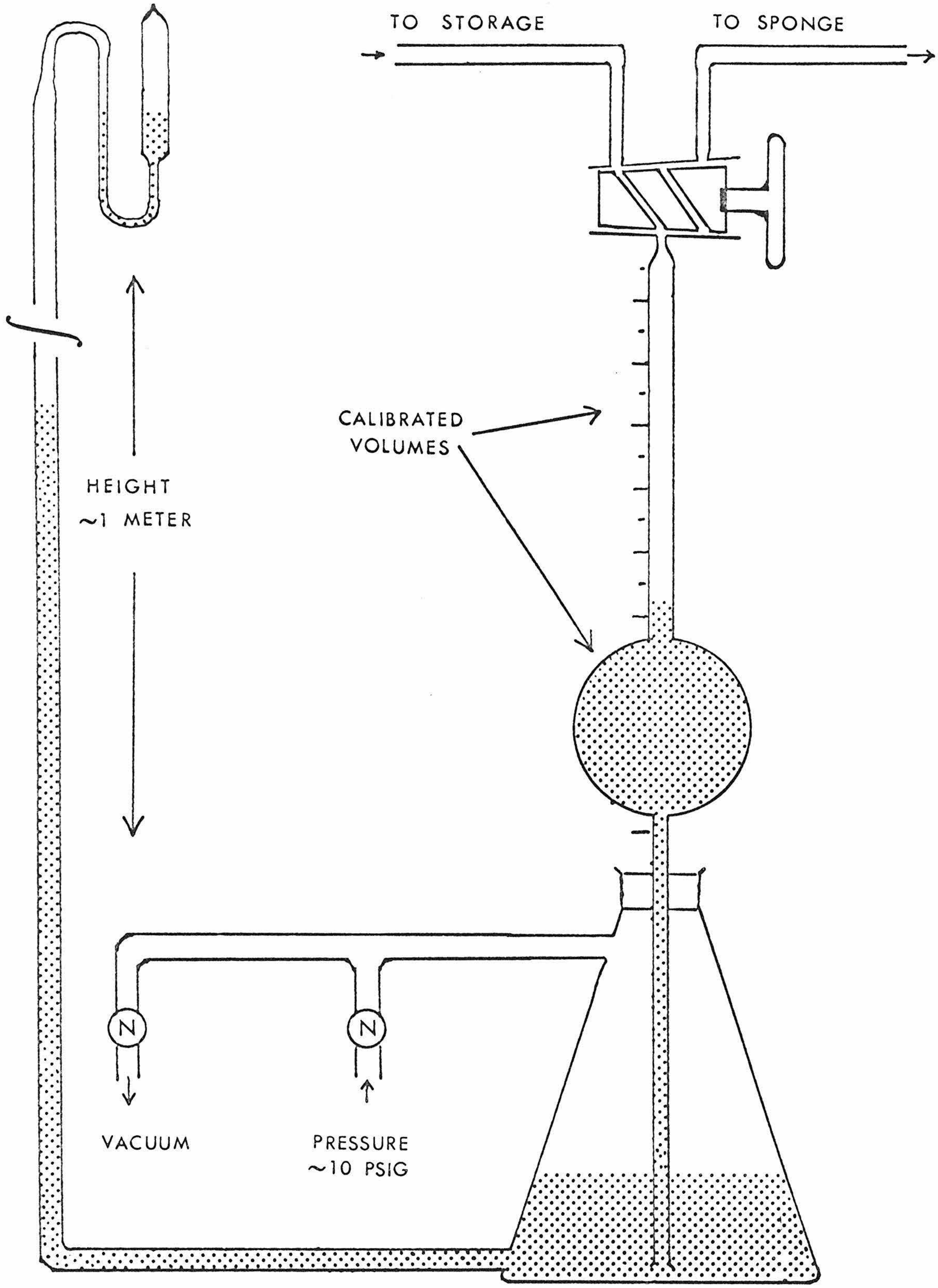

TO STORAGE
TO SPONGE
CALIBRATED VOLUMES
HEIGHT ~1 METER
VACUUM
PRESSURE ~10 PSIG
N
N

Figure (2-4)

Detail of special cold trap used with high vacuum gauges to minimize the effects of fluctuations in the liquid nitrogen level

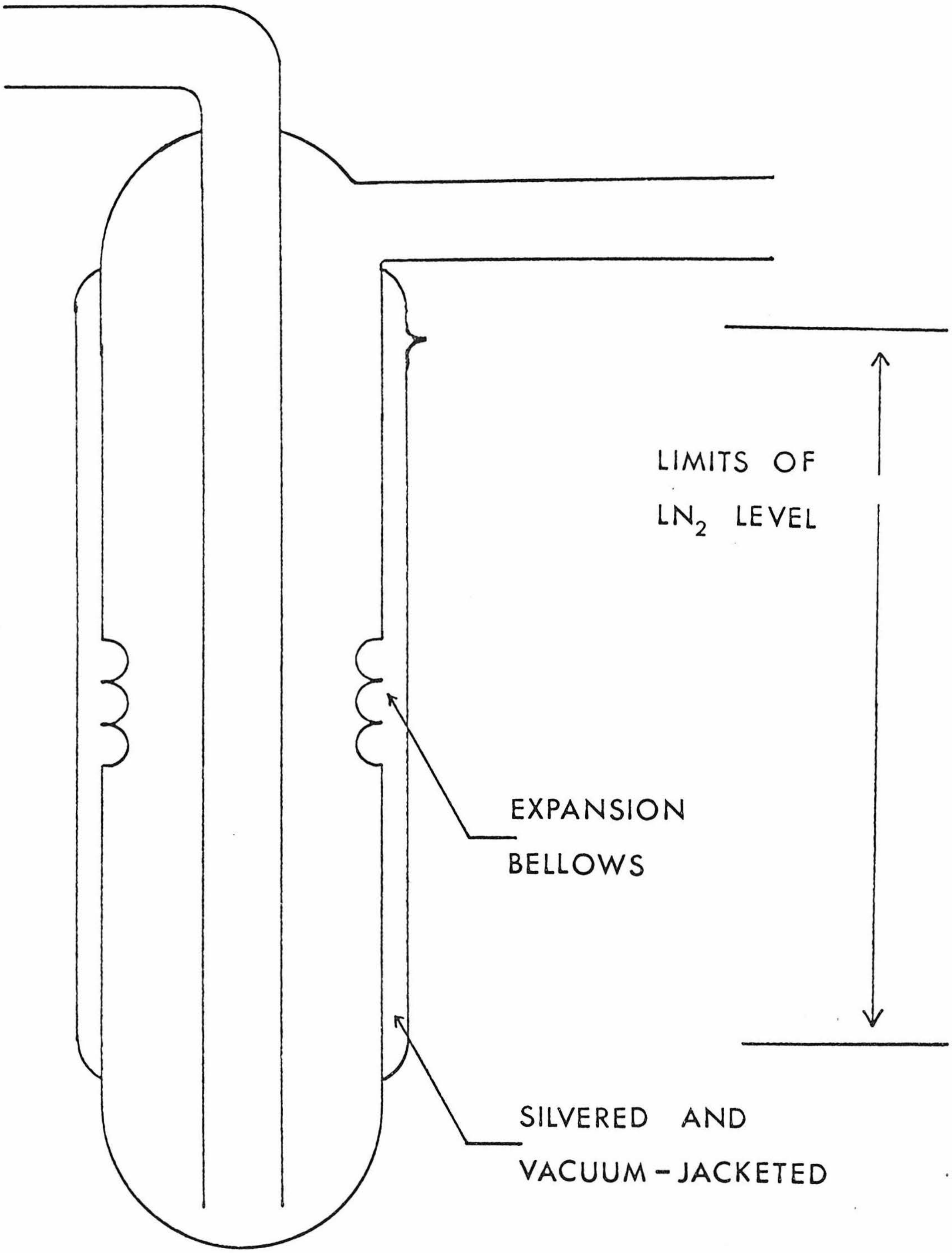

LIMITS OF
LN_2 LEVEL
EXPANSION
BELLOWS
SILVERED AND
VACUUM-JACKETED

Figure (2-5)

AC bridge circuitry

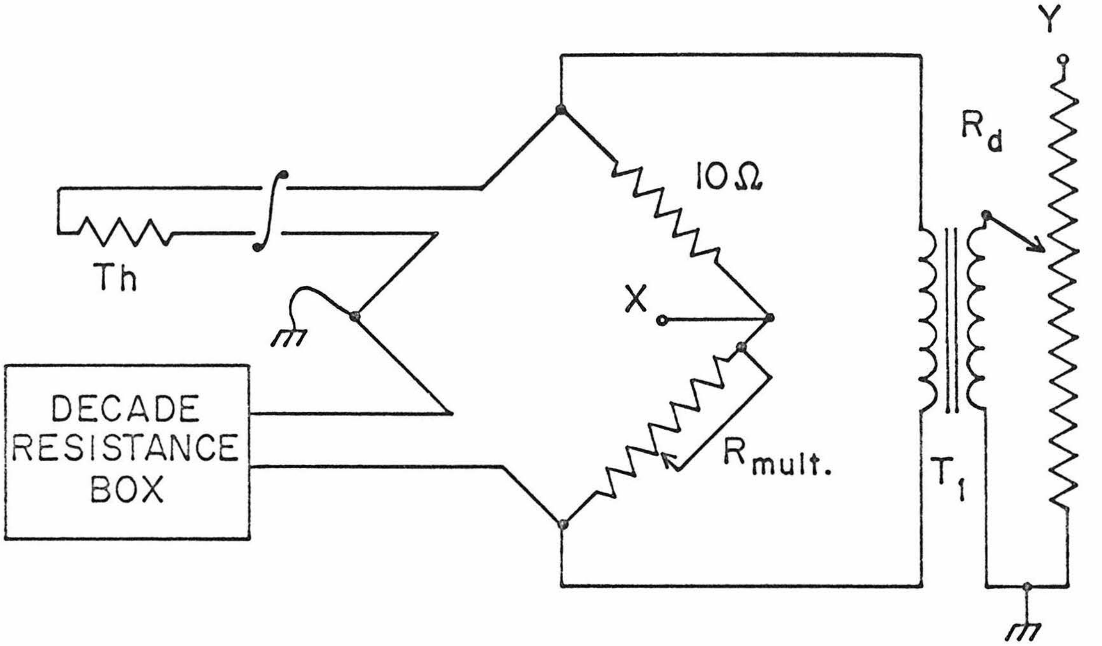
The abbreviations and symbols used in this figure are:

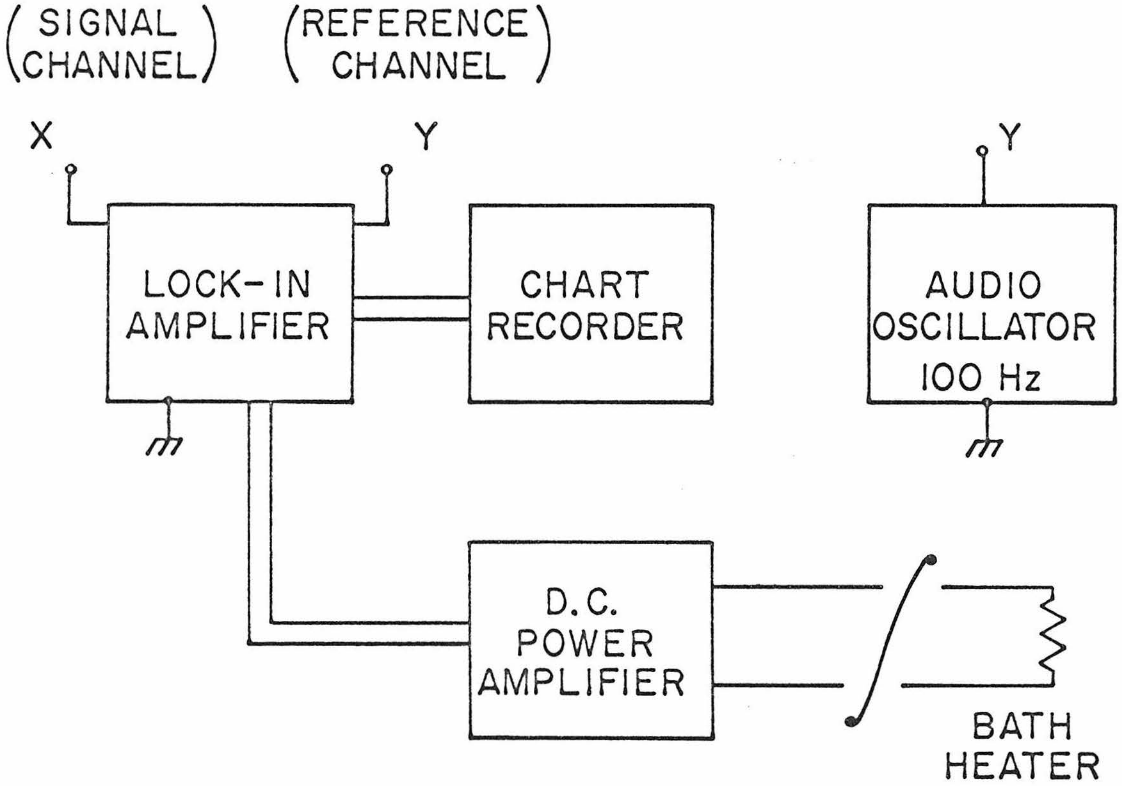
Rd - switch-selected to vary the power dissipation in Th from $\sim 10^{-5}$ W to $\sim 10^{-11}$ W (with accompanying loss in sensitivity).

$R_{mult.}$ - switch-selected values of 10, 100, and $1000\,\Omega$.

T_1 - transistor driver transformer #AR-104 (Argonne Electronics Manufacturing Corporation, Syosset, New York).

Th - switch-selected to be either a resistance thermometer on the sponge or one of several standard resistances.


Y
R_d
10Ω
Th
X
DECADE RESISTANCE BOX
R_mult.
T_1


(SIGNAL CHANNEL)
(REFERENCE CHANNEL)
X
Y
Y
LOCK-IN AMPLIFIER
CHART RECORDER
AUDIO OSCILLATOR 100 Hz
D.C. POWER AMPLIFIER
BATH HEATER

connects to a section of thin-walled cupro-nickel tubing which runs up through the top of the dewar. This tubing, the filling tube, is offset just above the sponge cap to reduce direct heat radiation from the room into the sponge.

The sponge is provided with two carbon resistance thermometers and a heating coil. One of the thermometers is a nominal 56 Ω ½W Ohmite(53) resistor which is used from about 30°K to 1.5°K. The other is a nominal 5600 Ω ½W Ohmite which is used from about 300°K to 20°K. The insulation was ground off of these resistors and they were coated with a thin layer of insulating varnish.(54) Then they were inserted into holes (110 mils in diameter) drilled through projections on the top and bottom of the sponge. These projections are an integral part of the cap and casing respectively. The thermometers were secured in the holes with an epoxy which takes a room temperature cure.(55) This epoxy is described by the manufacturer as having good thermal conductivity at cryogenic temperatures and a thermal expansion matching that of copper. It was found to be more satisfactory than certain other types including another by the same manufacturer.(56)

The resistances were measured with a sensitive ac bridge circuit. This circuit dissipates less than 10^{-5} watts in the thermometers, and yet it has a sensitivity of ~ 0.1%. It is composed of a homemade bridge circuit, used in conjunction with a commercial audio oscillator(57) and a commercial lock-in amplifier(58).

The sponge heater consists of approximately ten feet of #24 insulated Evanohm wire(59) with a total resistance of ~ 100 Ω . Since the insulation on this wire must be removed mechanically, at the solder joints, it was considered easier to use heavier gauge wire than the #40 which has often been used previously. A helical groove was machined in the wall of the sponge casing which was then coated with insulating varnish; the heater was laid in this groove.

Since the apparatus was designed to be usable for heat capacity measurements, provision was included for enclosing the sponge in an evacuable isolation container. The leads from the thermometers and heater were routed up the inside of the pumping line for this chamber until they were outside the dewar, where they went through a commercial Kovar-glass electrical feed-through; this was done because such feed-throughs have a reputation for being unreliable with respect to vacuum tightness at cryogenic temperatures--especially when immersed in superfluid helium These leads were made of relatively heavy gauge Evanohm wire, rather than the more conventional fine gauge copper in order to reduce handling problems. Presumably, the heat leak through heavy resistance wire should be about the same as that through lighter copper if the electrical resistances are the same. This assumption was not specifically tested, however no reduction in the liquid helium bath lifetime was noted in comparision with an earlier version of the apparatus which had used #40 copper leads, whereas the incidence of electrical short circuits was reduced to zero.

The gases to be used in the experiments were led from a storage manifold to a Toepler pump and thence to the filling tube. The Toepler pump, in addition to its primary task of measuring out the amount of gas to be admitted to the sponge, was used to measure the resulting pressure of the isotherm in the range of ~ 1 Torr to 760 Torr. Furthermore it can be used as a fairly good McLeod gauge for pressures down to ~ 10 millitorr (10 μ).

Pressures in the millitorr (micron) range and below are measured by a set of three gauges, contained in an oven which is capable of baking them out to ~ 500°C.(60) These are: a Pyrex thermocouple gauge with a useful range of ~ 0.2μ to 100μ;(61) an ionization gauge; and a monopole residual gas analyser.(62)

The residual gas spectrometer is necessary because the gauges acquire a background pressure of nitrogen (or carbon monoxide), which does not go away even when there is liquid helium in the dewar. The source of this background is uncertain but it may result from a large number of very small leaks to the atmosphere or it may result from the outgassing of tightly bound material within the vacuum system. Since the filling line to the sponge is long and thin, the effective pumping speed of the liquid helium is reduced to the point where the background can build up to appreciable pressures. In an earlier version of the apparatus which could be baked to only 150°C, this background was ~ 10^{-5} Torr; in the present system it is below 10^{-6} Torr. The spectrometer makes it possible to measure the partial pressure of the helium alone. At the present time, the lower limit of helium pressure which can be measured is on the order of 10^{-7} Torr. This limitation is due not to a lack of sensitivity on the part of the spectrometer, but rather to the presence of a background pressure of helium of about 10^{-8} Torr. The source of this background is also uncertain but it may be due to atmospheric helium permeating the Pyrex walls of the gauges. This matter is discussed further in appendix I.

All of the helium isotherms were done at temperatures below 4.2°K and depended on a pumped liquid helium bath for cooling. The bath is pumped through a mechanical manostat which is capable of holding a desired temperature to within about ± 10 m°K over the range of interest. A thermoregulator was constructed to maintain finer temperature control; it is shown as part of figure (2-5), and operated as follows: The dc output of the lock-in amplifier was fed to a special power amplifier which applied power to a bath heater at the bottom of the dewar when the bath became colder than the preset value. The output power was approximately proportional to the temperature error. Most of the time, however, it was not necessary to operate at a pre-determined temperature; and this circuit was not used. Instead, bath pressures were read on a mercury manometer and converted into temperature according to the 1958 scale.(63) An oil manometer was available for use at temperatures below the λ-point.

The preliminary noble gas isotherms, on the other hand, were done at various temperatures between 19°K and 145°K. Figure (2-6) shows the usable liquid range (i.e. between N.B.P. and T.P.) of the various practical liquid refrigerants available between 150°K and 0°K, as well as the temperature ranges within which it is possible to perform an isotherm on each of the noble gases. In order to do such an isotherm, the temperature should be such that the bulk vapor pressure of the adsorbate lies between ~ 760 Torr and ~ 0.1 Torr. (In addition the range of 1.0 Torr to 10 Torr is inconvenient with the existing apparatus.) In the case of neon, the bulk vapor pressure had to be kept below ~ 100 Torr because of the large effective dead volume at these temperatures.

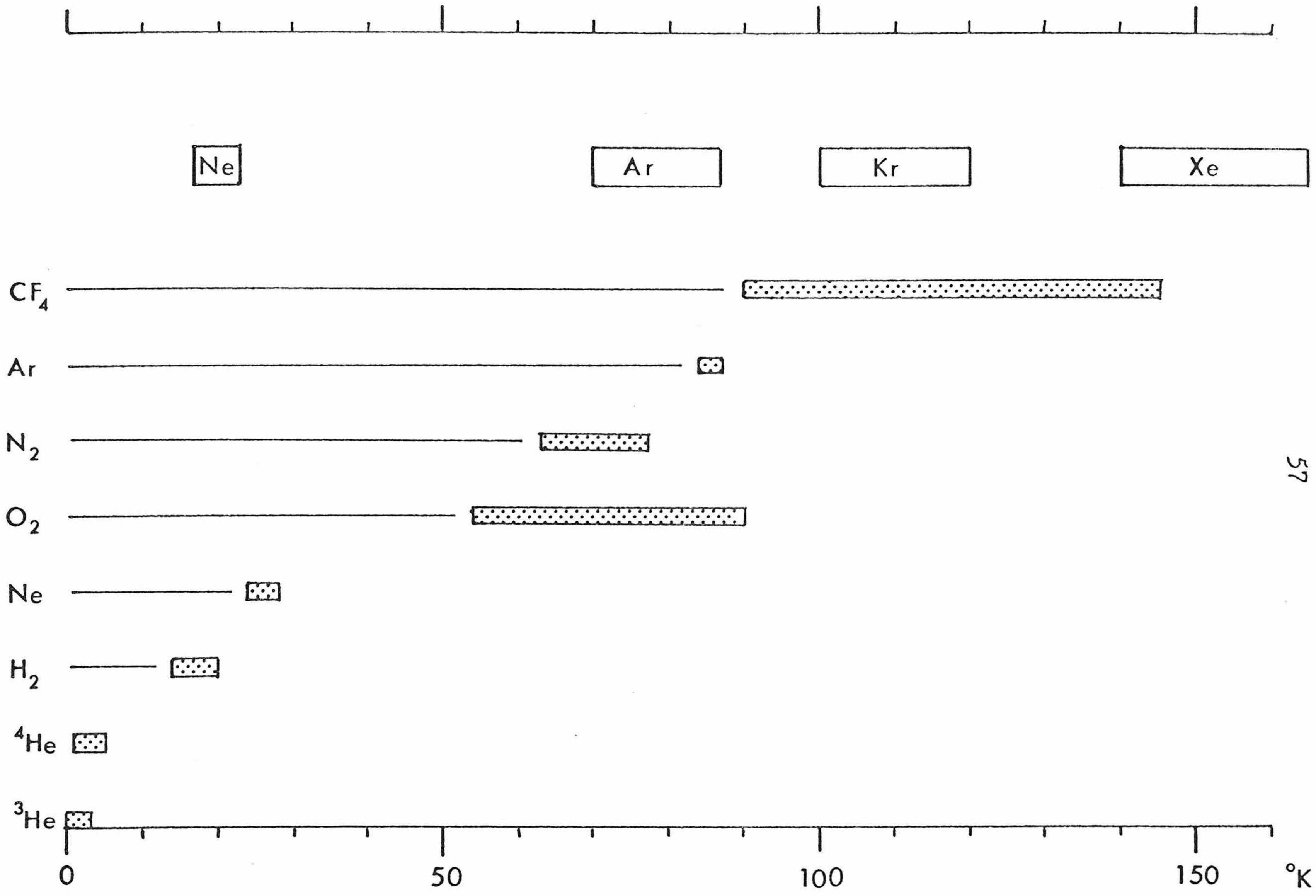
The cryostat used in this work could not be used in a continuously variable fashion; nor was it practical to use solidified refrigerants. Consequently it was necessary to use special procedures to obtain some of these isotherms. The compound tetrafluoromethane (carbon tetrafluoride, Freon-14) proved very

Figure (2-6)

Useful liquid refrigerants

in the range 0°K to 150°K

The open boxes show the temperature ranges within which the noble gas isotherms should be performed.


Ne
Ar
Kr
Xe
CF_4
Ar
N_2
O_2
Ne
H_2
^4He
^3He
0
50
100
150
°K

useful in the case of krypton and xenon. As shown on figure (2-6), its liquid range is ideally suited for these isotherms. Tetrafluoromethane is supplied as a compressed gas in cylinders; it is not known to be toxic, however it is relatively expensive and therefore had to be handled in a closed system. The method whereby this was done is diagrammed in figure (2-7) and discussed below.

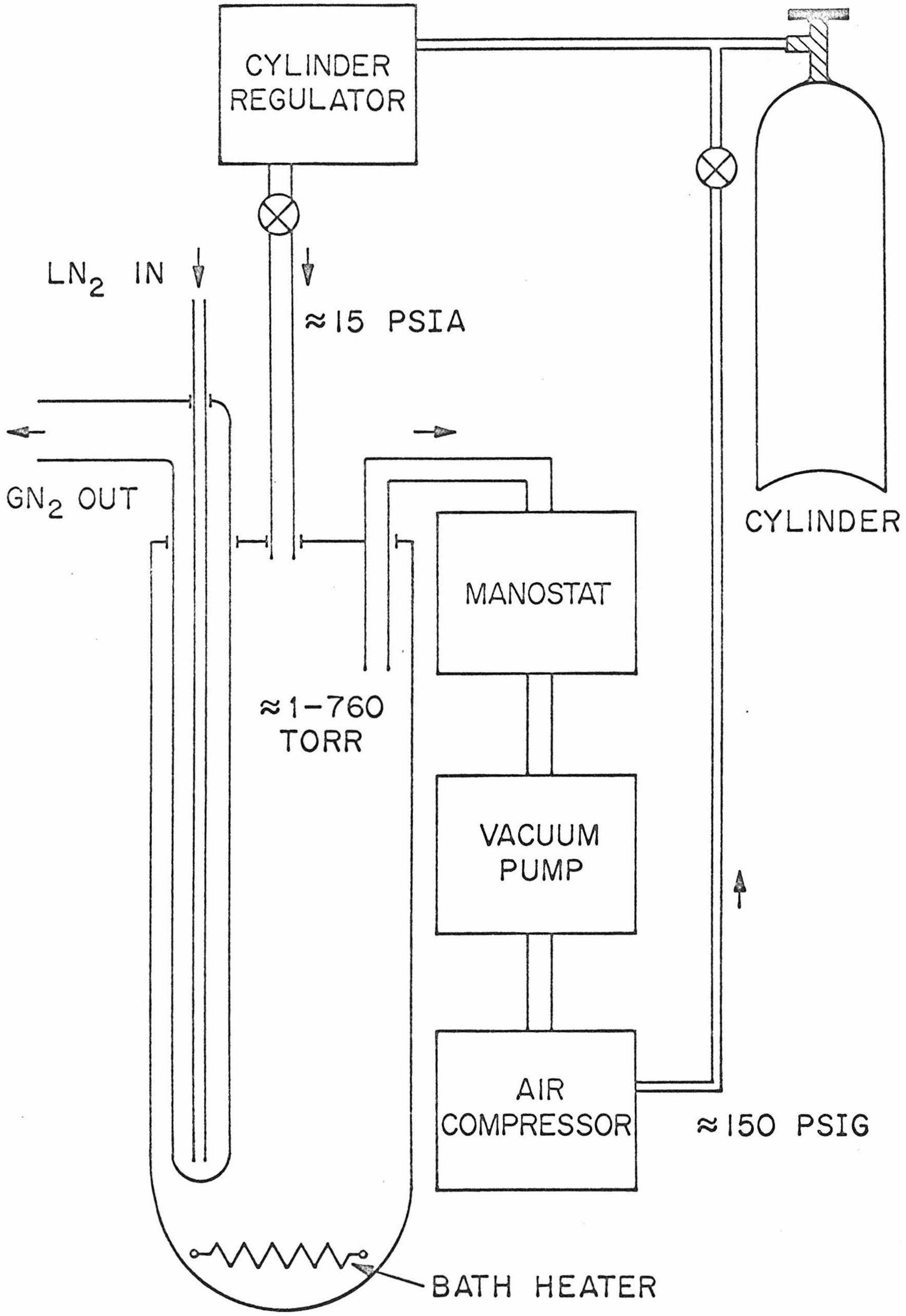
A closed, coaxial heat exchanger was temporarily inserted into the helium dewar, and the dewar evacuated. Liquid nitrogen was passed through the exchanger; while CF_4 at approximately atomospheric pressure was admitted to the dewar. By adjusting the respective flow rates, it was possible to condense liquid CF_4 in the bottom of the dewar at a reasonably fast rate. When a sufficiently large amount had been collected, the flows were turned off and the valve opened to the manostat which then controlled the bath temperature as the CF_4 was pumped out of the dewar, through an air compressor of the type used in older domestic refrigerators, and back into the cylinder at a pressure of ~ 150 psig; where it was stored until the next run.

All of the argon isotherms were taken using

Figure (2-7)

Closed-cycle freon-14 refrigeration system

When sufficient liquid freon had been collected, the liquid nitrogen flow was shut off and heat was temporarily applied at the bottom of the dewar to insure a uniform temperature throughout the bath.


CYLINDER REGULATOR
LN2 IN
≈15 PSIA
GN2 OUT
MANOSTAT
≈1-760 TORR
VACUUM PUMP
AIR COMPRESSOR
≈150 PSIG
CYLINDER
BATH HEATER

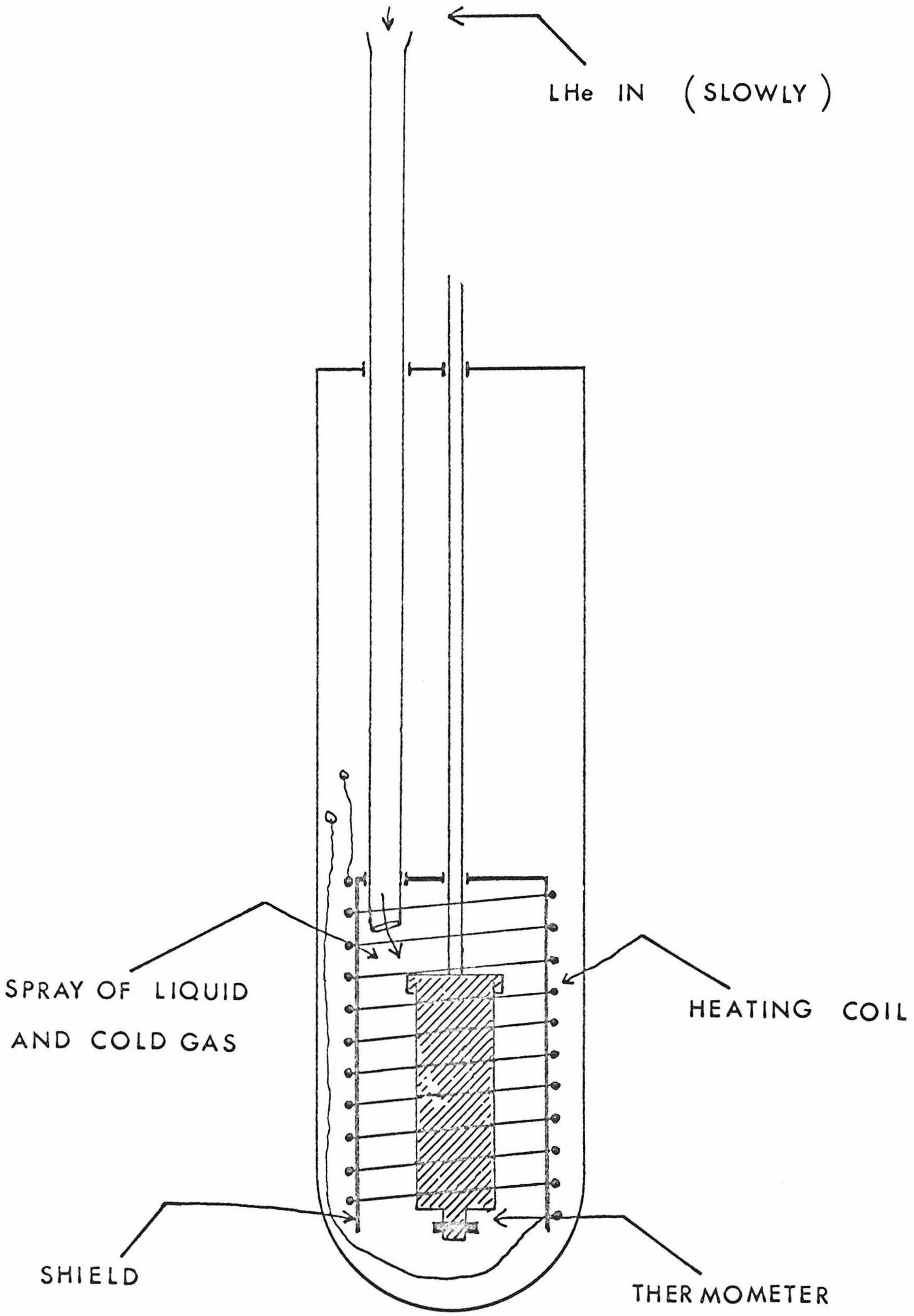
either liquid argon or liquid nitrogen as the refrigerant, since the use of oxygen would have involved certain hazards. Neon, however, presented a particular problem. Liquid neon itself is not suitable as a refrigerant in this apparatus because its vapor pressure at its triple point is quite high--324 Torr. Consequently it would have been necessary to measure the neon adsorbed in the sponge at pressures up to 324 Torr in order to get a complete isotherm. Since the dead volume within the sponge is approximately 50 cm^3, there is an effective volume of 50(273/27) $\simeq$ 500 cm^3 at $27^{o}K$. Such high pressures in such a large effective volume would have meant that nearly all of the gas being admitted to the system would have remained in the gas phase rather than adsorbing. Consequently the accuracy of the measurements would have been reduced to totally unacceptable levels. Since it can no longer cool the sponge effectively after reaching its triple point, liquid neon could not be used; furthermore the cost in sufficient quantities would have been extremely high.

Liquid hydrogen would have been ideal as far as its physical properties are concerned; however its chemical properties make its use in kilogram quantities undesirable in a general laboratory room with exposed motors, lights, etc. The method finally used (see figure 2-8) was satisfactory but far from ideal, and consequently the data for neon are probably slightly less accurate than those for the other noble gases. Liquid helium was transferred very slowly into the dewar while heat was being applied--not to the sponge directly, but to a sort of skirt surrounding the sponge. By adjusting the flow rate and the heating power manually, it was possible to hold the temperature in at least a quasi-static equilibrium while the data were being taken; using the resistance of the 5600 Ω thermometer as as indication of temperature. At the conclusion of each run when the isotherm had saturated, P_0 was recorded and was used to find out at what temperature one had been working. Needless to say, a variable temperature cryostat would have been a significant improvement here; however there is an additional complication: Not only is it necessary to regulate the temperature of the sponge, but one must also make sure that the temperature of the sponge is as low as, or lower than that of any other part of the system, e.g. the filling tube. If this is not done, the pressure readings will be too low.

The total internal volume of the vacuum gauges was on the order of 2000 cm^3. The normal operating

Figure (2-8)

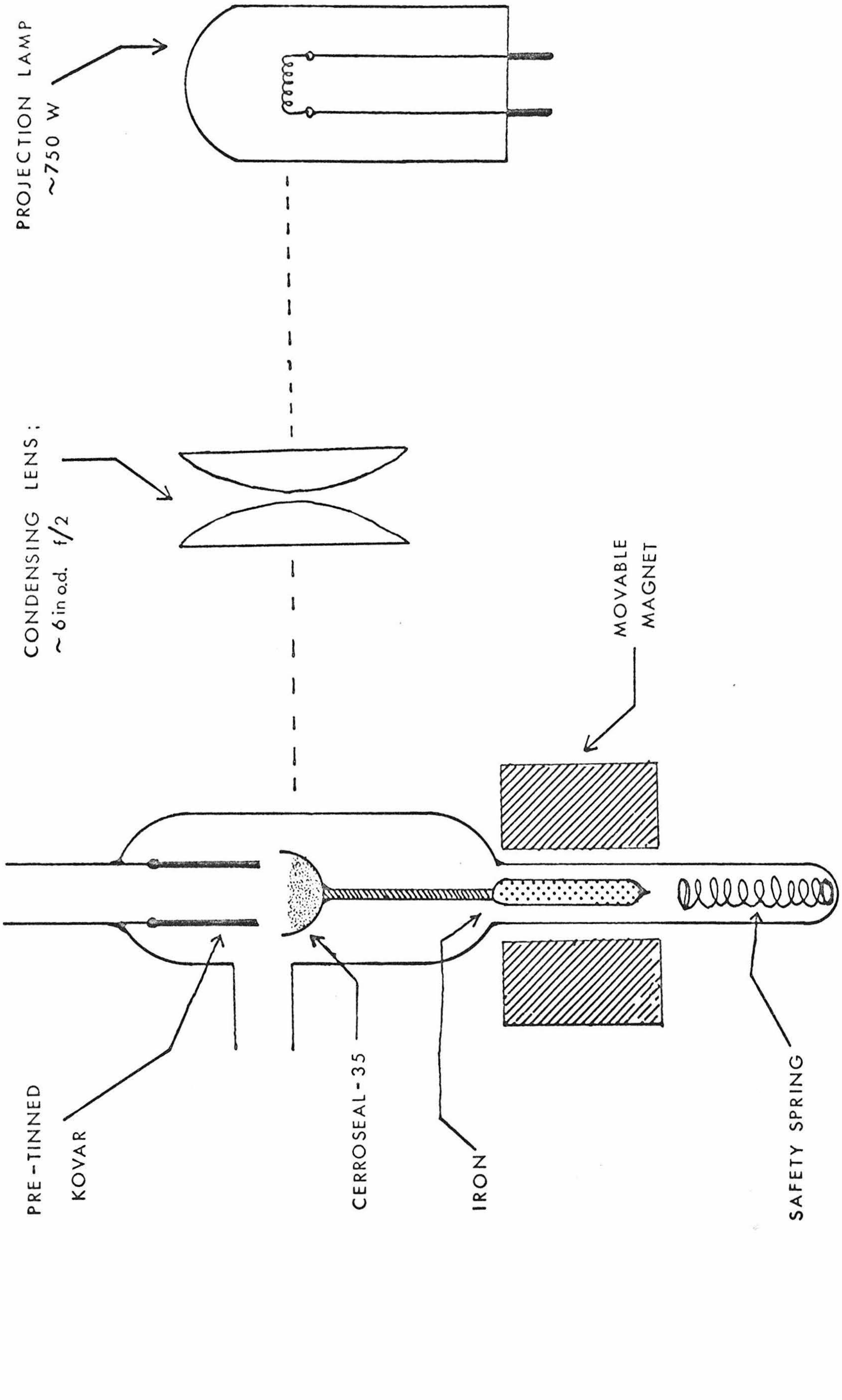
Method used to maintain temperatures in the 20°K range.


LHe IN (SLOWLY)
SPRAY OF LIQUID AND COLD GAS
HEATING COIL
SHIELD
THERMOMETER

procedure to do an isotherm of helium on, say, argon was to fill the outer dewar with liquid nitrogen and wait for the sponge to reach ~ 77°K. Then the correct amount of argon was metered into the system through the Toepler pump; presumably to be adsorbed as a monolayer on the bare copper sponge. In fact, however, a large portion of the argon would remain in the gas phase in the room temperature volume due to the large vapor pressure (~ 20 Torr) of an argon monolayer at 77°K. If liquid helium were to be transferred into the dewar in this condition, this argon would condense very rapidly. At best the distribution of the argon on the sponge would be very non-uniform; at worst, it could and often did completely block the narrow filling tube. Thus it was necessary to place a valve in the system to isolate the gauges from the sponge until after liquid helium temperatures had been reached. Most commercial high vacuum valves seal effectively on one side but not on the other; this is usually not a problem since the poorly sealed side can be placed in line with a pump. This system, however, was designed to maintain a good static vacuum for many weeks at a time, and any seals to the atmosphere would have degraded its performance. Consequently, the valve shown in figure (2-9) was used; it is a

Figure (2-9)

Liquid metal valve used to isolate the
sponge from the high vacuum gauges


PROJECTION LAMP
~750 W
CONDENSING LENS:
~6 in o.d. f/2
MOVABLE
MAGNET
PRE-TINNED
KOVAR
CERROSEAL-35
IRON
SAFETY SPRING

modification of a design which has appeared in the literature.(64) This valve is completely sealed from the atmosphere on both sides, and is capable of sealing atmospheric pressure differentials when closed, it also has a relatively low impedance when open. A proprietary alloy(65) having a nominal composition--indium 50%, tin 50%--was used rather than pure indium to reduce both cost and melting point. The vapor pressures of both components are quite negligible, even at several hundred degrees centigrade.(64) Such valves are frequently melted by flaming the glass envelope; however the method shown was found to be much safer, and more convenient, owing in part to the low melting point of the alloy ($\sim 120^\circ$C). This method applies the heat to the metal where it is needed, rather than to the glass.

CHAPTER III

DATA AND RESULTS

3.1 Preliminary noble-gas isotherms

An adsorption isotherm was taken at the most appropriate temperature on the bare copper for each of the four rare gases and for nitrogen. The only information required from these measurements was the monolayer capacity in each case, derived in a way that would be consistent for each gas and also consistent with the determinations made in previous studies. Hence the BET theory was used in each case to find N_m; these results are shown in figures (3-1) - (3-7).

In the case of argon, isotherms were taken at several temperatures, above and below the bulk triple point to see if this affected the monolayer capacity; the variation in N_m was found to be small. This family of isotherms was also used to contruct the q_{st} curve shown in figure (3-8).

Figure (3-1)

Nitrogen isotherm at 77°K

Dashed line shows location of N_m (21.5 STP cm^3) according to BET analysis (see figure 3-2).

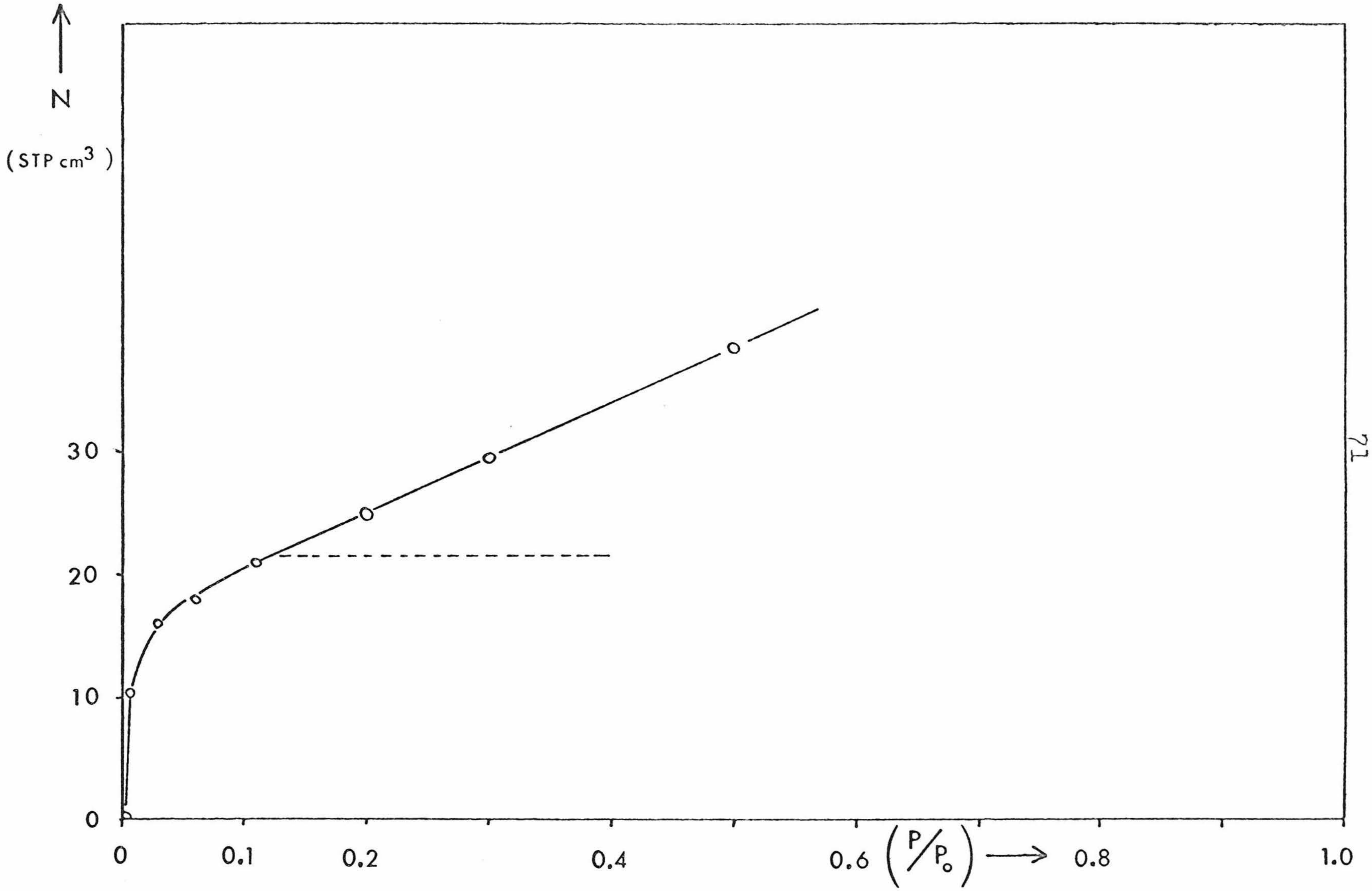

N
(STP cm³)
0
10
20
30
0
0.1
0.2
0.4
0.6
(P/Po)
0.8
1.0

Figure (3-2)

BET plot for nitrogen at 77°K

$N_m \equiv (\text{slope} + \text{intercept})^{-1} = 21.5$ STP cm^3.

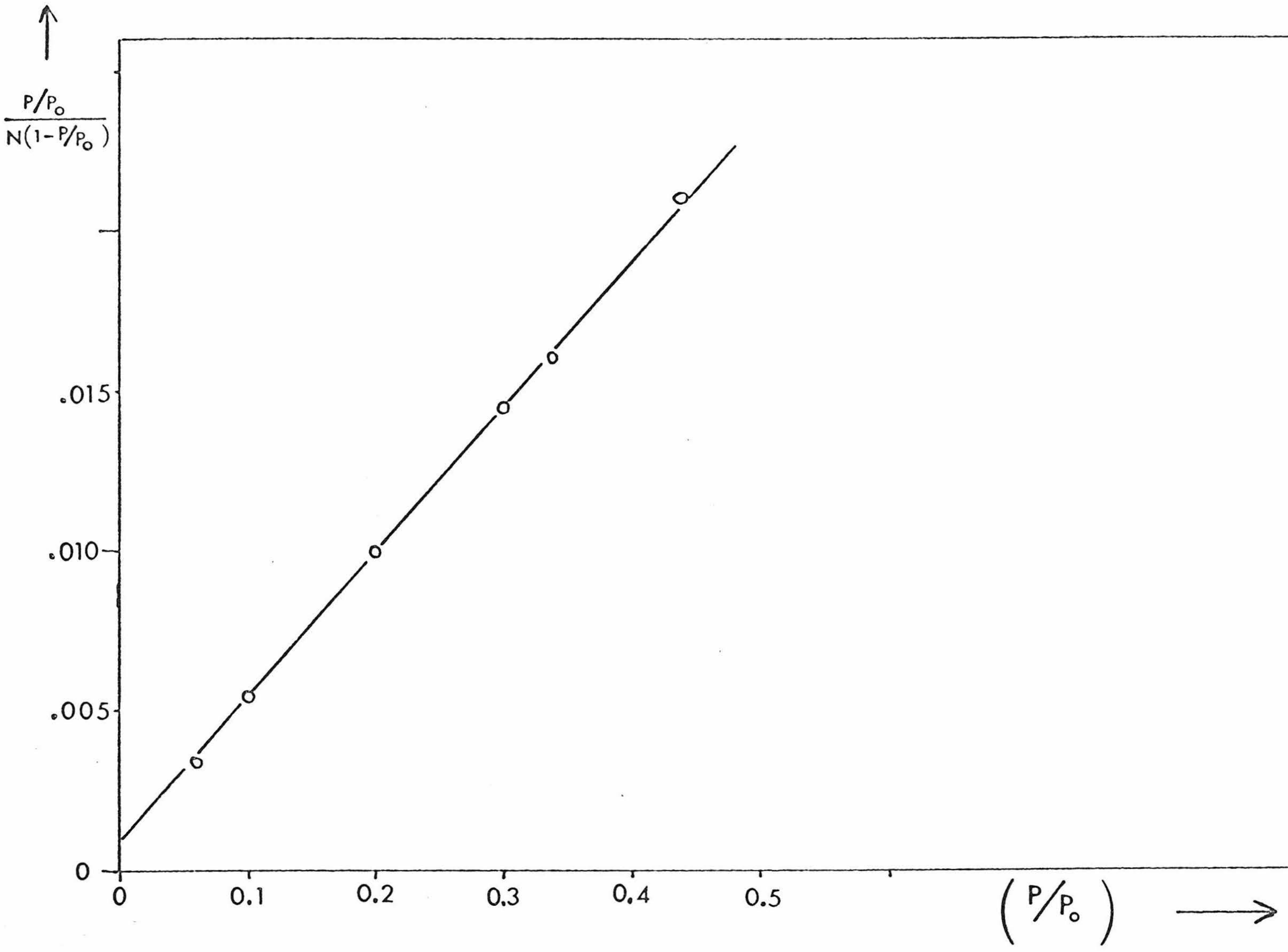

$\frac{P/P_o}{N(1-P/P_o)}$
.015
.010
.005
0
0
0.1
0.2
0.3
0.4
0.5
(P/P_o)

Figure (3-3)

Neon isotherm at 24.6°K

BET N_m = 30 STP cm^3

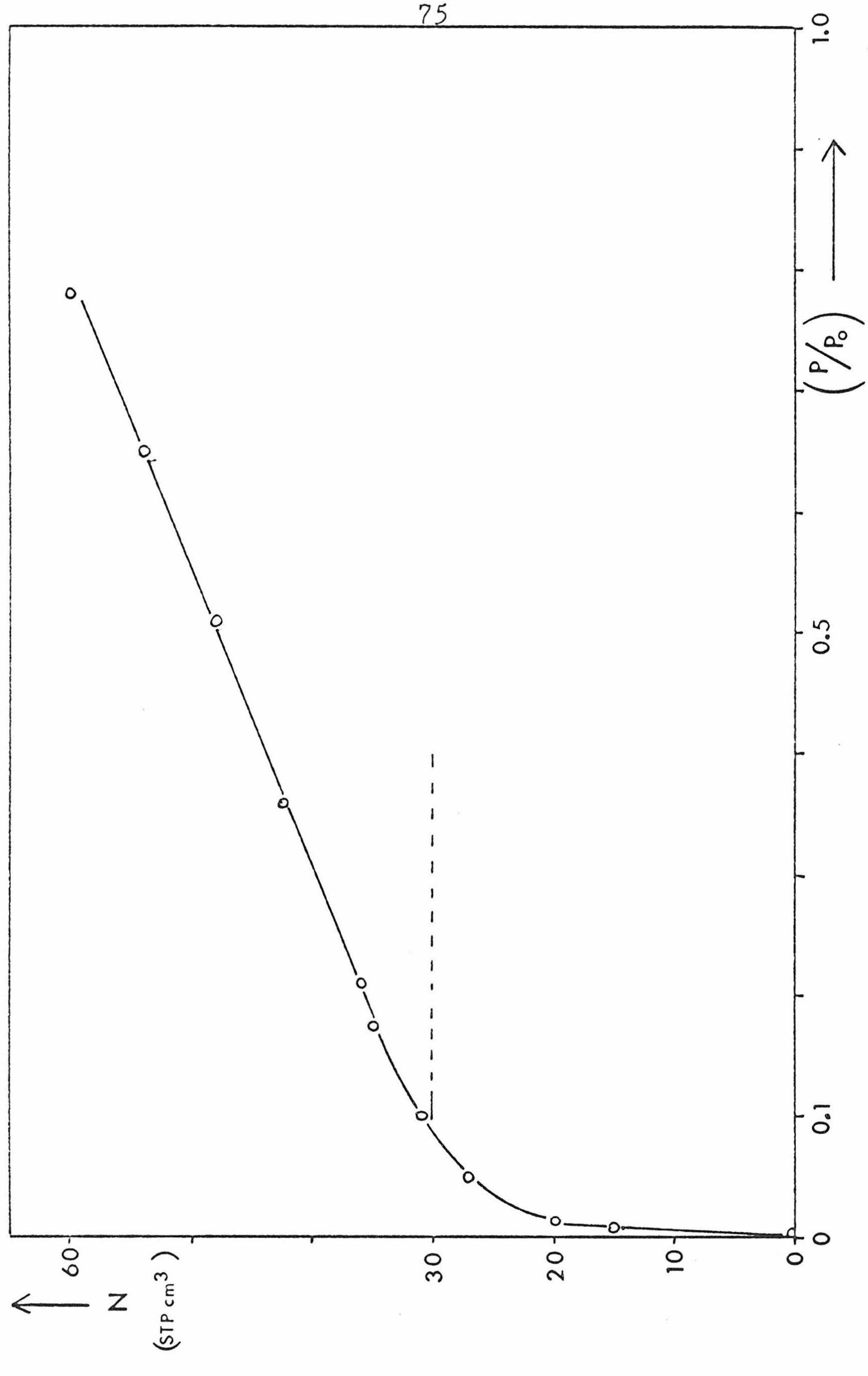

N
(STP cm^3)
60
30
20
10
0
0
0.1
0.5
1.0
($^P/_{P_o}$)

Figure (3-4)

Neon isotherm at 19.8°K

BET N_m = 31 STP cm^3

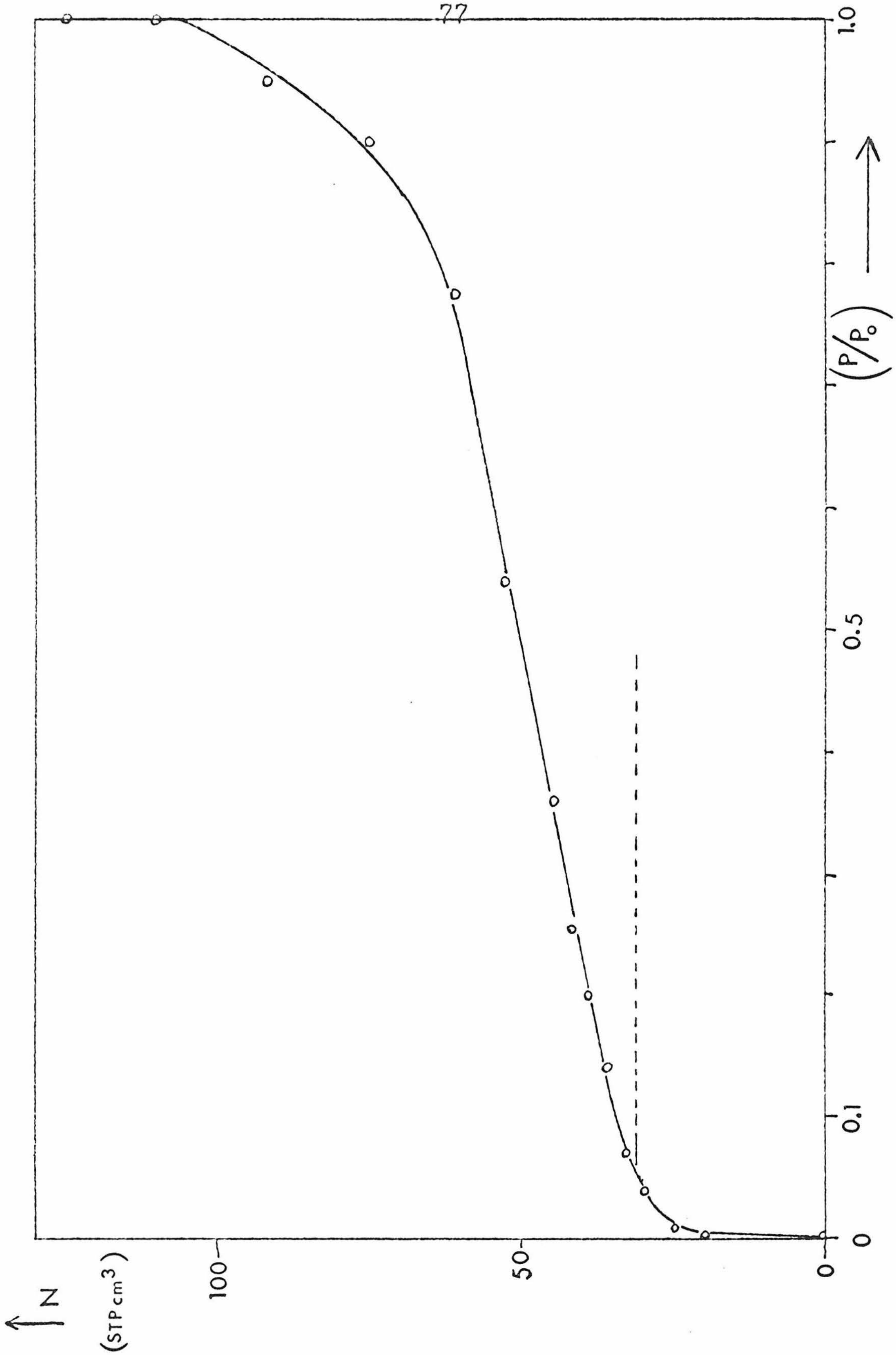

N
(STP cm^3)
100
50
0
0
0.1
0.5
1.0
(P/P$_o$)

Figure (3-5)

Family of argon isotherms at $73^{\circ}K \leq T \leq 87^{\circ}K$

BET $N_m = 22$ STP cm^3 at $87^{\circ}K$

BET $N_m = 21$ STP cm^3 at $73^{\circ}K$

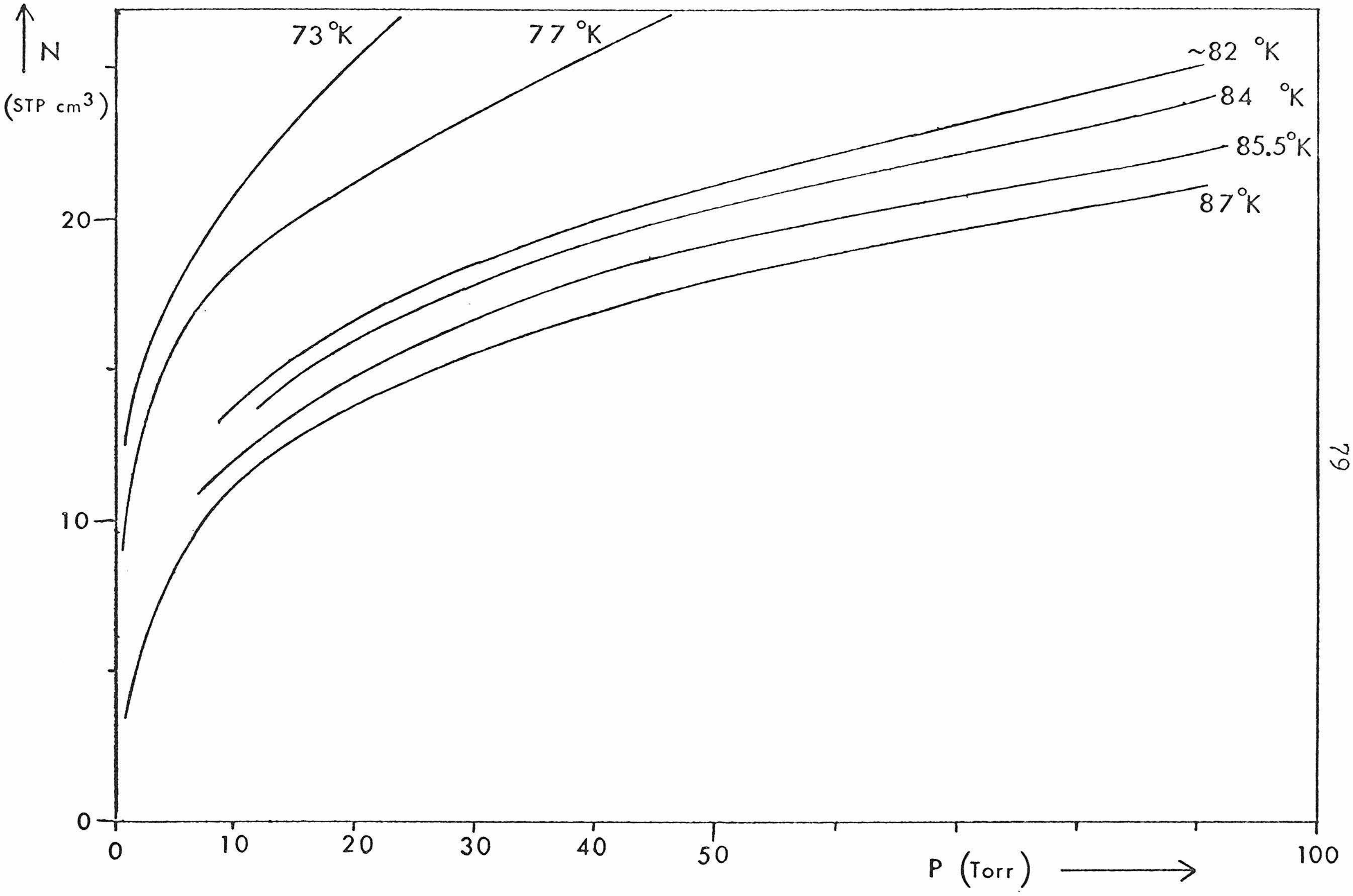

N
(STP cm^3)
0
10
20
0
10
20
30
40
50
100
P (Torr)
73°K
77 °K
~82 °K
84 °K
85.5°K
87°K

Figure (3-6)

Krypton isotherm at 109°K

BET $N_m = 16.7$ STP cm^3

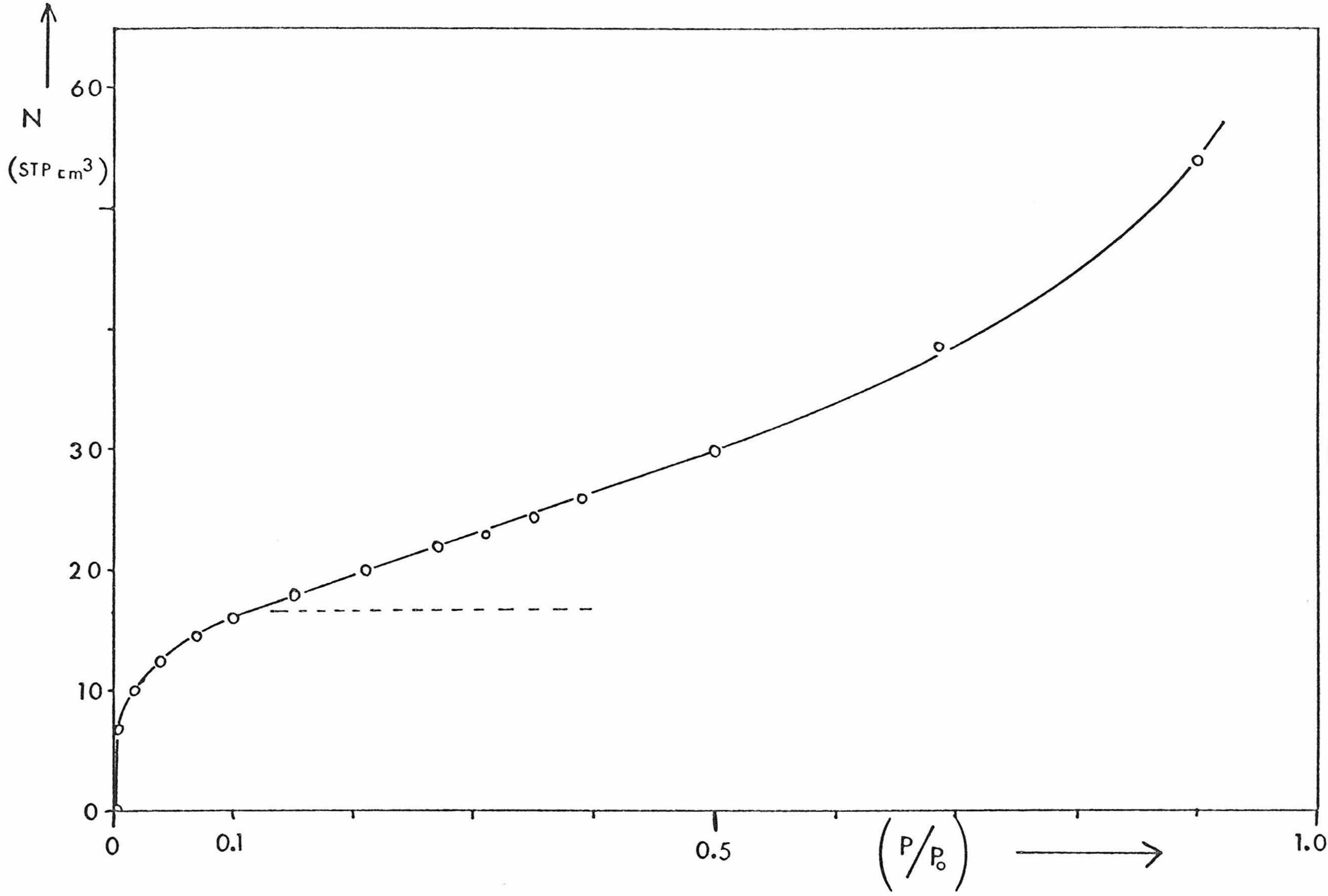

N
(STP cm^3)
60
30
20
10
0
0
0.1
0.5
1.0
(P/P$_o$)

Figure (3-7)

Xenon isotherm at 145°K

BET N_m = 12.5 STP cm^3

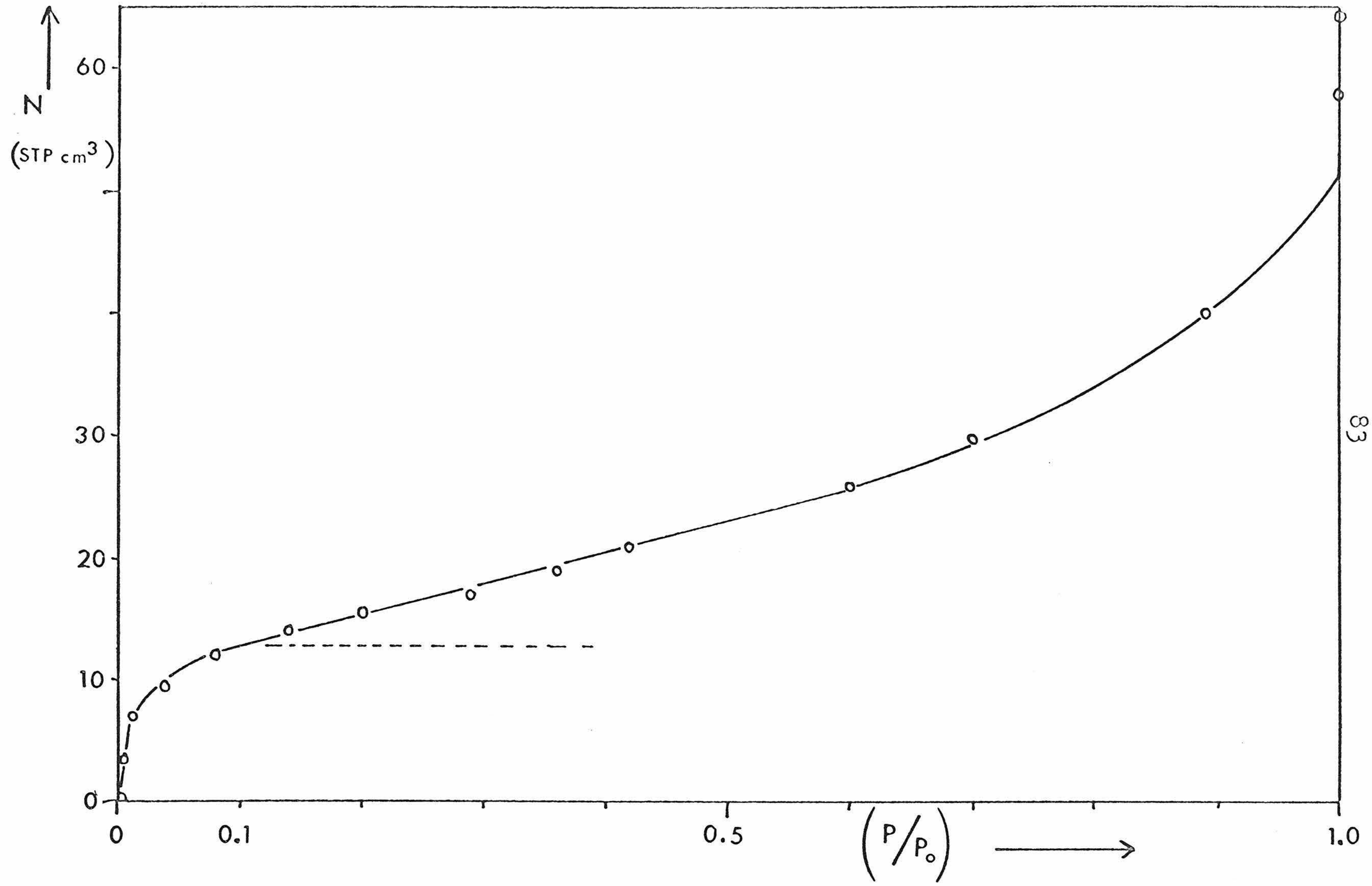
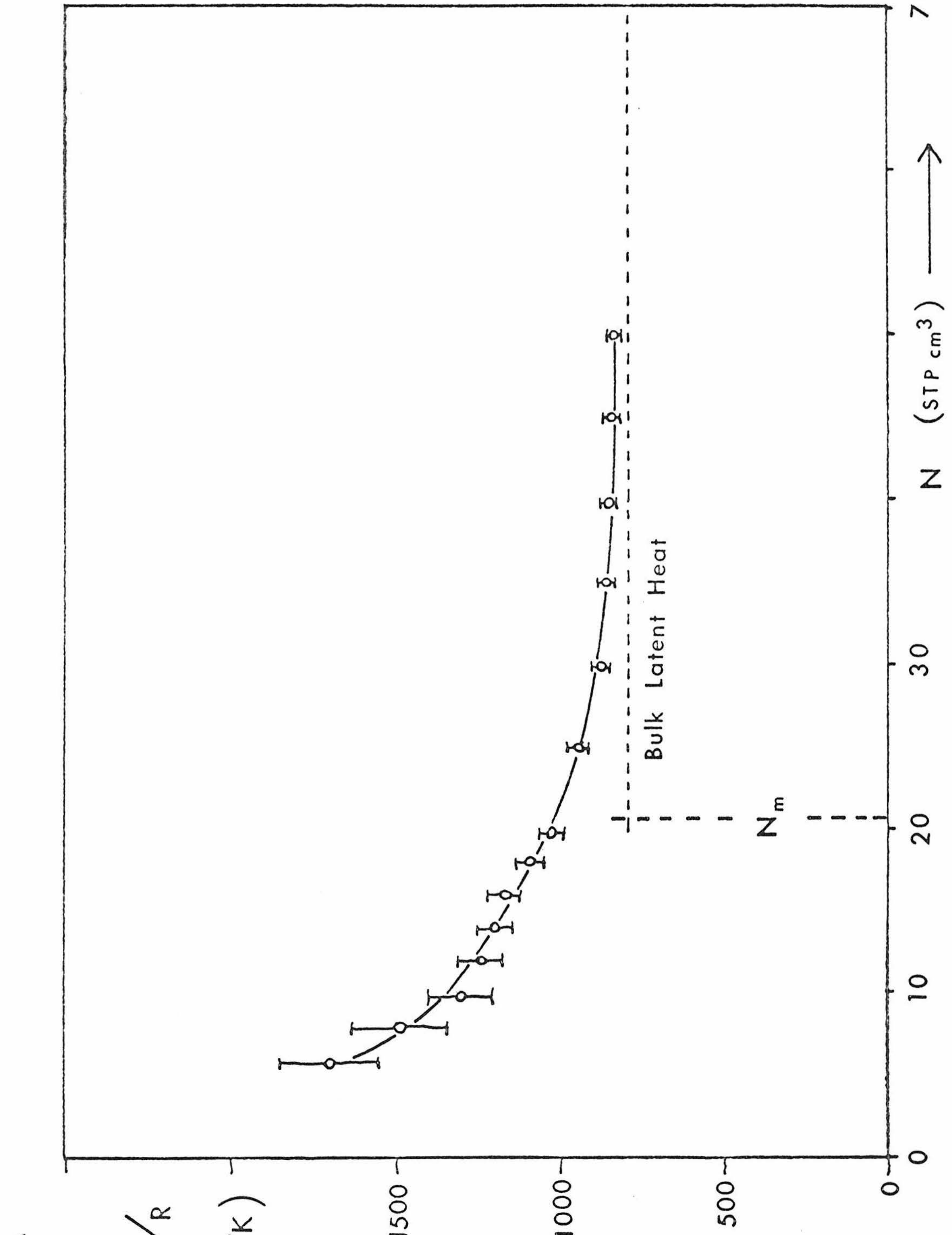

N
(STP cm^3)
60
30
20
10
0
0
0.1
0.5
1.0
(P/P_o)

Figure (3-8)

Isosteric heat of adsorption of argon on bare copper; derived from the data of figure (3-5)

Note that q_{st} is practically equal to the bulk latent heat for $N/N_m > 1.5$.


q_ST/R
(°K)
1500
1000
500
0
0
10
20
30
70
N (STP cm³)
Bulk Latent Heat
N_m

If suitable assumptions are made concerning the way in which the atoms are packed on the surface and in the bulk state at the same temperature, then the known bulk state densities can be related to the areal density on the surface; conventionally, the following equation is used(66):

$$\sigma_m = 3.46 \times 10^{16} \left[\frac{M}{4\sqrt{2}\, N_o \rho_b} \right]^{2/3} \qquad (3\text{-}1)$$

where:

σ_m is the area/molecule in $\mathring{A}^2$

M is the molecular weight

N_o is Avogadro's number

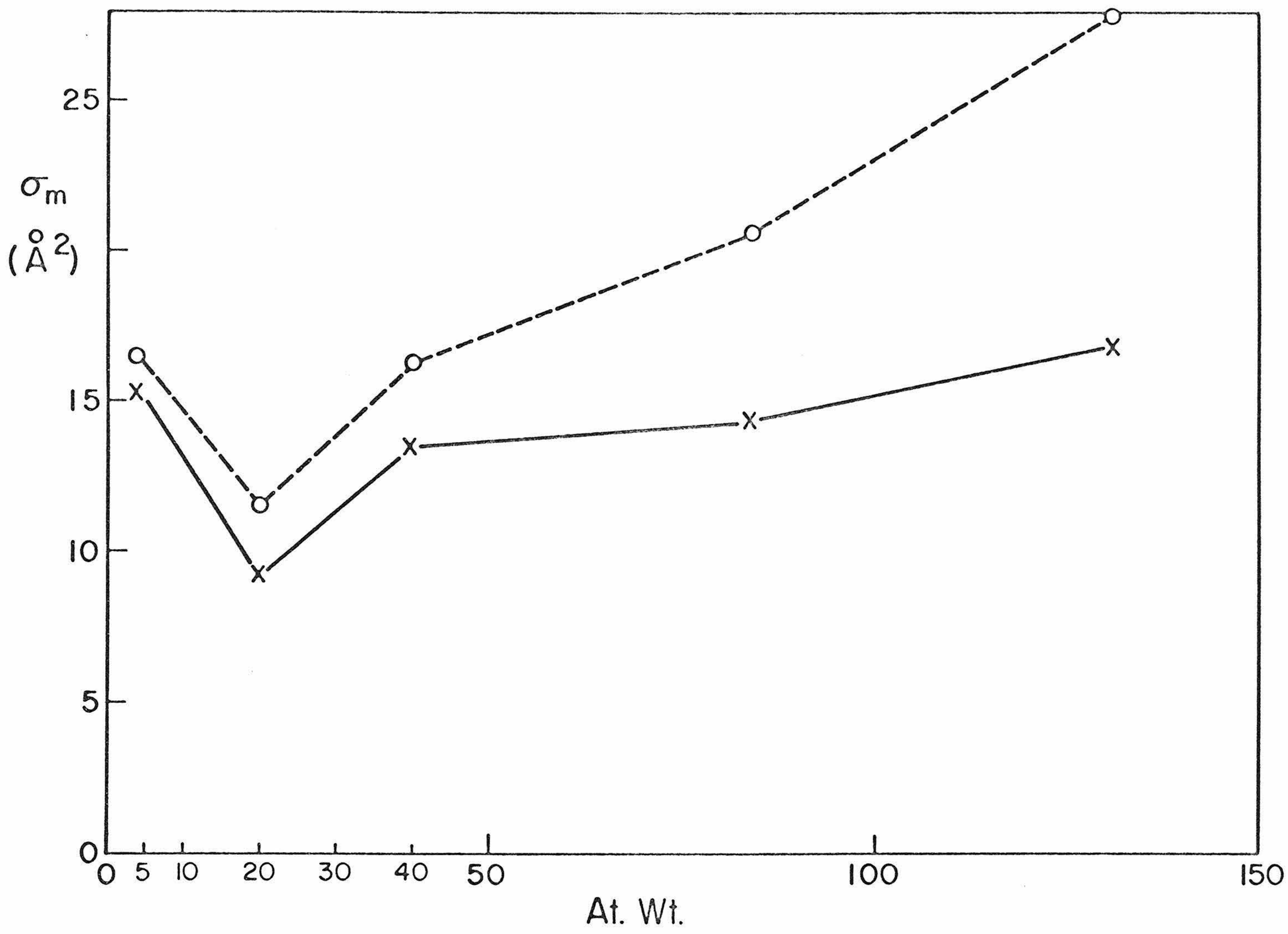
ρ_b is the bulk density in grams/cm^3

The areal density, σ_m, together with the monolayer capacity, N_m, may be used to derive the surface area of the substrate; conversely if the area is known, N_m may be used as a check on the value of σ_m determined by equation 3-1. In accordance with common practice, the nitrogen BET monolayer capacity at 77°K was used to determine the area of the sponge, resulting in a value of 0.94×10^6 cm^2 = 94 m^2. This area was used with the other monolayer values to determine an experimental σ_m for each noble gas which is compared with the results of equation 3-1 in figure (3-9). The

Figure (3-9)

The area occupied per molecule for
the various rare gases

The dashed curve shows the area found experimentally from the monolayer values and the surface area estimate of 94 m^2; the solid curve shows the areas predicted by equation 3-1.


σ_m
($\mathring{A}^2$)
25
15
10
5
0
0
5
10
20
30
40
50
100
150
At. Wt.

point for He^4 was actually taken on Ar-plated copper rather than on bare copper but it nevertheless maintains the good agreement set by the other data.

3.2 Main helium results

In any adsorption study the adsorbing surface is necessarily enclosed in a dead volume; this includes the volume of the measuring instruments at room temperature, the volume of the filling tube (partly at room temperature and partly at bath temperature), and the volume of the pores separating the sintered copper flakes as well as the volume of the hole in the center of the sponge. Whenever a charge of gas is admitted to the sponge, some of it remains in the gas phase. Since the adsorption measurements are concerned only with that portion of the gas which is adsorbed, a gas phase correction must be subtracted. In general, this fact makes it impossible to measure isosteres directly since the coverage will change with temperature; happily however, in the case of helium submonolayers below $4.2^{\circ}K$, the gas phase correction is so small that it can be ignored.

However there are still important considerations which must be applied to the raw experimental pressure data before the isosteres can be presented. Aside from the obvious and routine (if somewhat tedious) task of calibrating the pressure gauges there are also the problems of the thermomolecular effect and of ensuring true equilibrium. (The discussion of this last point will be deferred to section 3.3.)

Whenever one attempts to measure the pressure of a gas at low temperature with a gauge at room temperature, the thermomolecular effect (thermal transpiration) must be considered. Briefly, the pressure measured by the warm gauge is always greater than the actual pressure in the cold system. The magnitude of this effect is determined by: the nature of the gas being measured, the two temperatures (T_h and T_c), the actual pressures (P_h and P_c), the radius of the connecting tubing (R), and (possibly) the material of which the connecting tube is composed. If the connecting tube (the filling tube in our case) is of constant diameter in those regions where the temperature is changing, then the Weber-Schmidt equation, as quoted for helium by Keesom,(67) has been used in the past:

$$\text{Log}\,\frac{P_h}{P_c} = \tfrac{1}{2}\,\text{Log}\,\frac{T_h}{T_c} + 0.1813\,\text{Log}\,\frac{y_h + .1878}{y_c + .1878}$$

$$+ \quad .428 \operatorname{Log} \frac{y_h + 1.831}{y_c + 1.831} \quad - \quad .1582 \operatorname{Log} \frac{y_h + 4.993}{y_c + 4.993} \qquad (3\text{-}2)$$

where:

R = radius of filling tube in centimeters

$y_i = R/L_i$

$$L_i = \frac{17.85\ (T_i/273.1)^{1.147}}{P_i}$$

(the pressures, P_i are expressed in microbars)

This set of implicit equations was solved numerically on the IBM 360/50 computer(68) for the temperatures of interest. If the pressures at both ends of the filling tube are so low that the gas therein is in the region of free molecular flow ($L_i \gg R$) then the equation is considerably simplified:

$$P_h/P_c = (T_h/T_c)^{\frac{1}{2}} \qquad (3\text{-}3)$$

This condition prevailed for many of the measurements; it can magnify the pressure seen by the gauges by factors of ten or more.

Recent work(69,70) has indicated that the magnitude of the thermomolecular correction may be influenced by the material of which the connecting tube is constructed. Weber and Schmidt made their classic study with glass tubing but many recent experiments have used stainless steel or cupro-nickel (present work) tubing. The preliminary results of reference (70) indicate that these are second order effects in the pressure ranges with which we are concerned--smaller than the scatter of the data points--but that they may be more important at slightly higher pressures or in more refined studies.

In any event, all of the data in this paper with the exception of figure (3-22) were analyzed on the basis of the original Weber-Schmidt equation and constants. The basic data--families of isosteres--are shown in figures (3-10) - (3-14). The same measurements were performed on a substrate consisting of bare copper, precoated with ~ 1.0 monolayer of the noble gas in each case; for the argon precoat, a second run was carried out with a precoating of ~ 1.4 monolayers in order to examine the effects of changing this parameter. These runs will be referred to as: Ne, Ar 1.0, Ar 1.4, Kr, and Xe. Most of the other results in this paper were derived from these isosteres, including the isosteric heat of adsorption, the partial molar entropy, the entropy, and the heat capacity of the film; as well as the adsorption isotherms.

Figure (3-10)

The family of isosteres for helium
on neon-coated copper

Notes:

The third parameter is the coverage in STP cm^3.

A few points have been left out for clarity, but the scatter shown is representative.

The connecting lines are only for clarity and are not necessarily identical to the computer-derived fits discussed in the text.

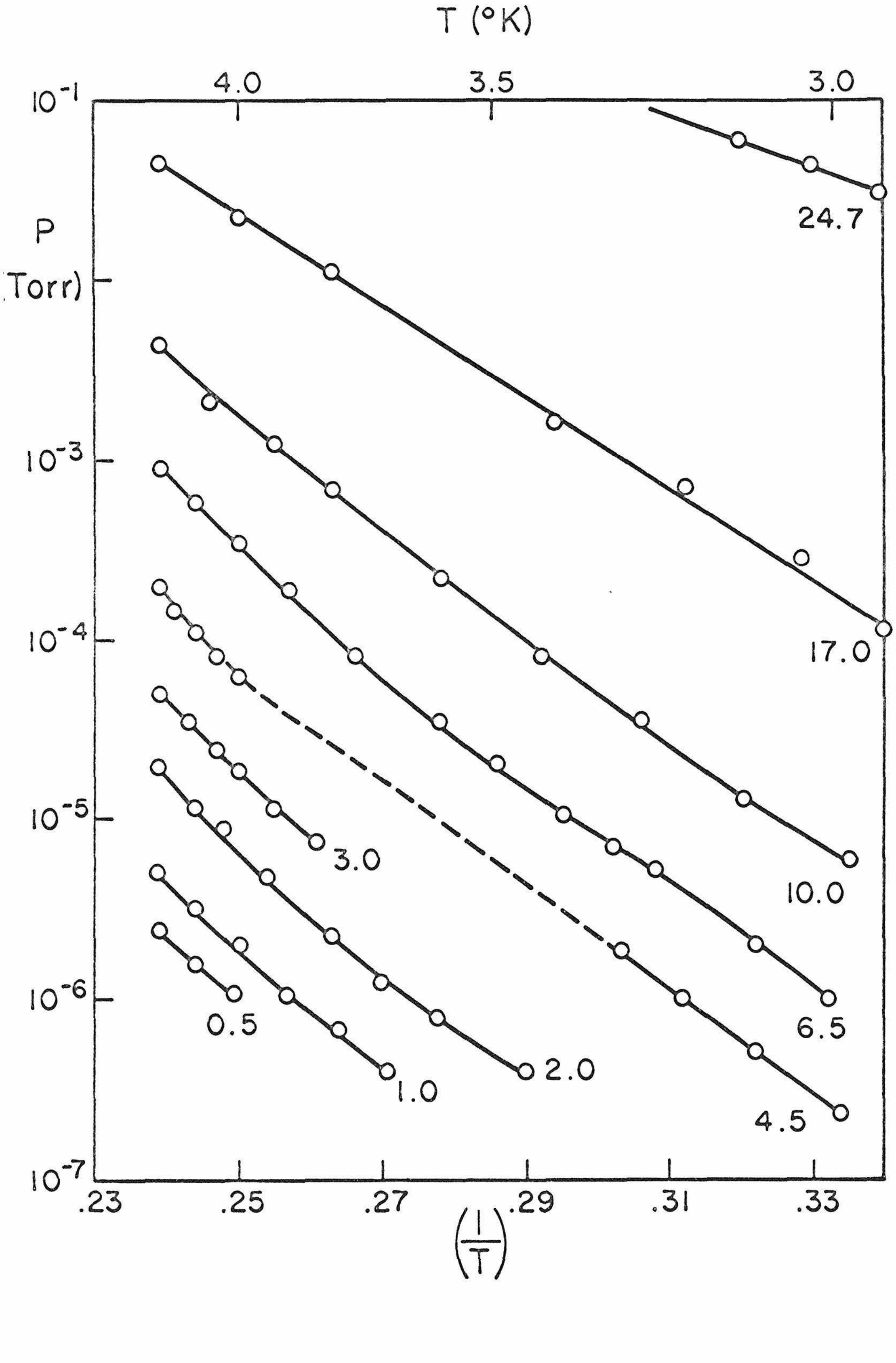
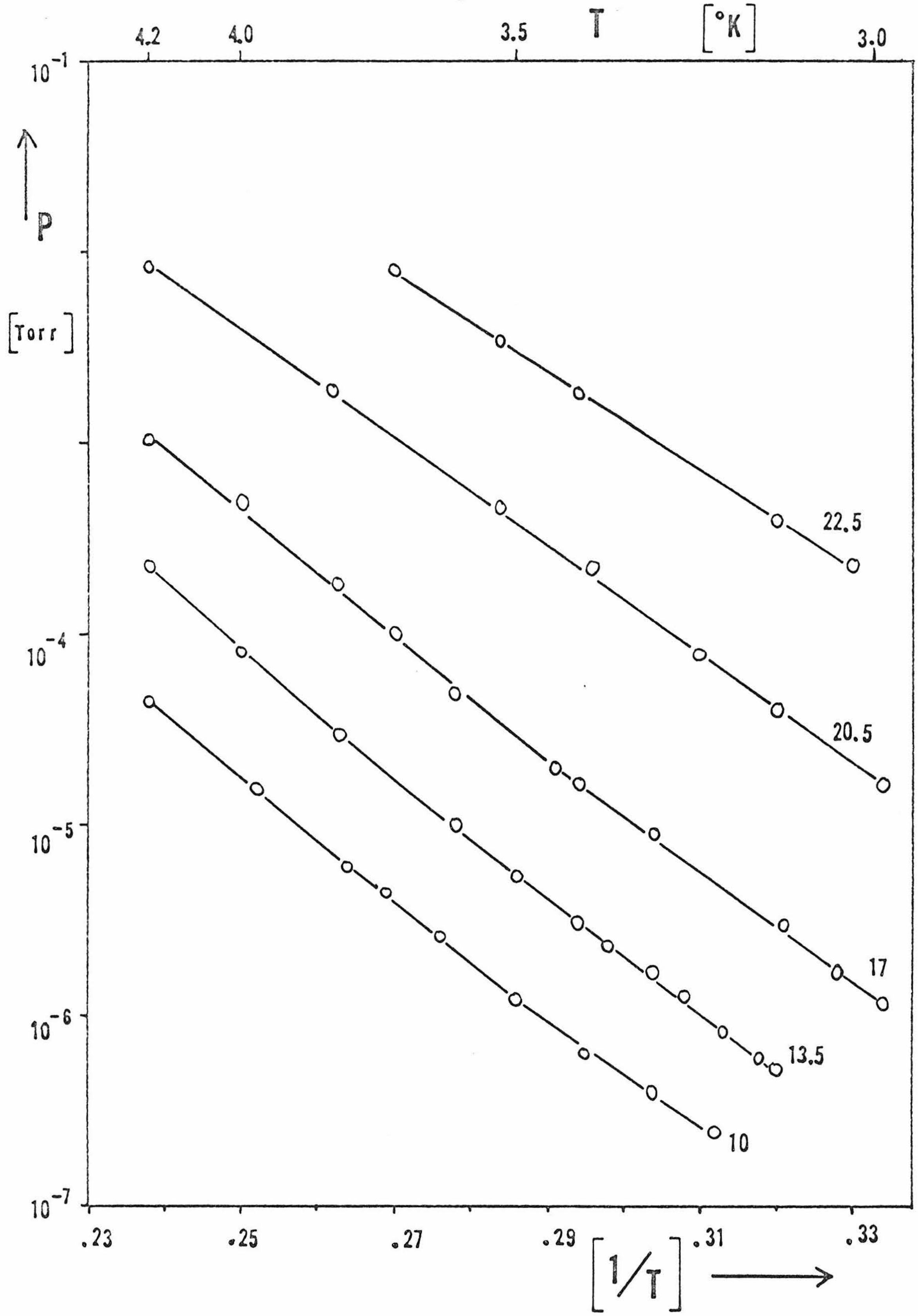

T (°K)
4.0
3.5
3.0
10^{-1}
P
(Torr)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
24.7
17.0
10.0
6.5
4.5
3.0
2.0
1.0
0.5
.23
.25
.27
.29
.31
.33
$\left(\frac{1}{T}\right)$

Figure (3-11)

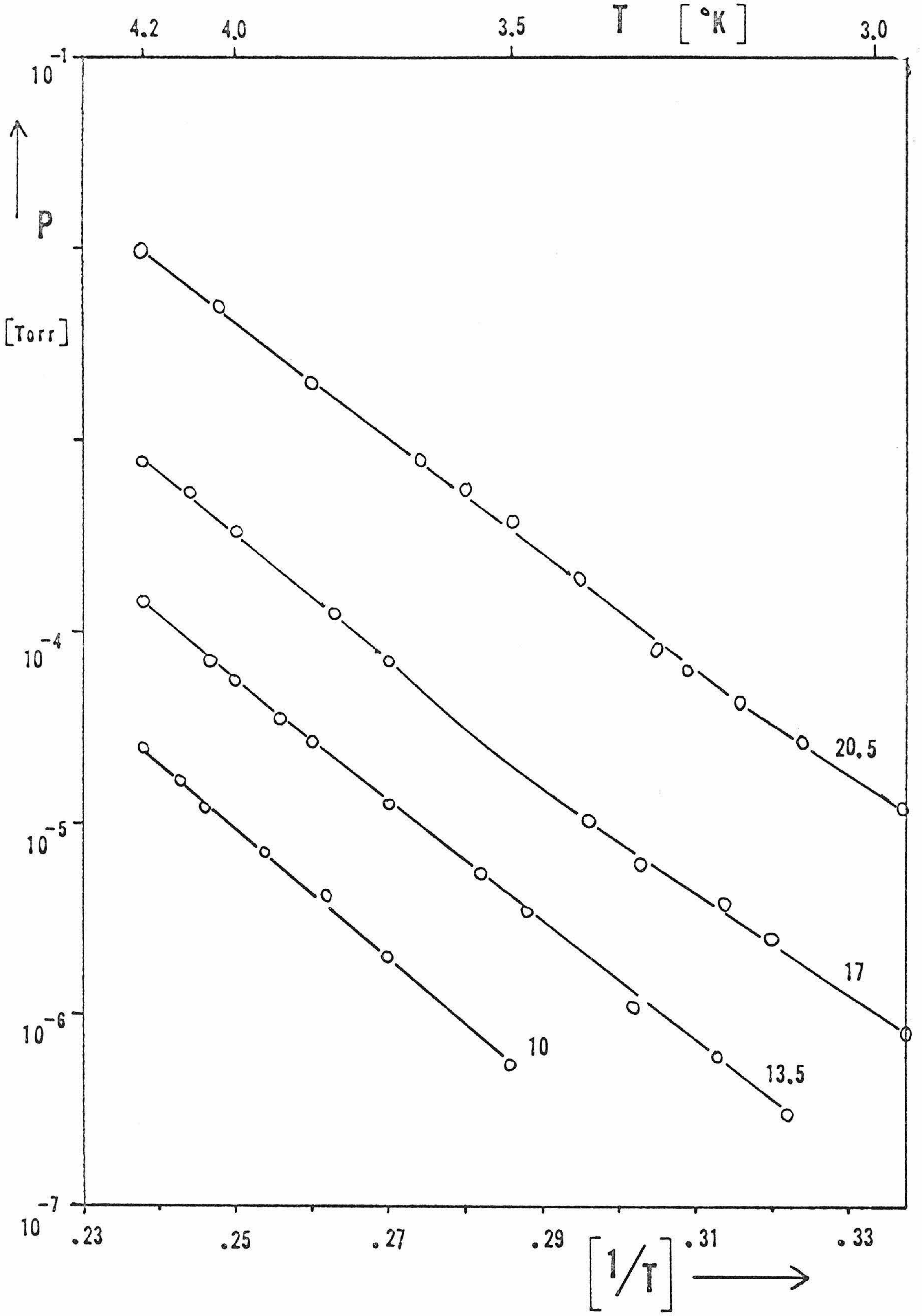
Isosteres on Ar 1.0



4.2
4.0
3.5
T
[°K]
3.0
10^{-1}
P
[Torr]
10^{-4}
10^{-5}
10^{-6}
10^{-7}
22.5
20.5
17
13.5
10
.23
.25
.27
.29
.31
.33
[1/T]

Figure (3-12)

Isosteres on Ar 1.4



T [°K]
4.2
4.0
3.5
3.0
P [Torr]
10^{-1}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
20.5
17
13.5
10
.23
.25
.27
.29
.31
.33
[1/T]

Figure (3-13)

Isosteres on Kr

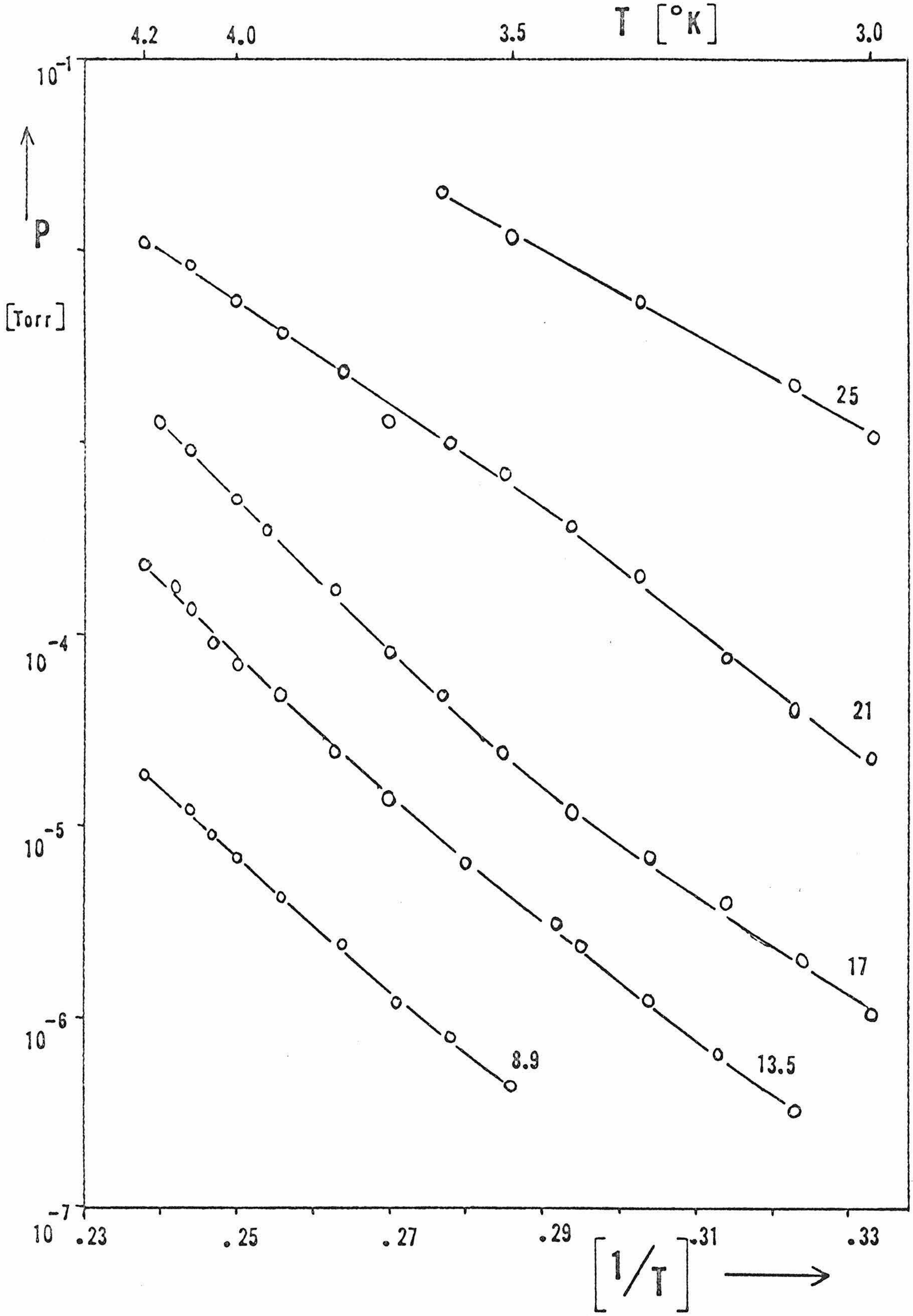
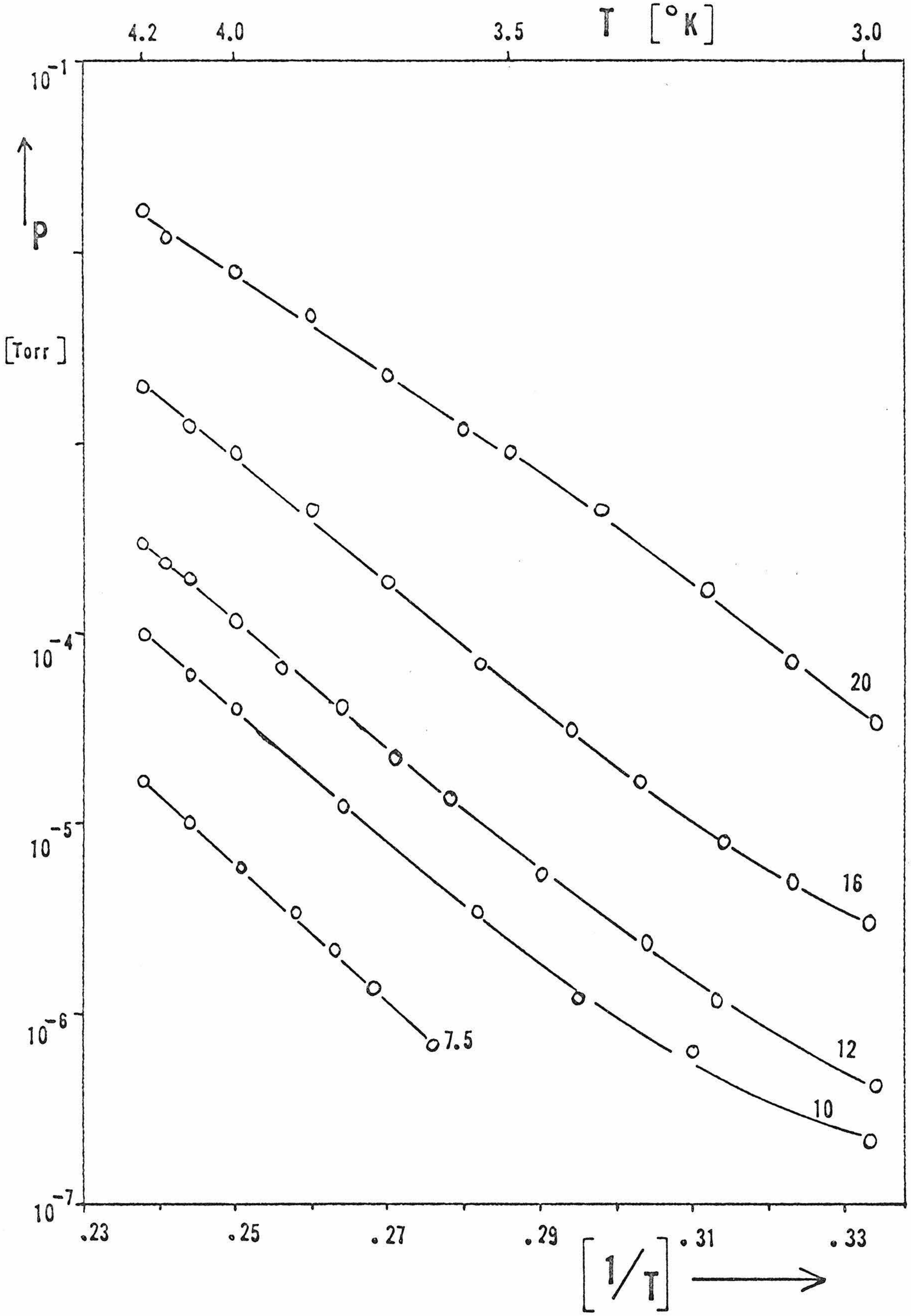

T [°K]
4.2
4.0
3.5
3.0
P
[Torr]
10^-1
10^-4
10^-5
10^-6
10^-7
.23
.25
.27
.29
.31
.33
[1/T]
25
21
17
13.5
8.9

Figure (3-14)

Isosteres on Xe


4.2
4.0
3.5
T [°K]
3.0
10^{-1}
P
[Torr]
10^{-4}
10^{-5}
10^{-6}
10^{-7}
.23
.25
.27
.29
.31
.33
[1/T]
20
16
12
10
7.5

To a first approximation, the isosteres are straight, parallel lines free from any observable steps or discontinuites. The errors in the data are small enough, however, that the departures from constant slope--i.e. variations in q_{st} with N and T--may be analyzed. In order to accomplish this, the points from each of the 28 isosteres were fitted to a polynomial of the form:

$$\mathrm{Ln}\ (P) = a_1 + a_2 \left[\frac{1}{T}\right] + a_3 \left[\frac{1}{T}\right]^2$$

using a modification of the standard "REGRES" and "INVERT" programs of the Citran version of the IBM 360/50 computer. This procedure produced values for the a_i, as well as standard errors, $\sqrt{(\Delta a_i)^2}$ and correlations, $\sqrt{(\Delta a_i)\ (\Delta a_j)}$. The isosteric heat of adsorption and its error were then determined at selected temperatures along each isostere according to the relationships:

$$\frac{q_{st}}{R} \equiv - \frac{\partial \mathrm{Ln}(P)}{\partial(1/T)}_N = -a_2 - 2a_3 \left[\frac{1}{T}\right]$$

and

$$\Delta(q_{st}/R) = \sqrt{(\Delta a_2)^2 + (4/T)(\Delta a_2)(\Delta a_3) + (4/T^2)(\Delta a_3)^2}$$

Finally, $\partial S/\partial NR$ and its standard error were determined from q_{st}/R using equation 1-3 and 1-4; the error in $\partial S/\partial NR$ contains an additional term of ±0.2 due to the estimated uncertainty of ~ 20% in the absolute value of the pressure which appears in equation 1-4. The results of these manipulations appear in figures (3-15) - (3-19) and (3-20) - (3-24); additionally, figure (3-22) shows $\partial S/\partial NR$ calculated from a set of isosteres reduced with the preliminary data of reference (70) for the thermomolecular effect rather than with the Weber-Schmidt data. It can be seen that the differences are small. The results for all five substrates are reproduced in figure (3-25) where it can be seen that the curves behave similarly for each substrate. In all the figures (3-15 to 3-25) a coverage of 20 STP cm^3 corresponds roughly to one monolayer (see pp. 132 and 135).

If the curves for $\partial S/\partial NR$ could be extended to zero coverage, it would be a simple matter to integrate them numerically and obtain absolute values for the total entropy, S as a function of coverage. Even the Ne data which extend to the extremely low coverage of ~ 0.025 monolayer can not be extrapolated to zero coverage, however. (The reason for this, as well as our meaning of the term monolayer in this

Figure (3-15)

q_{st}/R as a function of coverage on Ne

○ at 4.2°K.

× at 3.0°K.

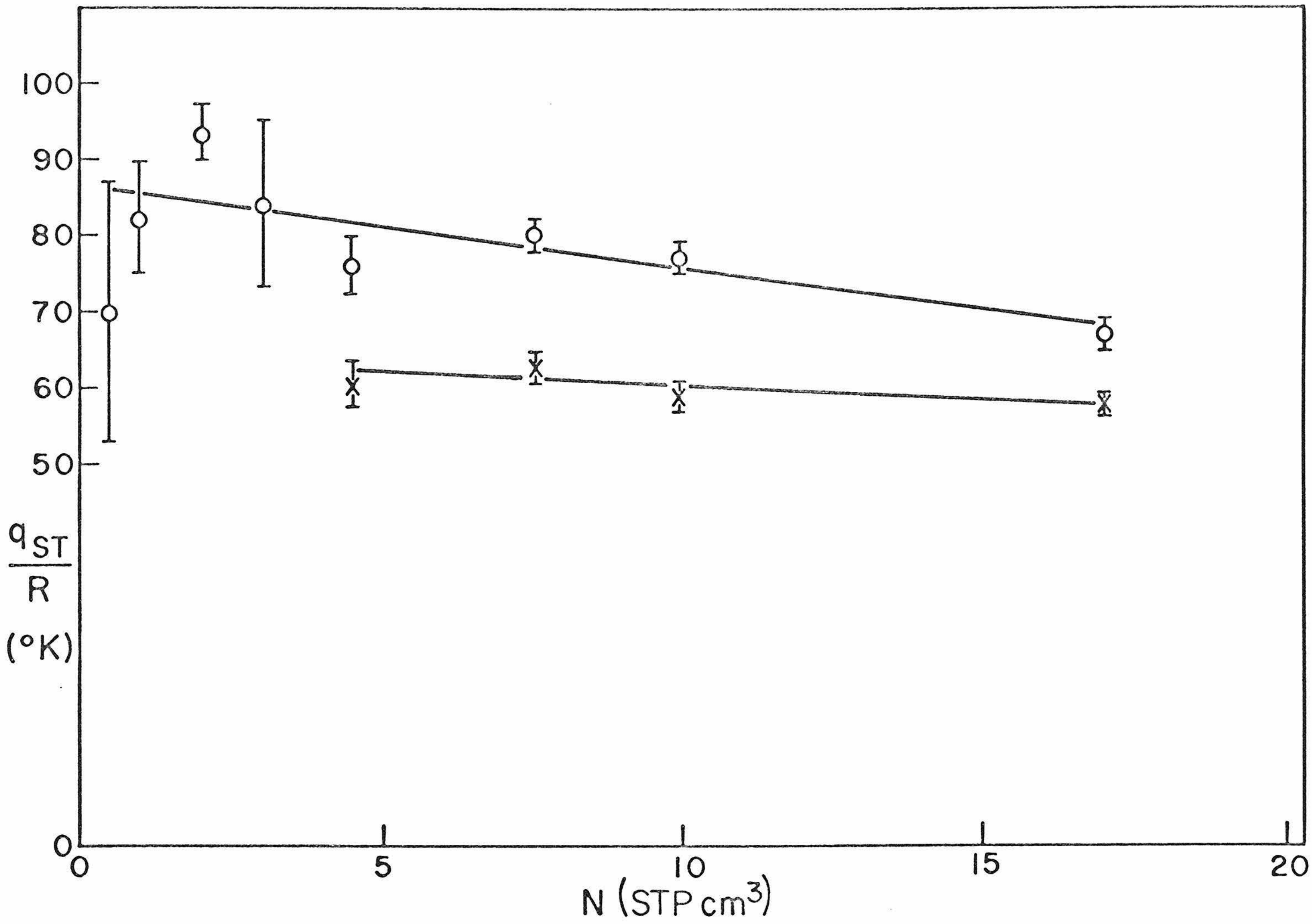

100
90
80
70
60
50
0
$\frac{q_{ST}}{R}$
(°K)
0
5
10
15
20
N (STP cm^3)

Figure (3-16)

q_{st}/R as a function of coverage on Ar 1.0

○ at $4.2^{\circ}K$.

× at $3.0^{\circ}K$.

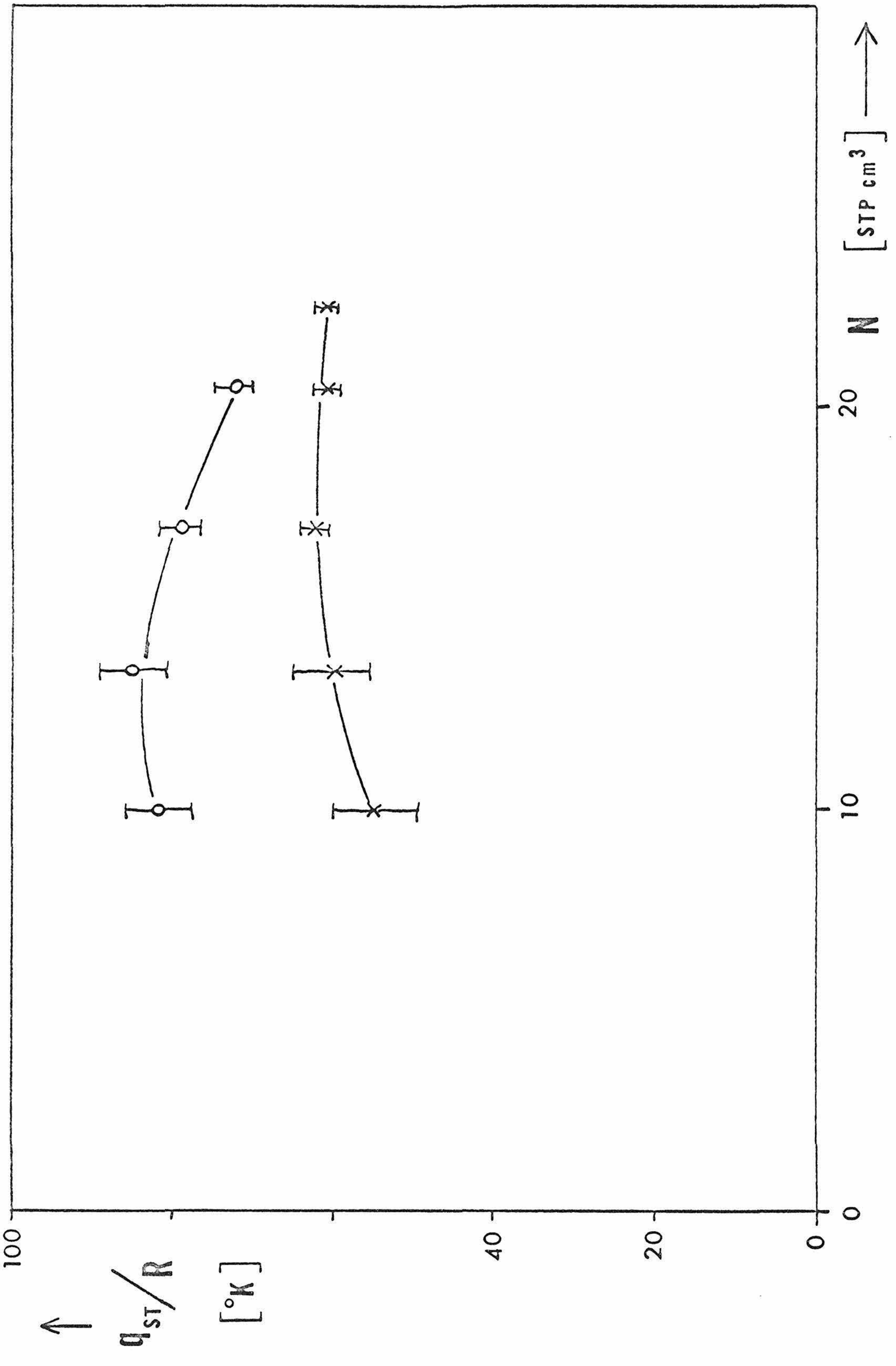

100
40
20
0
0
10
20
q_{ST}/R [°K]
N [STP cm^3]

Figure (3-17)

q_{st}/R as a function of coverage on Ar 1.4

○ at 4.2°K.

× at 3.0°K.

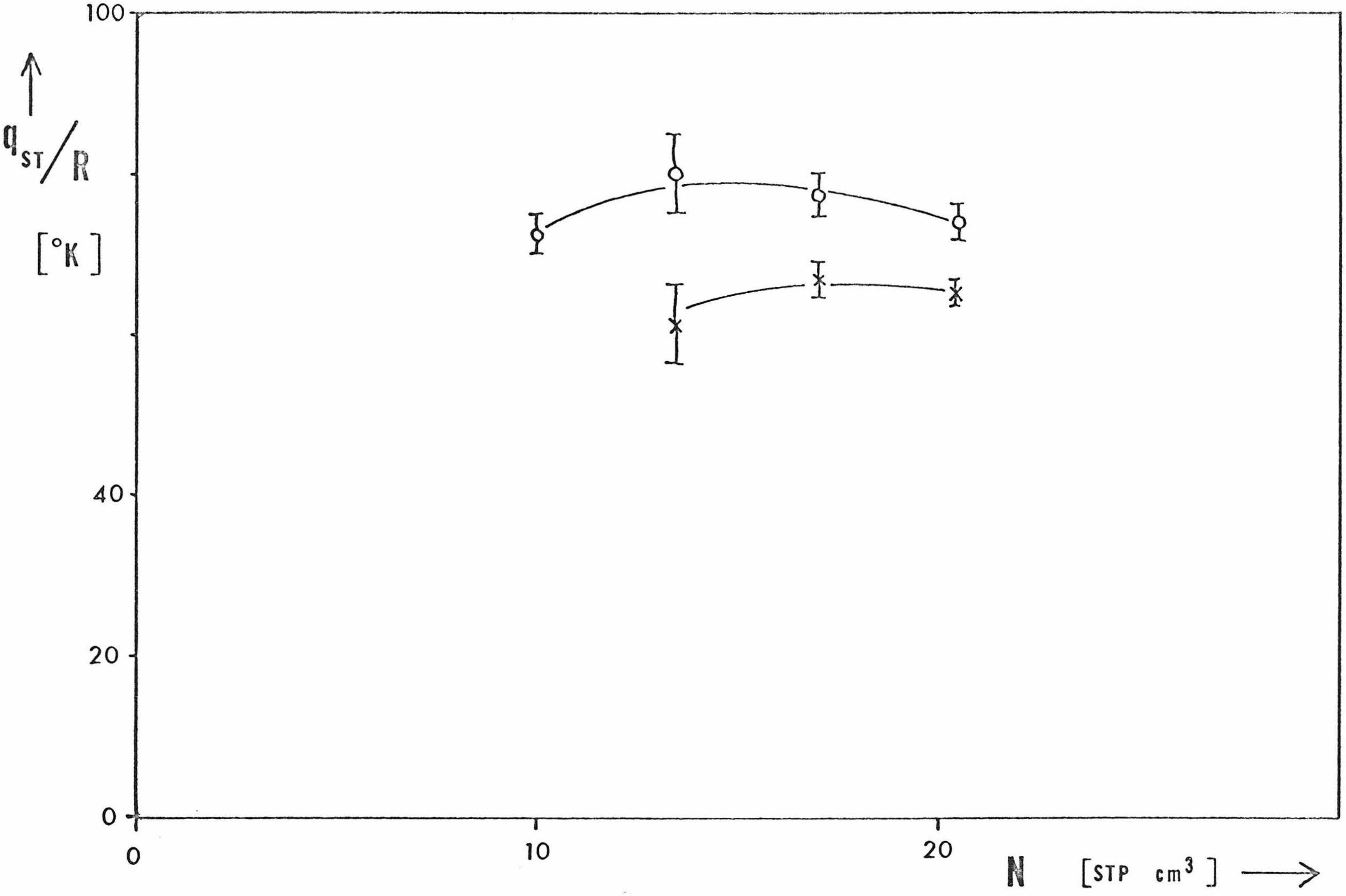

100
40
20
0
q_{ST}/R
[°K]
0
10
20
N [STP cm^3]

Figure (3-18)

q_{st}/R as a function of coverage on Kr

○ at 4.2°K.

× at 3.0°K.

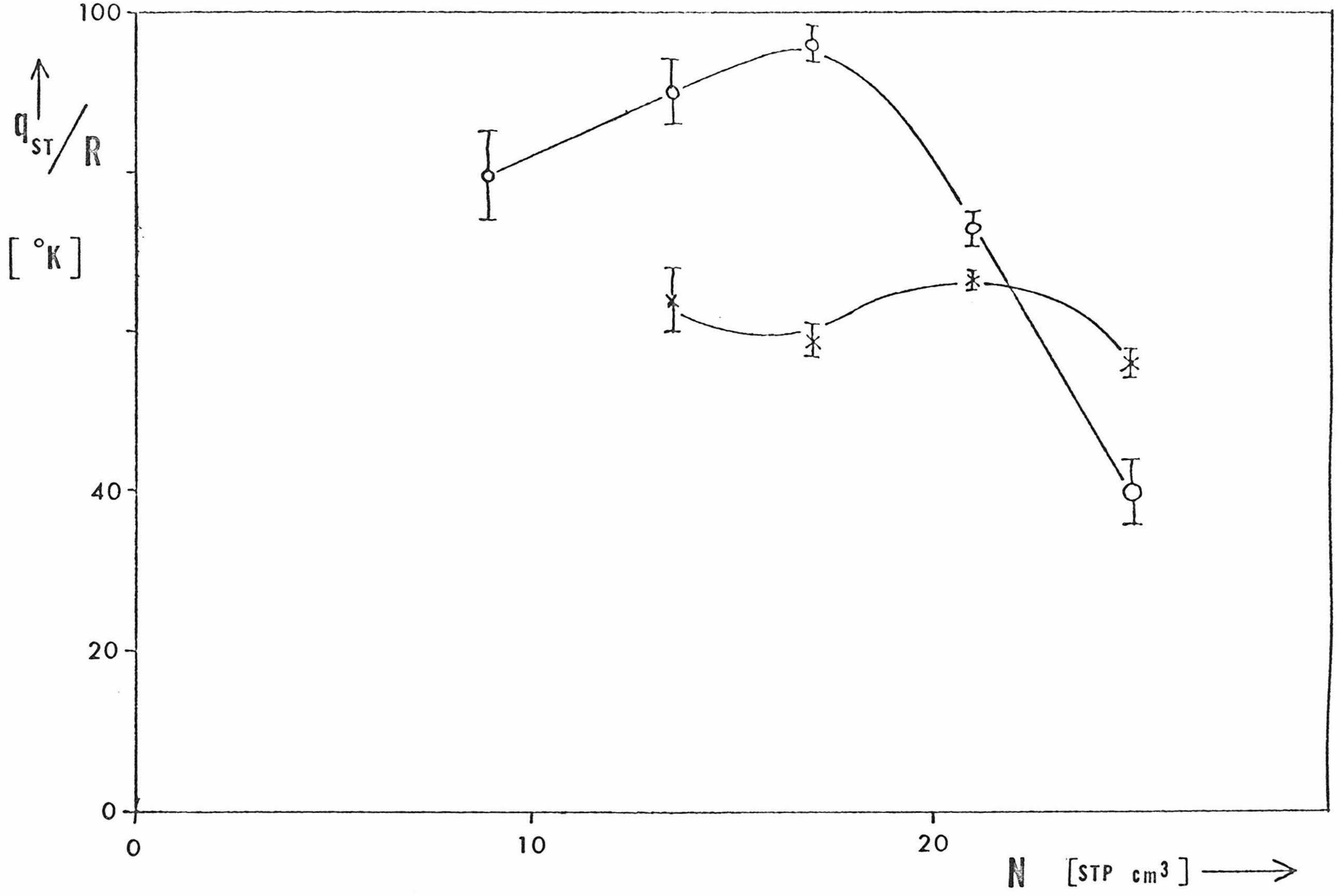

q_{ST}/R
[°K]
100
40
20
0
0
10
20
N [STP cm^3]

Figure (3-19)

q_{st}/R as a function of coverage on Xe

○ at 4.2°K.

× at 3.0°K.

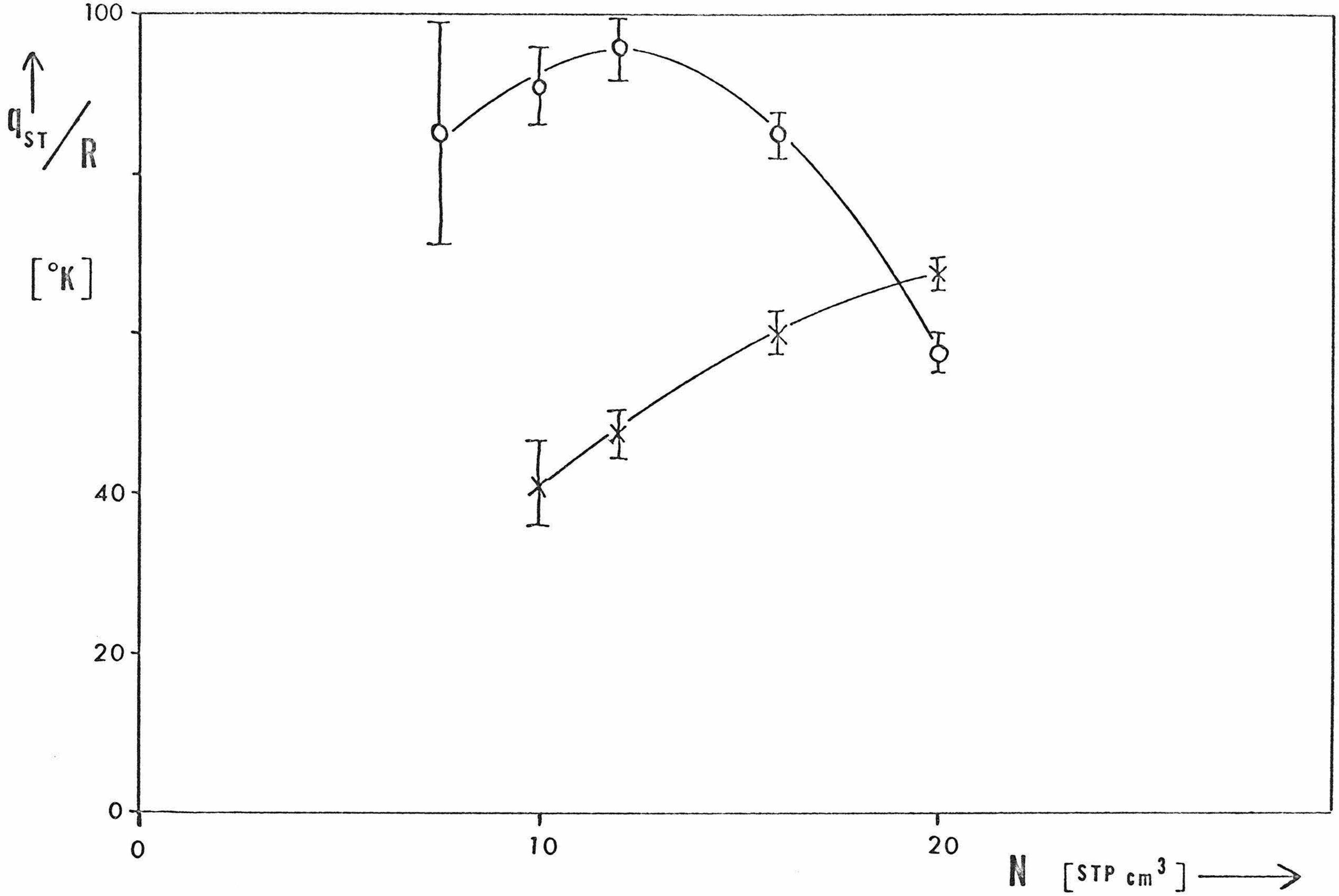

q_{ST}/R
[°K]
100
40
20
0
0
10
20
N [STP cm^3]

Figure (3-20)

The partial molar entropy, $\partial S/\partial NR$ as a function of coverage for helium on neon

○ at 4.2°K.

× at 3.0°K.

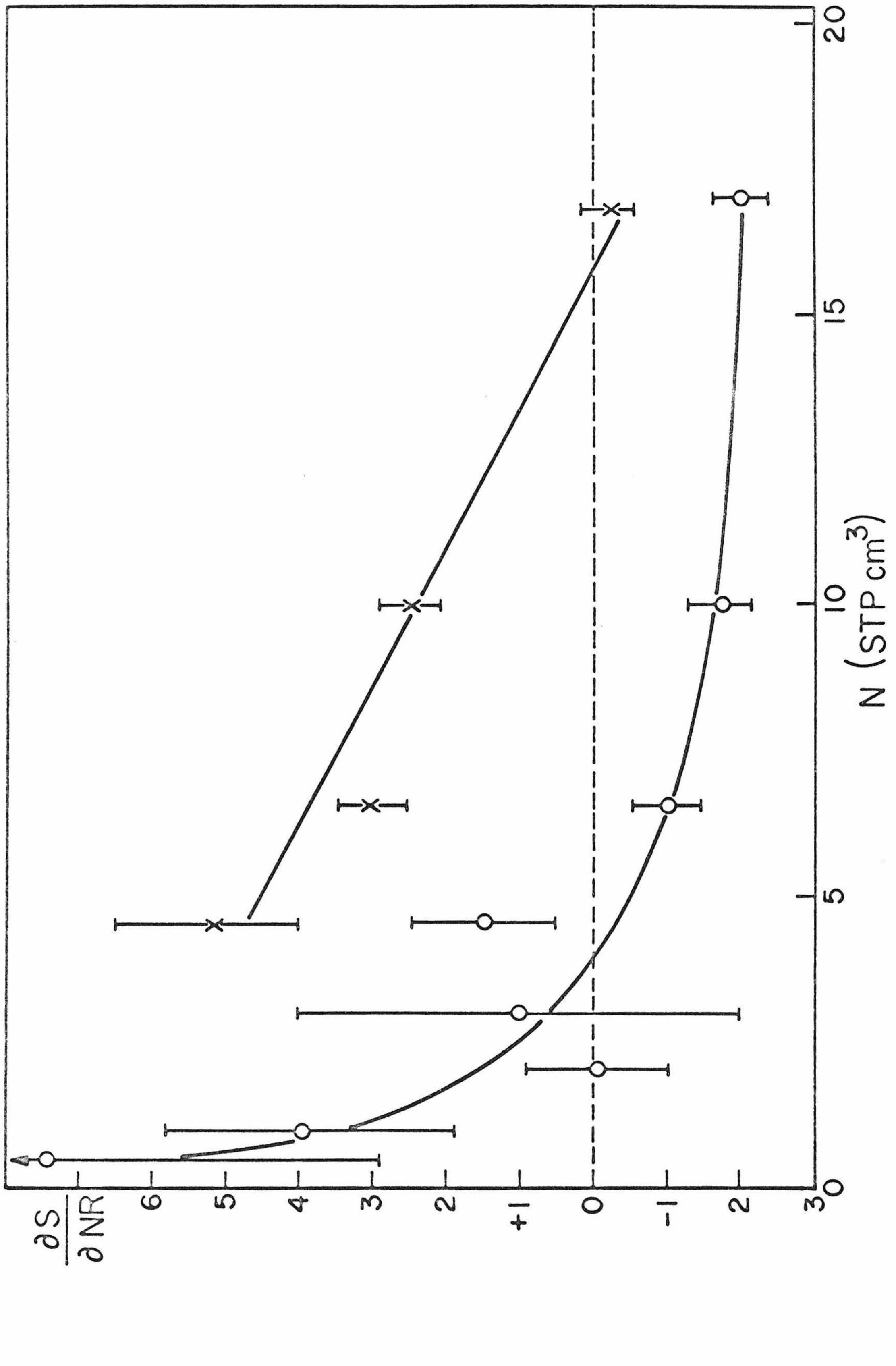

$\frac{\partial S}{\partial NR}$
6
5
4
3
2
+1
0
-1
2
3
0
5
10
15
20
N (STP cm^3)

Figure (3-21)

The partial molar entropy, $\partial S/\partial NR$ as a function of coverage for helium on argon 1.0

○ at 4.2°K

× at 3.0°K

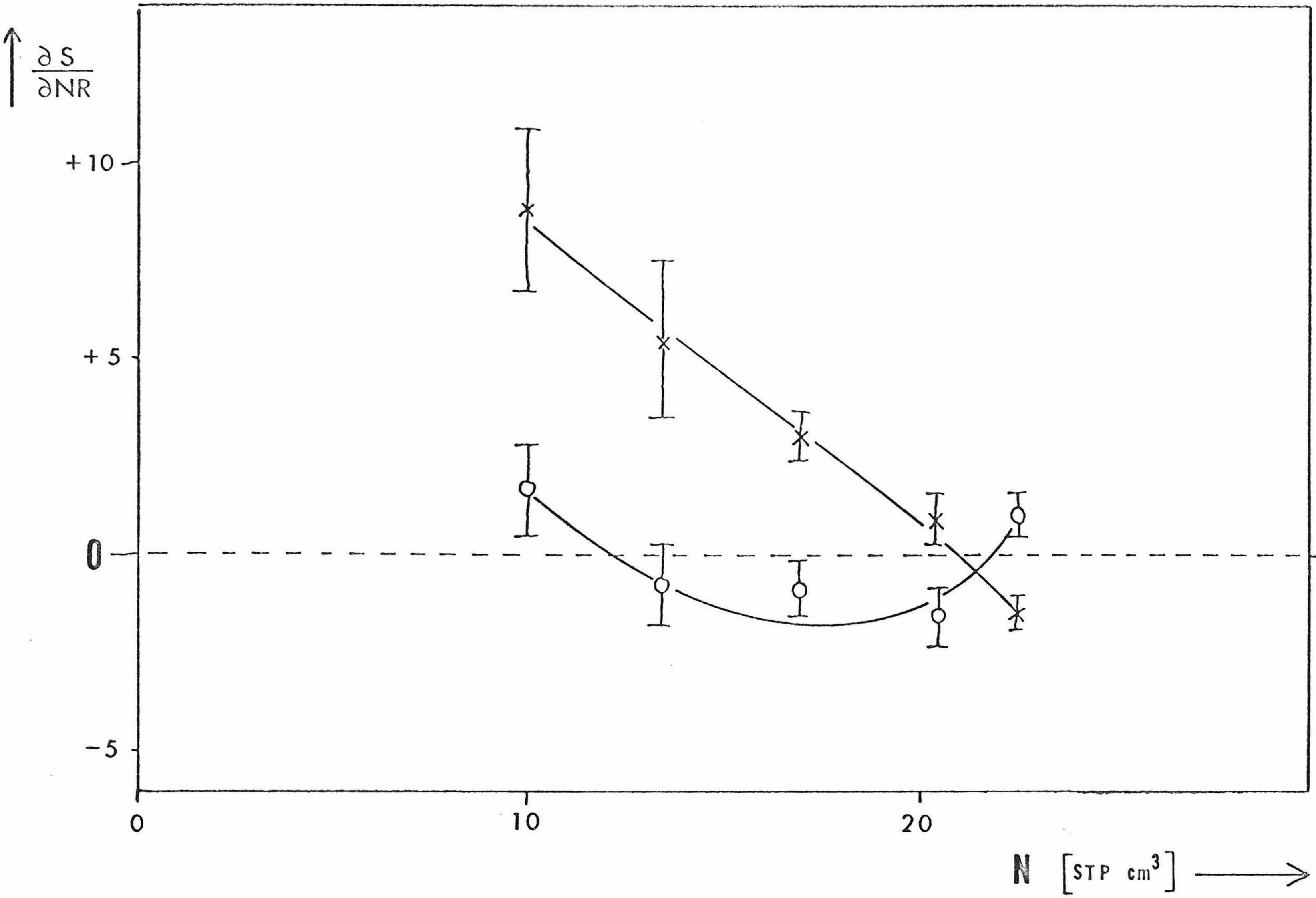

$\frac{\partial S}{\partial NR}$
+10
+5
0
-5
0
10
20
N [STP cm^3]

Figure (3-22)

∂S/∂NR as a function of N on Ar 1.4

$\overset{\top}{\underset{\bot}{\circ}}$ at 4.2°K.

$\overset{\top}{\underset{\bot}{\times}}$ at 3.0°K.

The dotted portion shows the change which would result from having used the preliminary results of reference (70) instead of the Weber-Schmidt results in the data reduction. See text.

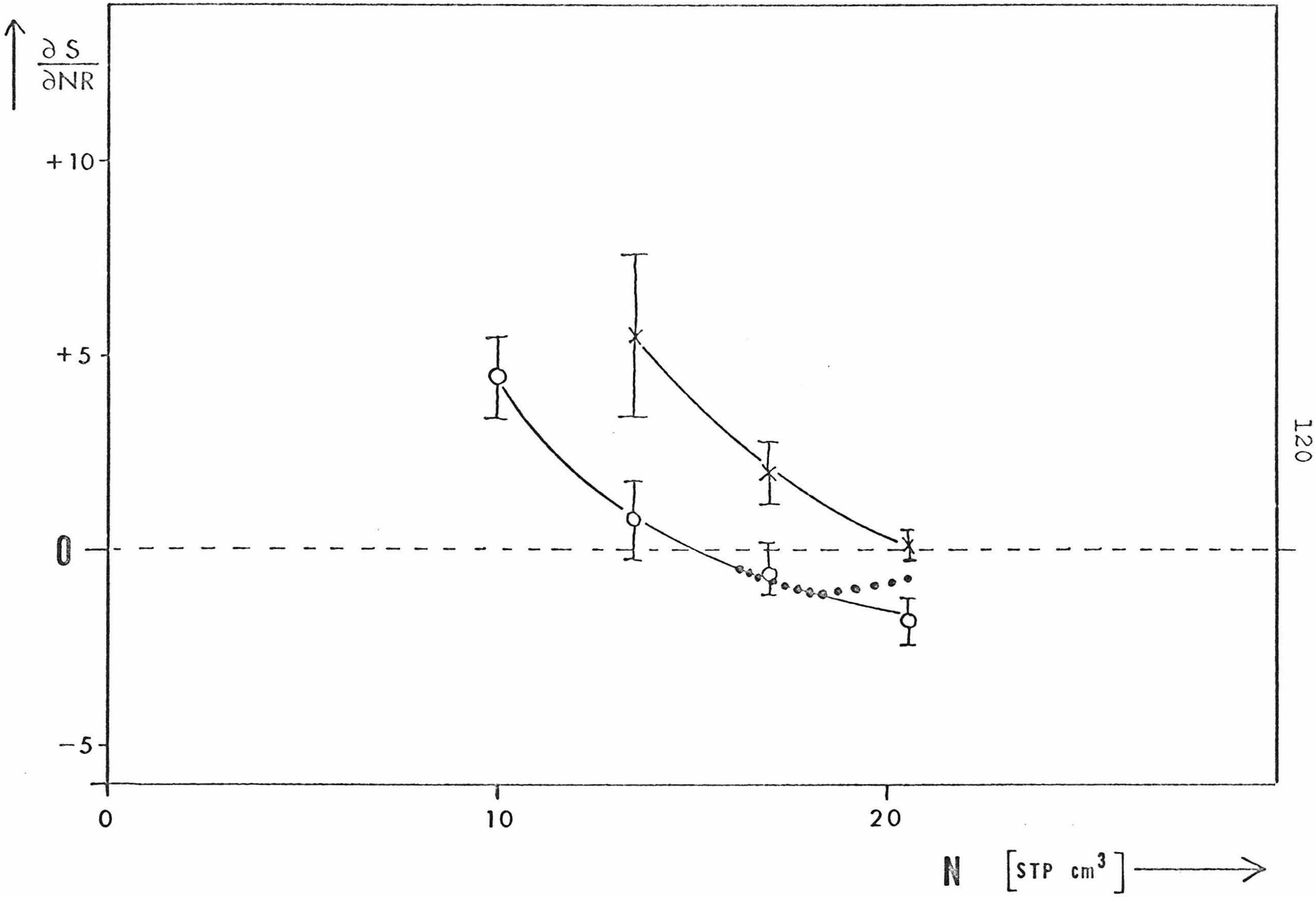

$\frac{\partial S}{\partial NR}$
+10
+5
0
−5
0
10
20
N [STP cm^3]

Figure (3-23)

The partial molar entropy, $\partial S/\partial NR$ as a function of coverage for helium on krypton

$\underset{\perp}{\overset{\top}{\circ}}$ at 4.2°K.

$\underset{\perp}{\overset{\top}{\times}}$ at 3.0°K.

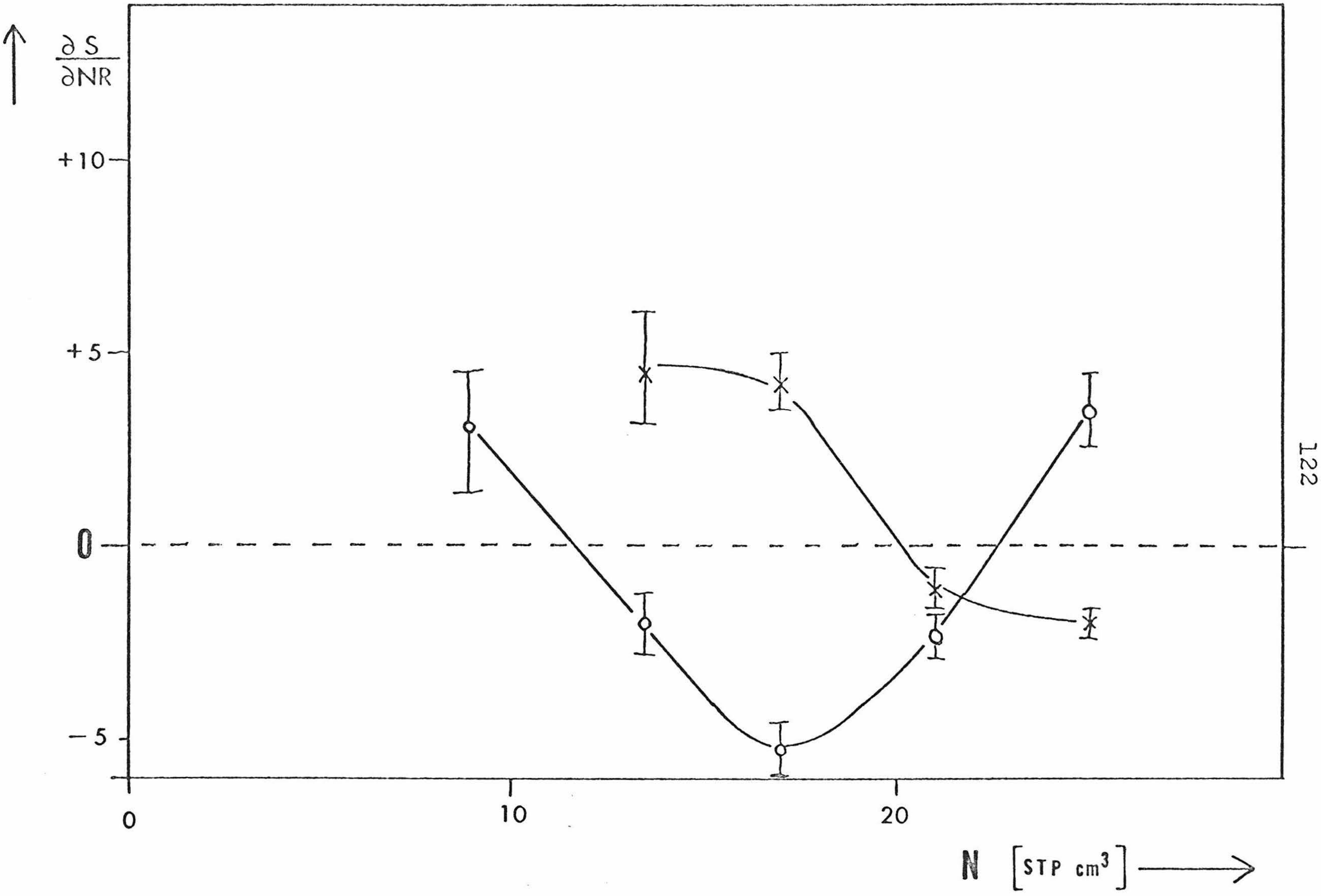

$\frac{\partial S}{\partial NR}$
+10
+5
0
−5
0
10
20
N [STP cm^3]

Figure (3-24)

The partial molar entropy, ∂S/∂NR as a function of coverage for helium on xenon

○ at 4.2°K.

× at 3.0°K.

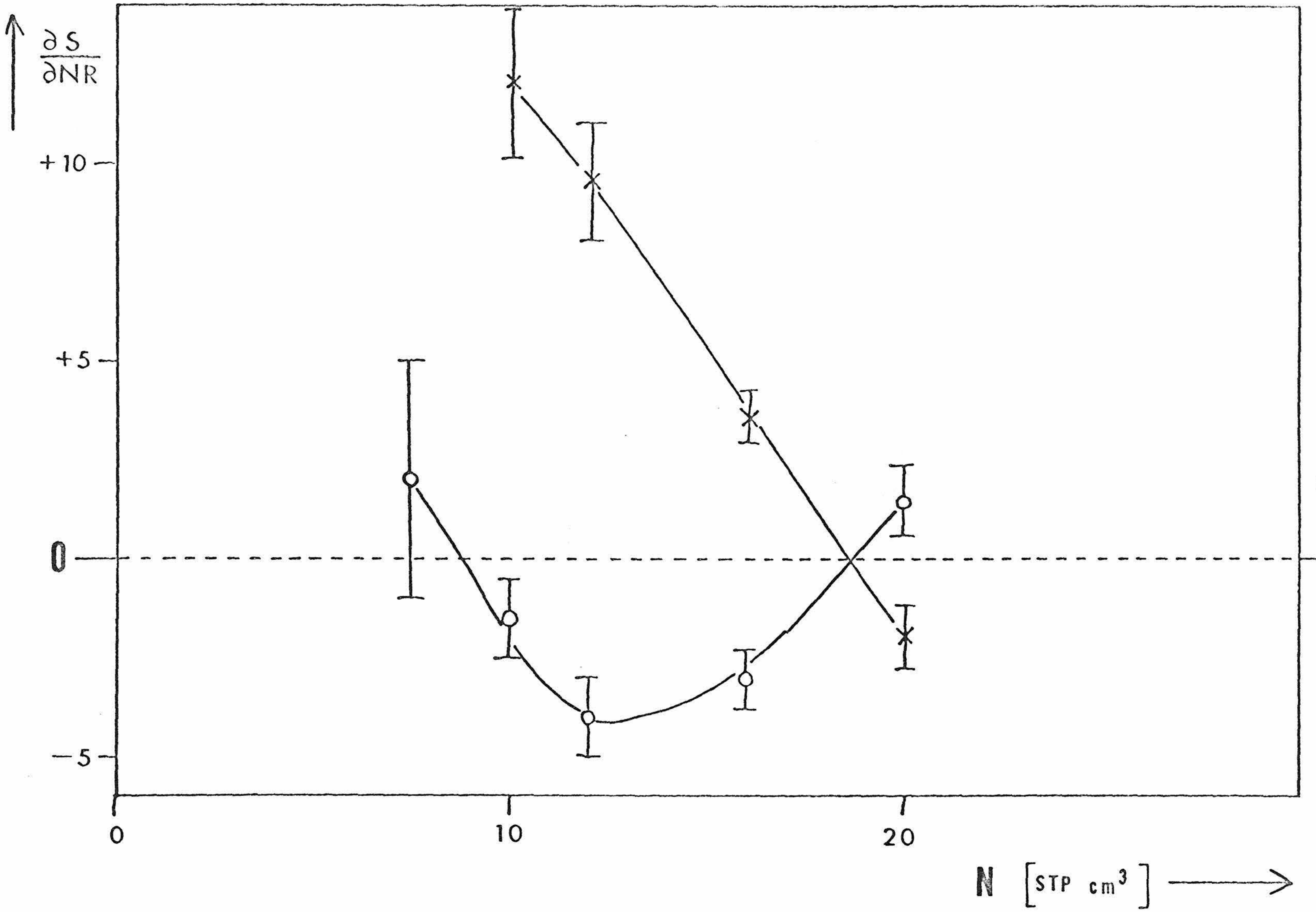
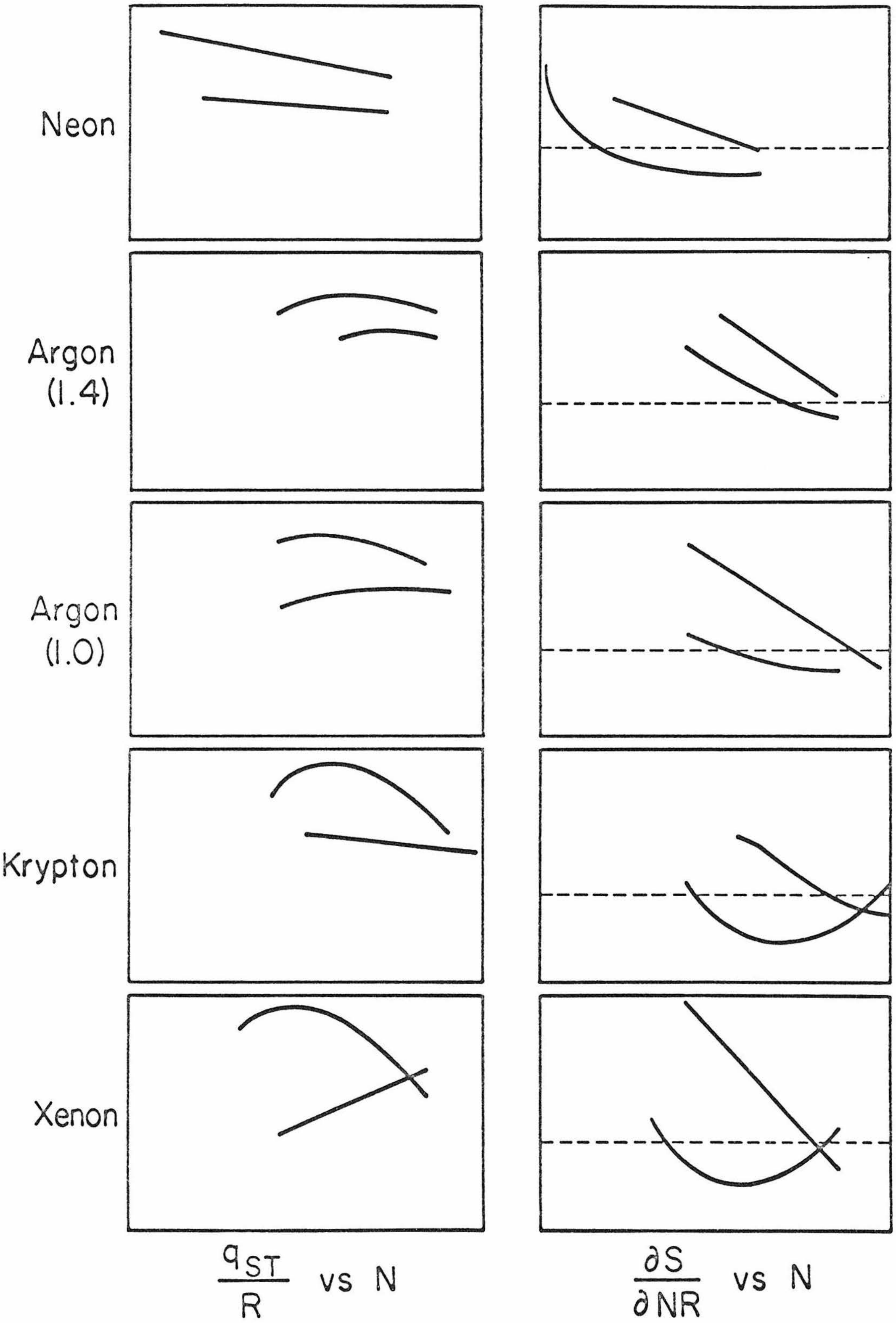

$\frac{\partial S}{\partial NR}$
+10
+5
0
−5
0
10
20
N [STP cm^3]

Figure (3-25)

The data of figures (3-15) to (3-24) reproduced together to show the basic similarity of the film behavior as the substrate is changed

Full scale on the abscissae is approximately one monolayer.


Neon
Argon (1.4)
Argon (1.0)
Krypton
Xenon
$\frac{q_{ST}}{R}$ vs N
$\frac{\partial S}{\partial NR}$ vs N

context will be discussed in the next section.) Nevertheless, we can still derive some information about the general behavior of S from that of $\partial S/\partial N$, and this is done in figure (3-26). Except for the coverages at which the extrema occur--which can be precisely located as the zero-crossings of the $\partial S/\partial N$ curves--these curves are not intended to be quantitative in any way; in particular the way in which the two curves approach the point of minimum separation is unknown except in so far as the monotonic dependence of entropy on temperature demands that they do not cross. Since the average total heat capacity (or, more properly the average of C/T) is given by $\Delta S/\Delta T$, and since the two curves of figure (3-26) correspond to a constant temperature difference, ΔT, it is also possible to derive a qualitative, schematic curve for C/T versus N as shown in figure (3-27). Here again the only quantitative features are the coverages at which the extrema occur and, in this instance, the point (0,0). The extrema now are located where the $\partial S/\partial N$ curves interlace since $\partial S/\partial N$ independent of T implies $\partial S/\partial T$ ($\equiv$ C/T) independent of N.

The occurence of extrema and declining regions

Figure (3-26)

Schematic behavior of the total entropy, S as a function of coverage and temperature; derived from the typical shape of the $\partial S/\partial N$ curves of figure (3-25)

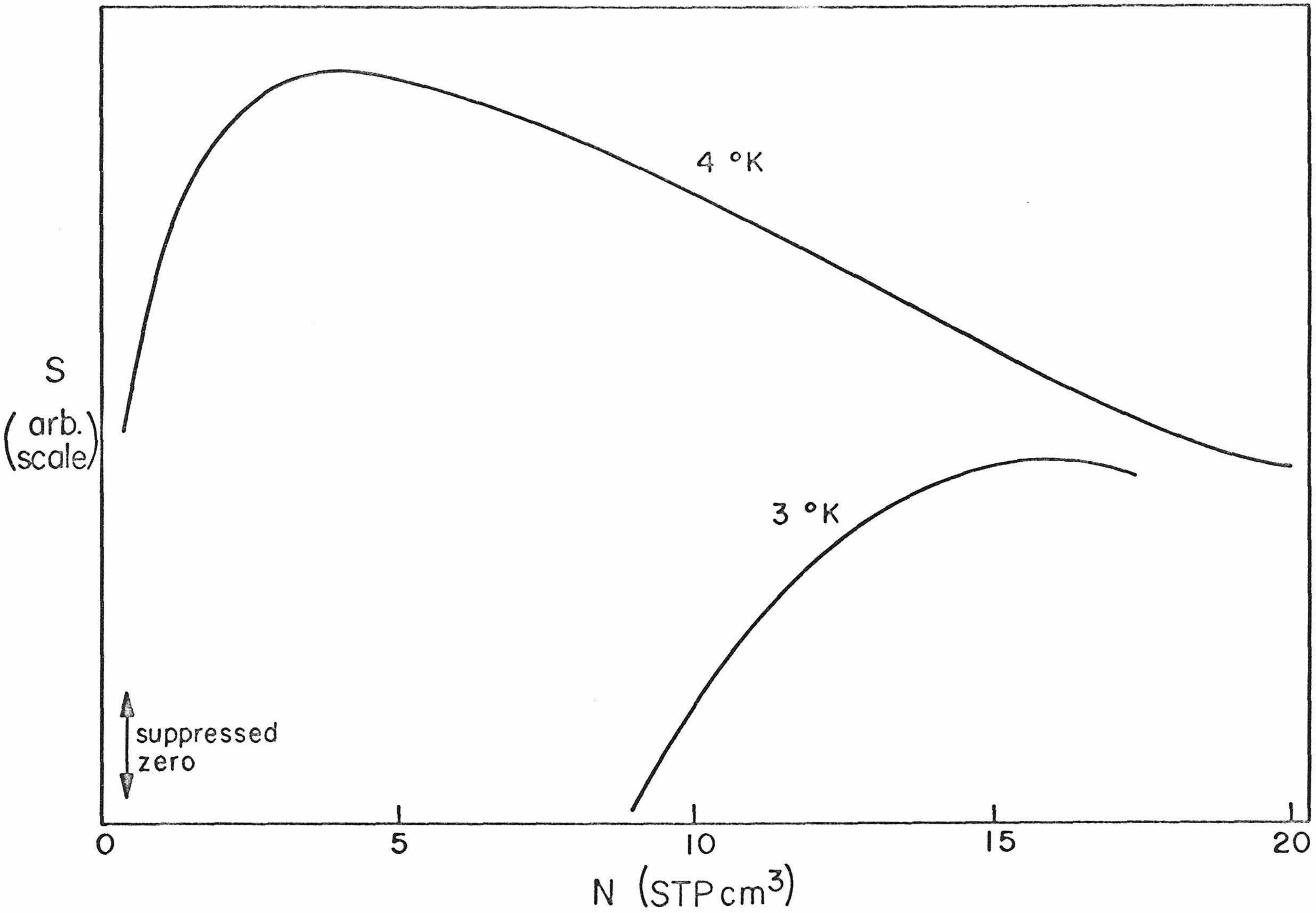
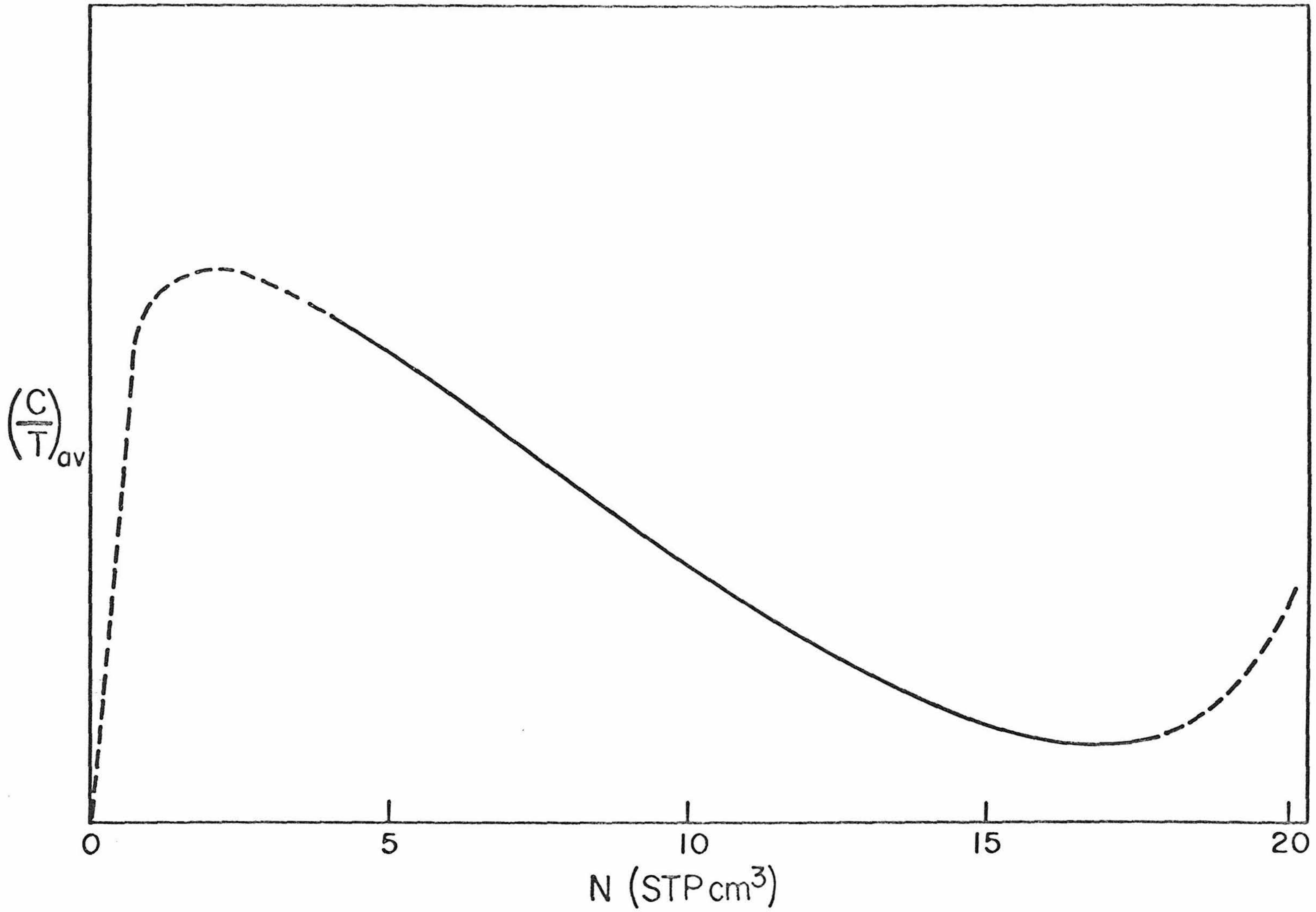

S
(arb. scale)
4 °K
3 °K
suppressed zero
0
5
10
15
20
N (STP cm3)

Figure (3-27)

Schematic behavior of the average total heat capacity at ~ 3.5°K, derived from the behavior of S versus N and T in figure (3-26)


$\left(\frac{C}{T}\right)_{av}$
0
5
10
15
20
N (STP cm^3)

in the curves of S and C is interesting and will be discussed in the next chapter. However we must emphasize once again that we are talking about total entropy and heat capacity, since this behavior would be much less surprising in the molar entropy or specific heat, S/N and C/N.

3.3 Miscellaneous results and observations

The isosteres and related quantities discussed in the preceding section constitute the bulk of the numerical data of this work; there were, however, a number of other incidental results which will be reported below.

Given a family of isosteres, it is a trivial matter to derive an isotherm at any temperature within the range of the data; figure (3-28) shows the 4.2°K isotherms for helium on each of the substrates. These curves show that changing the substrate has a much greater effect on the pressure than it did on the isosteric heat of adsorption. The isotherms were also analyzed according to the (undoubtedly inadequate) Langmuir model to obtain crude values for the monolayer capacity. As discussed in chapter I, the monolayer capacity for any non-ideal substrate is a very poorly defined quantity both experimentally

Figure (3-28)

The 4.2°K isotherms on the various substrates:

✱ Bare Copper

■ Ar 1.4

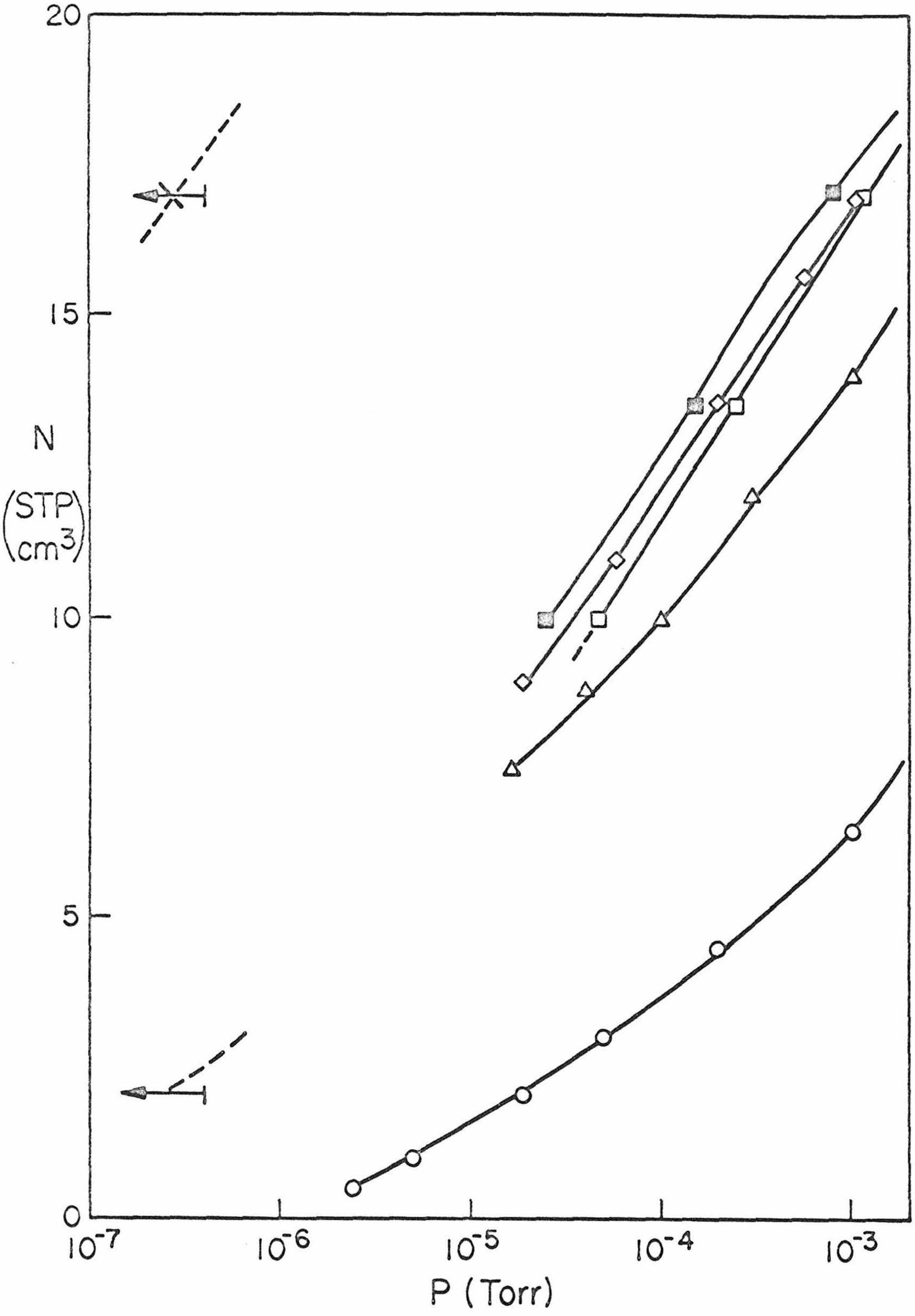
◇ Kr

□ Ar 1.0

△ Xe

○ Ne

The two points on the extreme left side are non-equilibrium upper limits; see text and figure (3-29).


20
15
10
5
0
N
(STP / cm^3)
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
P (Torr)

and theoretically; consequently the results of the analysis can most realistically be described by saying that in each case N_m appears to be in the vicinity of 20 STP cm^3 and displays much less variation with precoat than did that of the precoats themselves on the bare copper. When helium coverages in this paper are referred to as fractional monolayers it is to be understood that the value of 20 STP cm^3 is being assumed.

We have already mentioned in chapter II that one of the limits imposed upon this experiment was that of a background partial pressure of helium. There is a second limit which affects some of the measurements--the equilibrium time. The pores of the sponge are on the order of microns in size and consequently it may take very long times for the gas to diffuse uniformly throughout the sponge at low pressures. Since the helium dewar must be refilled at intervals of $\sim$ 10 to 30 hours, and since the act of transferring liquid helium disturbs the equilibrium (especially at very low pressures or at temperatures below 4.2^oK), there are definite limits on the length of time within which equilibrium may occur. While this slow diffusion rate might be advantageous in an experiment to measure the mobility of atoms along the surface, it is a problem in the measurement of isotherms. The problem could, of course, be alleviated by fabricating the sponge with much larger pores, but this would degrade the surface to volume ratio. This is discussed further in appendix I.

If, however, the helium atoms have lateral mobility on the substrate; then this may supplement the gas diffusion and bring about more rapid equilibrium.(35) Figure (3-29) shows the rate of approach to equilibrium for a variety of precoat-helium coverage combinations. These curves were actually monitored continuously and displayed large transients whenever the liquid helium bath was refilled; the points shown are representative averages. The two lowest curves were actually pursued for more than ten days (~ 260 hours) each and were still falling; the final observed values appear at the extreme left hand side of figure (3-28) as upper limits of the pressures.

These curves represent extreme cases of waiting for equilibrium; generally speaking attempted data at 4.2°K were aborted if they required more than two or three days to reach equilibrium. At temperatures below 4.2°K the time limit was about 20 hours

Figure (3-29)

The rate of approach to pressure equilibrium for various combinations of helium coverage and substrates:

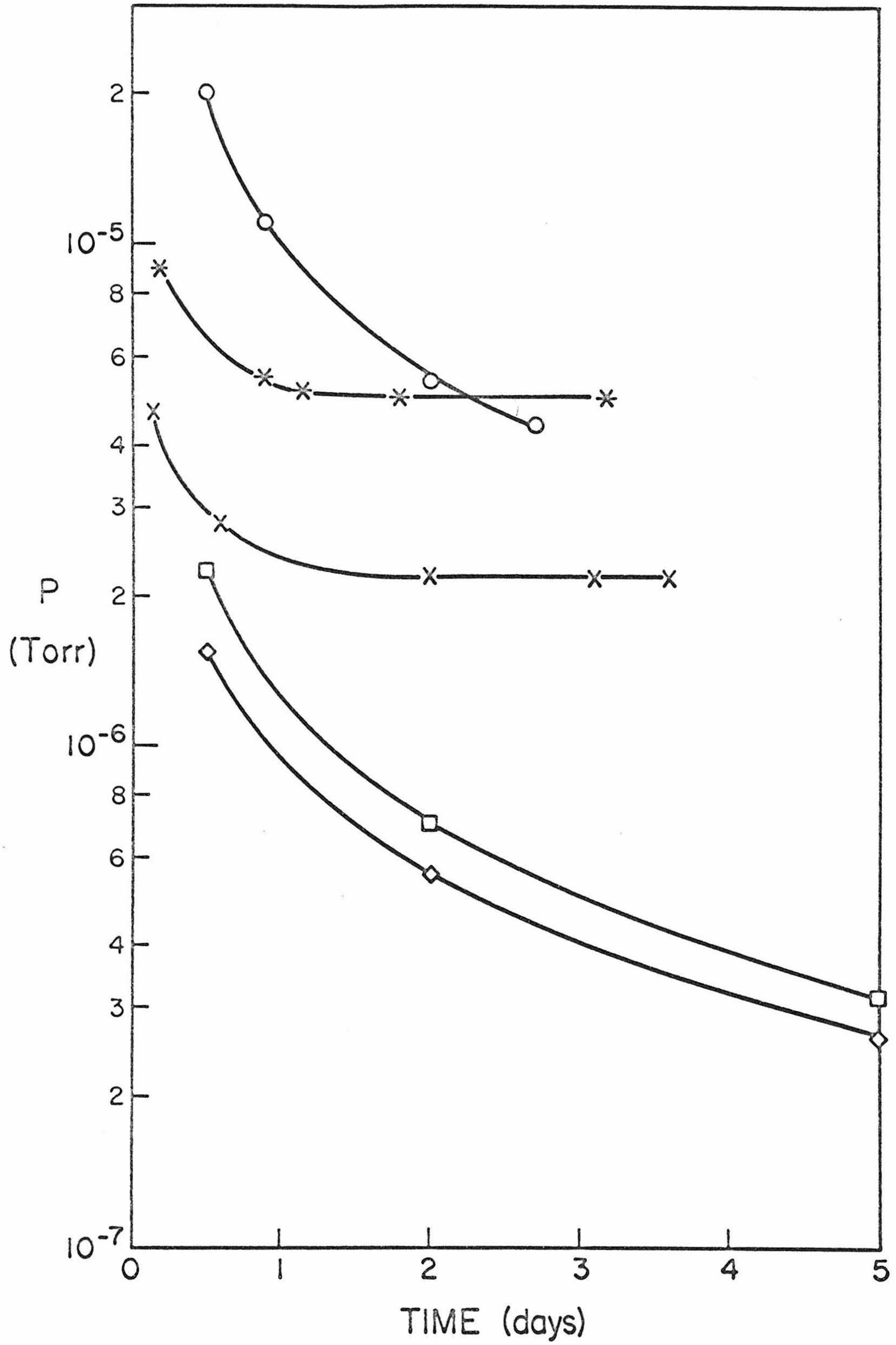
○ 0.3 He on 1.4 Ar

✳ 0.05 He on 1 Ne

× 0.025 He on 1 Ne

□ 0.1 He on 1 Ar

◇ 0.8 He on Cu


P
(Torr)
10^{-5}
8
6
4
3
2
10^{-6}
8
6
4
3
2
10^{-7}
0
1
2
3
4
5
TIME (days)

(one bath lifetime) due to the increased disturbance caused by transferring fresh liquid helium into a bath already below the normal boiling point. However once equilibrium had been attained at 4.2°K for a given coverage it generally required much less time at the lower temperatures due to the fact that at these low gas pressures virtually no reorganization of mass within the sponge is required to compensate for the infinitesmal increase in coverage caused by the lowering gas pressure. At higher pressures, the equilibrium became practically instantaneous i.e. an hour or less at the highest pressures measured.

The implications of the rapid approach to equilibrium of the two Ne curves will be discussed in the next chapter; however from a strictly experimental point of view, this made it possible to pursue the Ne data to unprecedentedly low coverages as shown in figure (3-30). This figure also shows the reason for our previous assertion that the data cannot be quantitatively extrapolated to zero coverage: The isotherm is still non-linear even at 0.05 layers, and in fact does not seem to be following any simple relationship.

Finally, figure (3-31) shows the 4.2°K heat

Figure (3-30)

The 4.2°K isotherm on Ne at extremely low coverage

1 STP $cm^3 \simeq 0.050$ layer.

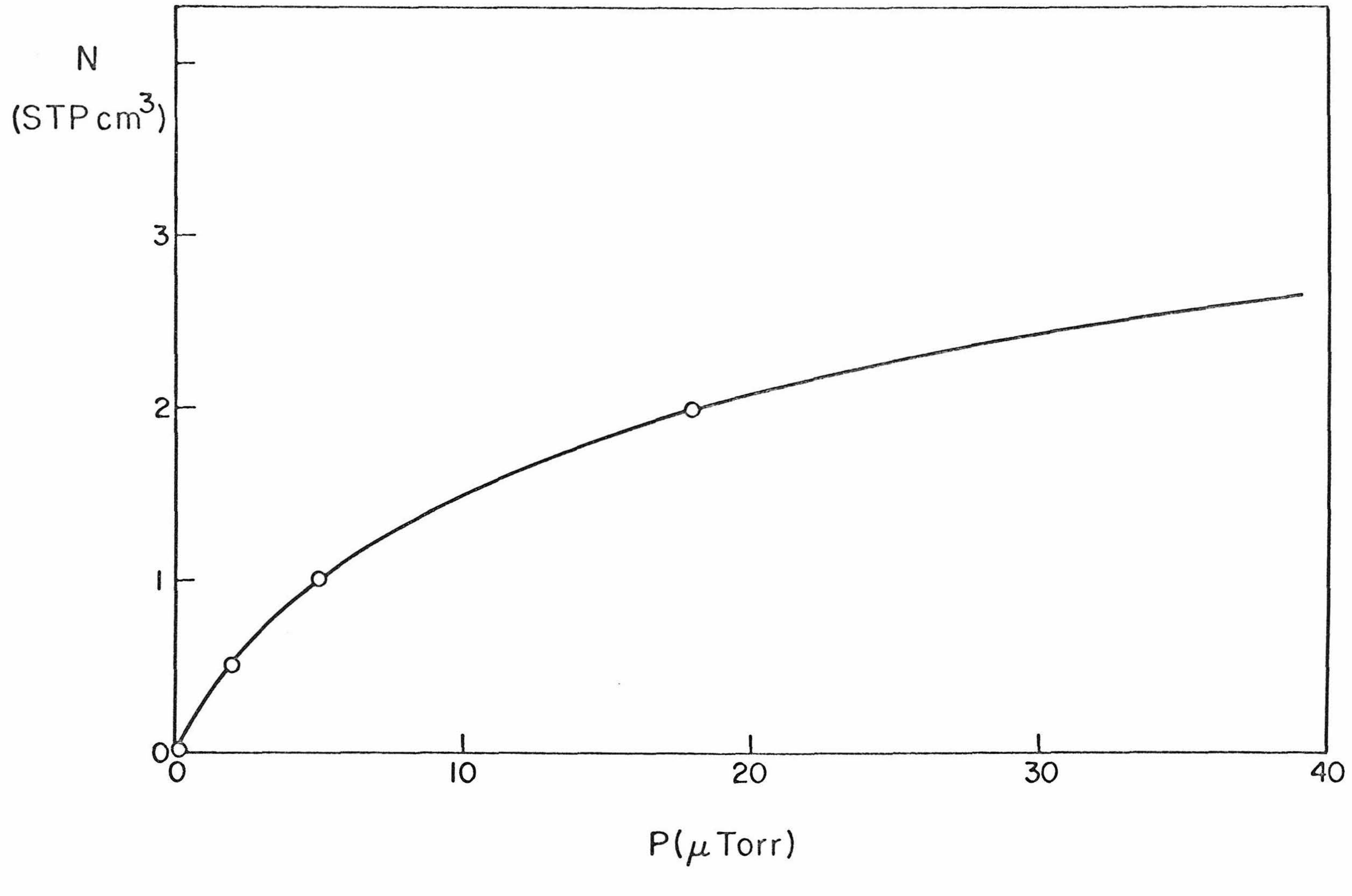
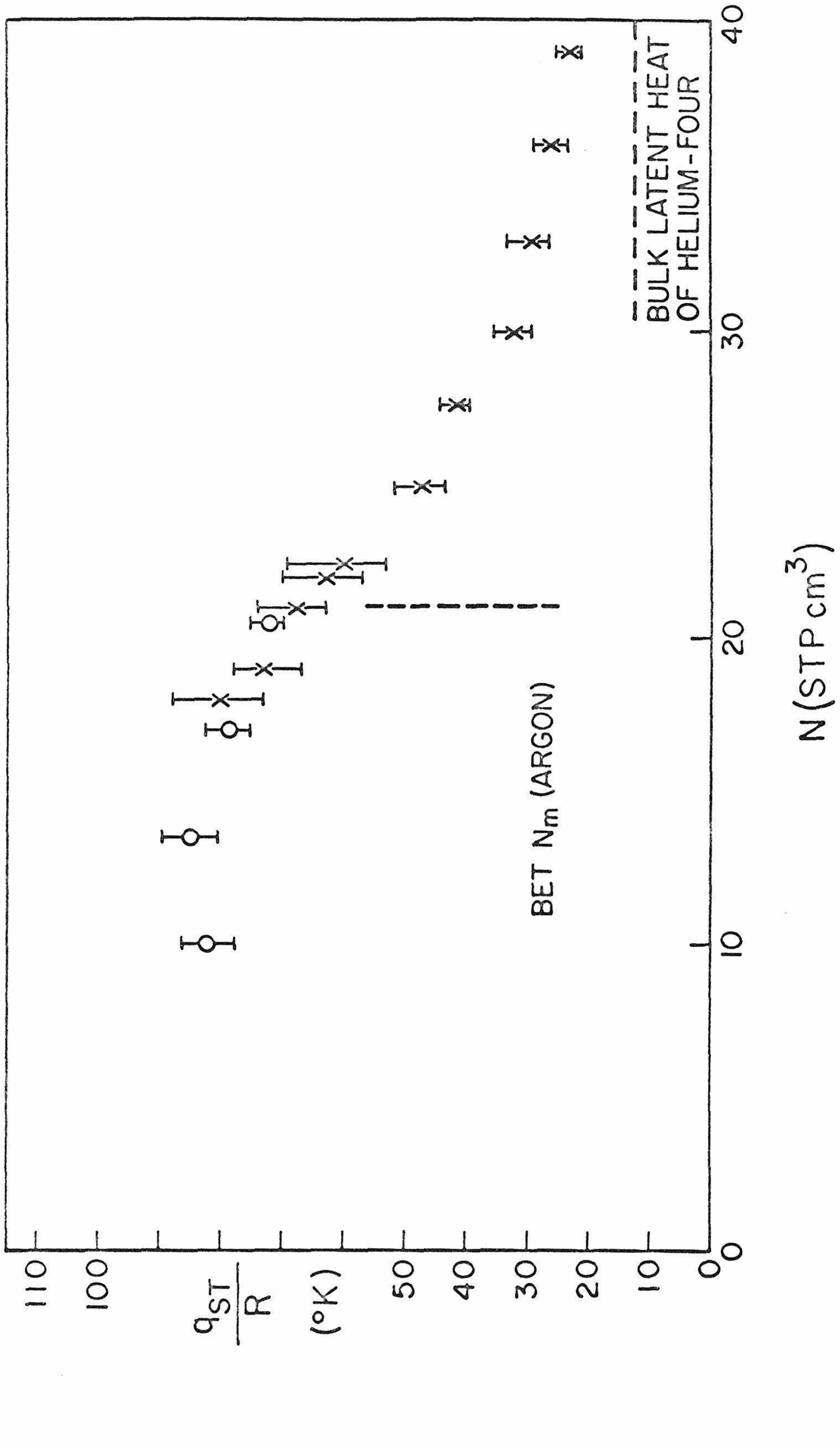

N
(STP cm^3)
0
1
2
3
0
10
20
30
40
P(μ Torr)

Figure (3-31)

The isosteric heat of adsorption, q_{st}/R, of helium on Ar 1.0 over a wide range of coverage

The difference between q_{st} and the bulk latent heat at ~ 2 layers should be compared to that difference in the case of argon on copper in figure (3-8).

The vertical dashed line locates the coverage at which the number of helium atoms equals the number of argon atoms.


110
100
$\frac{q_{ST}}{R}$
(°K)
50
40
30
20
10
0
0
10
20
30
40
$N(\mathrm{STP\ cm^3})$
BET N_m (ARGON)
BULK LATENT HEAT
OF HELIUM-FOUR

of adsorption on Ar 1.0 at coverages up to ~ 2 layers. The higher coverage data were taken on a different sponge prepared according to the same recipe as the one described in chapter II but with a geometry more suited to the higher pressures. This curve shows why many early studies obtained erroneous results for the monolayer capacity of adsorbed helium: An uncritical application of the BET theory essentially assigns monolayer status to the coverage at which q_{st} becomes nearly equal to the bulk latent heat; but this clearly has not yet occurred even at two layers.

CHAPTER IV

CONCLUSIONS

4.1 General

The purpose of this research was to survey the behavior of the adsorbed sub-monolayer film on various substrates; we will, in this chapter, discuss these results and point out the conclusions which can be drawn from our data about the properties of the film. Our ultimate goal--probably unattainable at this time--will be to provide a description of the nature of the film and the laws which it obeys. We will first discuss the new findings which have arisen from this work and their relationship to previous studies. Finally we will examine some of the questions which have been either raised or left unanswered at the present time.

An examination of figure (3-25) shows that there are many quantitative changes which take place in the system as the substrate is changed. However these are quite minor in comparison to the crucial observation that there is an amazing similarity in the basic behavior of the film on different substrates. The main phenomena which the five systems have in common are: The heat of adsorption at 4°K is significantly greater than at 3°K except at the highest coverages, and has approximately the same value for each substrate at typical temperatures and coverages; the curves of $\partial S/\partial NR$ each display an inverted region wherein the quantity is less at 4°K than it is at 3°K; and in most cases the $\partial S/\partial NR$ curves pass through zero and become negative for a while. (The points where the $\partial S/\partial NR$ curves cross zero represent extrema in the entropy as a function of coverage; the points where the $\partial S/\partial NR$ curves cross one another represent extrema in the heat capacity as a function of coverage.)

The anomalous behavior in $\partial S/\partial NR$ indicates that the system is becoming ordered very rapidly as the coverage is increased and that the ordering process is shifted to higher coverages as the temperature falls. This process and the fact that it occurs for all substrates consititutes one of the most important observations resulting from the research and will be discussed subsequently; for the moment we will point out that figure (3-25) indicates that the film obeys a fixed set of rules which are only slightly modified as the substrate is changed.

There are several other conclusions which may be derived from our data: The mobility reported by McCormick <u>et al</u>.(30) for helium on Ar 1.0 was apparently not an isolated instance; our equilibrium curves of figure (3-29) show that the mobility of the film is much greater on Ne than on Ar 1.0 and lacking any information to the contrary we assume that at these temperatures mobility is also a general property of the film, differing only quantitatively as the substrate is changed. This will also be discussed below. To a first approximation it appears that the actual monolayer capacity is not a sensitive function of the precoating since all of the isotherms in figure (3-28) gave approximately the same value for N_m when subjected to a Langmuir analysis. This must be regarded as an open question, however, because the Langmuir analysis (or any other determination of N_m on a non-ideal surface) is quite crude and because the location of the maxima in the $4.2^\circ K$ q_{st} curves on Kr and Xe occurs at coverages suggestively close to the amount of the respective precoats.

Finally, the smoothness of the isosteres and isotherms leads to the conclusion that to within the accuracy of the data there are no observable first order phase transitions or other phenomena which would produce discontinuities or sudden changes of slope in these functions. As discussed in chapter I, this fact does not preclude the possibility of such things taking place on a microscopic level.

By less direct arguments we can demonstrate that, at least on Ne, the adsorbed He atoms continue to interact with one another even at the extremely low coverage of ~ 0.05 layer [where the average separation is $\mathcal{O}(15\ \text{Å})$] : In the case of non-interacting particles adsorbed on a homogeneous substrate (Langmuir adsorption) we would expect the heat of adsorption to be a constant, independent of coverage; we would also expect the pressure over the adsorbed atoms to be proportional to the coverage, at low coverage because the probability of an atom evaporating would be proportional to the number of atoms in the film. Figure (3-30) shows the adsorption isotherm of helium adsorbed on neon at extremely low coverage; the curve is clearly non-linear, in fact it is bending downward which indicates a nonhomogeneous surface and/or a repulsive interaction between the adsorbed helium atoms. The isosteric heat of adsorption (figure 3-15), on the other hand, is clearly not falling with increasing coverage in this range contrary to what would be expected if the system consisted of non-interacting particles on a heterogeneous substrate where the stronger sites would be filled first with a large binding energy. Thus we are forced to the conclusion that the particles do interact even at very low densities, and that any heterogeneity which the substrate may possess is masked by the effects of this interaction.

4.2 Two dimensional Debye solids

Calorimetric specific heat measurements(30,31) on submonolayer films of He^4 (as well as He^3) have often displayed a T^2 temperature dependence at low temperatures. Since this is also the behavior to be expected of a two-dimensional Debye solid, such models have been intensively discussed. It must be remembered, however, that materials may display Debye-like behavior without being solid in the ordinary sense (consider bulk He II, for example).

The present data do not permit us to study the specific heat, C/N, of the film over a wide temperature range. However we can derive some information about the general behavior of the specific heat (actually the total heat capacity divided by the temperature, C/T) as a function of coverage. This is shown, schematically, in figure (3-27). The most striking feature is the large region of coverage where the total heat capacity is decreasing with increasing coverage. By comparing the derivation of figure (3-27) with the information shown in figure (3-25), it can be seen that this behavior is typical of all of our substrates with but minor variations. In order to compare this result with earlier studies, figure (4-1) shows a quantity proportional to C/T which has been derived from the published data of references (30) and (31). The data of McCormick _et al_. show a definite maximum and declining region at temperatures and coverages similar to the present work. The data of Stewart and Dash, on the other hand, at comparable temperature and coverage show no indication of being anything other than perfectly monotonic with coverage. This is characteristic of all of their data at all temperatures for both isotopes of helium--with one intriguing exception: for He^3 at the lowest temperatures they found that

Figure (4.1)

Heat capacity as a function of coverage found calorimetrically in previous studies

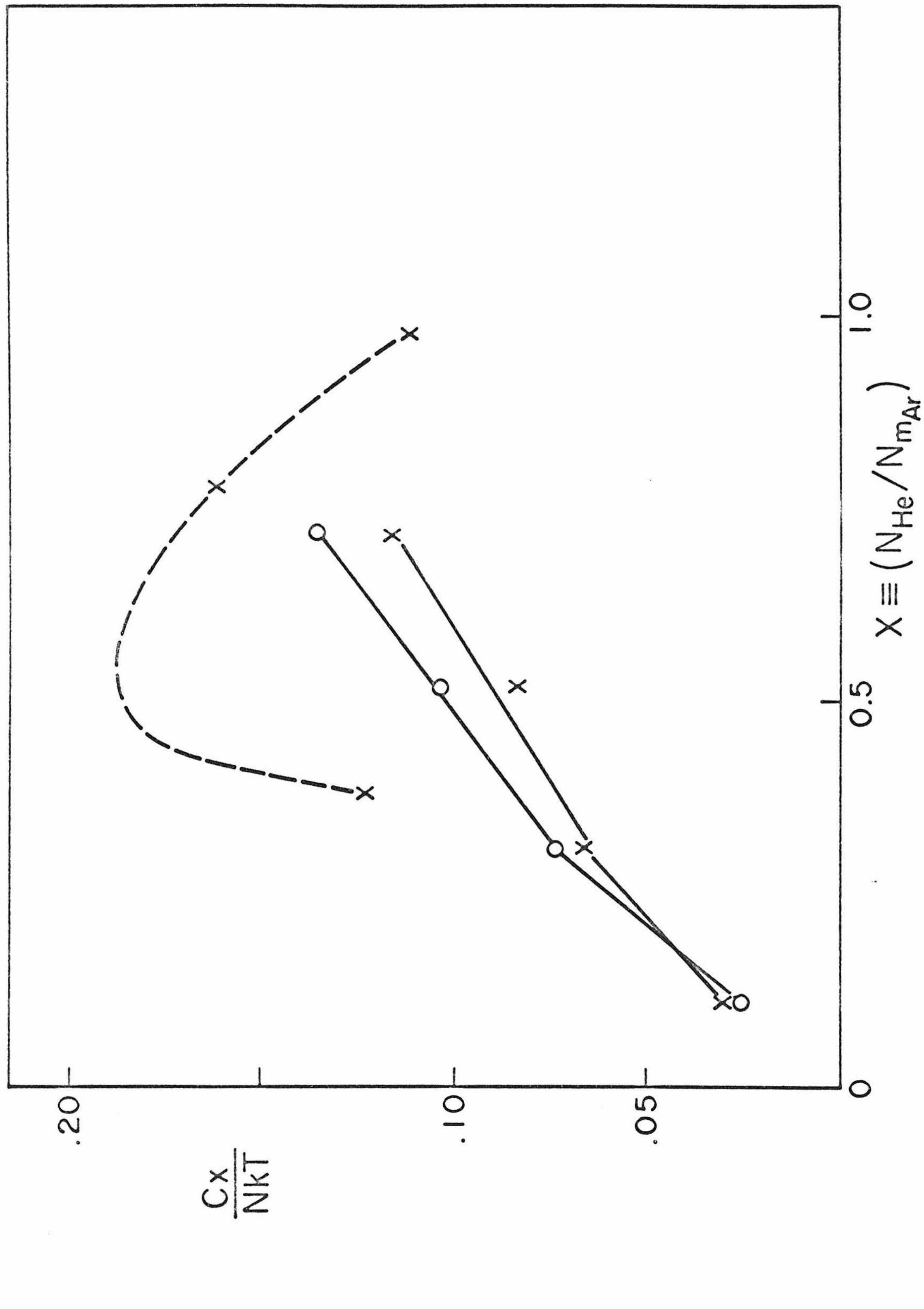
The ordinate is proportional to C/T; the abscissa is in monolayers, scaled for the various sponges used.

The points on the dashed curve are derived from the published data of McCormick _et al_.

The points on the solid curves are derived from the published data of Stewart and Dash.

○ at 4^{o}K

× at 3^{o}K


.20
.10
.05
0
0.5
1.0
$\frac{Cx}{NkT}$
$X \equiv (N_{He}/N_{m_{Ar}})$

the heat capacity had a maximum and then decreased over the range $0.5 \lesssim X \lesssim 1.0$.

When seeking an explanation for the serious discrepancy between these data, it must be considered that there were some differences in the construction of the copper sponges used by Stewart and Dash on the one hand versus McCormick et al. and the present study on the other hand. In particular Stewart and Dash used a finer grade of copper powder and a lower sintering temperature. The lower sintering temperature should tend to preserve whatever discontinuities and facets were present initially in the powder. Hence both this, and the smaller flakes, should tend to reduce the area over which a collection of adsorbate atoms can freely interact without feeling the various damping effects which no doubt arise from the strongly non-uniform fields at the edge of a flake or a flake face. Some possible implications of this hypothesis will be discussed shortly.

Simple two dimensional Debye behavior would require the entropy and heat capacity of the film to be monotonically increasing functions of coverage and in fact both reference (30) and (31) found departures from ideal Debye behavior in their respective studies. McCormick _et al_. found Debye behavior only at $\theta \gtrsim 0.5$ while the temperature dependence of C/N at lower coverages contained a significant linear-in-T term as well as other anomalies. Stewart and Dash have not published an analysis of the size of the linear-in-T term, if any, in their data; however they found it necessary to postulate the co-existence of two distinct Debye solids in their film (as well as one or two low density surface phases) in order to fit their observed data. The shape of our entropy and heat capacity curves seems to indicate that there is one type of film behavior at low coverages which is supplanted at higher coverage by a second which is much more highly ordered (note the rapidly decreasing total entropy). It is most intriguing, however that this transition makes its appearance at successively _higher_ coverages as one lowers the temperature. In summary: we find ordered behavior at high coverages and disordered behavior at low coverages; McCormick _et al_. found Debye-like behavior at high coverage and more complicated behavior at low coverage; and Stewart and Dash--with their finer-grained substrate--find modified Debye behavior at all coverages.

Considering the first two cases together, we get a picture of an ordered phase with Debye-like behavior at high coverage and a disordered phase with a more complex temperature dependence at low coverage. Searching for an analogy to this behavior in conventional three dimensional systems we might first speculate that the film has a gas (liquid) -like phase which condenses to a two dimensional solid at higher coverage. However such an analogy is completely at variance with the observation that the process takes place at higher coverage (average density) as the temperature is lowered. Similarly, any attempt to relate the high coverage region with bulk He II and the low with an uncondensed liquid or gas meets with the same objection. In fact, this anomalous temperature dependence leads to the conclusion that if it is possible to understand these results by three-dimensional analogy then the higher coverage phase must be considered to have become configurationally disordered in spite of its lower entropy. It is not unusual at these temperatures for a liquid phase to have a lower entropy than the corresponding solid phase, however we must have an explanation for a process which produces melting as the coverage is increased. For example, it is well known that, due to thermal fluctuations, a crystalline solid in two dimensions can not grow to arbitrarily large size for $T > 0$.

We would like to explore the consequences of the assumptions that the He adsorption on the surface proceeds in the form of clusters or patches as suggested by Stewart and Dash(31) and that as these patches grow they eventually reach a size where they are large enough to be broken up by thermal fluctuations. This requires that the relevant parameter become the size of a patch rather than the mean density of the surface since the distribution of adsorbate is no longer presumed uniform. If multiple patches can form on the substrate then these two concepts are no longer simply related at submonolayer coverage. This point of view explains nicely the observation that the entropy maximum shifts to higher coverage at lower temperature since higher coverage now implies larger patches which are more readily broken up at lower temperatures. Furthermore each individual crystal face of the polycrystalline substrate should now be considered as an independent system with its own patch or patches;

and if, at low coverage, there are a large number of small patches it is possible that edge effects may account for the linear-in-T specific heat term observed by McCormick et al. Finally: if, in fact, the sponge used by Stewart and Dash has smaller adsorbing facets than the others then it may be that their patches simply cannot grow to a large enough size to be affected by fluctuation.

A calculation by Dash(71) indicates that (neglecting the effects of substrate periodicity) at 4^{o}K the root mean square particle displacement due to thermal fluctuations should become comparable to the interparticle separation when a patch grows to have $\sim 10^4 - 10^6$ atoms on a side. (Dash also points out that a two dimensional polycrystalline mass consisting of many small crystals would be more stable and might be indistinguishable from a large single crystal as far as the temperature dependence of its specific heat is concerned.) The sponges used in the present study and by McCormick et al. were estimated by Goodstein et al.(50) to contain flakes a few microns on a side--i.e. $\sim 10^4$ atomic diameters. Thus a patch growing on one surface of a flake might be only marginally capable of growing large enough to be disrupted by fluctuations. If the flakes used by Stewart and Dash were, say, 30% smaller than ours in linear dimensions then a completed monolayer would consist of a patch the same size as that in a half monolayer on our sponge and higher temperature would be required in order to see the effects of fluctuations. For example, an examination of the $\partial S/\partial NR$ curves of figure (3-25) shows that we would not have observed extrema in the entropy had we accidentally confined our data to temperatures and coverages below, say, $3^{\circ}K$ and 0.8 layers.

If the adsorbate atoms do indeed tend to cluster then there must be some lateral binding energy holding the patches together. Stewart and Dash have suggested the "mattress effect" as a possible source. Compression of the substrate by a helium atom brings a neighboring atom closer to the underlying copper. They have estimated this binding from their data to be $\sim 8^{\circ}K$. We have also made a crude estimate of this energy from our observed lower limit of pressure difference (see figure 3-28) between He on bare copper and He on Ar-plated copper and the change in binding energy implied thereby together with the published(72) value for the compressibility, κ , of (bulk) argon:

$$\exp(\Delta E/kT) \sim P_{Ar}/P_{Cu} \geq 10^4$$

$$\Delta E/kT > \ln 10^4 > 10$$

On argon, a helium atom is $\sim 3\ \mathring{A}$ away from the copper and occupies an area $\sim 10\ \mathring{A}^2$, thus the pressure which it exerts on the argon is, approximately:

$$P \gtrsim 10kT/30\ \mathring{A}^3 \sim 200\ \text{ATM}$$

$$P \gtrsim 200 \times 10^6\ \text{dyne/cm}^2$$

$$\kappa_{(\text{bulk Ar})} \simeq 6 \times 10^{-11}\ \text{cm}^2/\text{dyne}$$

$$\kappa P = \Delta t/t \gtrsim 1.2\%.$$

A second helium atom, near the first would thus find itself at least 1.2% closer to the copper and in a $1/Z^3$ field. If its binding energy is of the order of 100°K then the increase at this location would be at least:

$$1.2\% \times 3 \times 100^\circ K \simeq 4^\circ K.$$

This is a crude lower limit on the lateral binding.

If this compressibility of the precoat is the source of the lateral binding it should persist to arbitrarily low temperature. It is interesting to speculate on what the effects of this would be on the properties of a collection of adsorbed He^3 atoms in view of the fact(73) that an attraction between Fermions should eventually produce something like Cooper pairs obeying Bose statistics at some sufficiently low temperature.

4.3 Mobility, binding, tunneling, and related details

As mentioned previously, many studies reached the conclusion that the helium film should be localized rather than mobile whereas the calorimetric specific heat measurements of McCormick *et al.*(30) indicated that submonolayer films on Ar-plated copper below $4.2^\circ K$ did in fact possess lateral mobility. The present data show qualitatively that this was not an isolated instance and that helium on neon-plated copper has even more mobility than helium on argon-plated copper. Figure (3-29) shows the rate at which pressure equilibrium was approached at $4.2^\circ K$ for various combinations of coverage and substrate. In view of the construction of the sponge (chapter II), it follows that pressure-driven diffusion provides a lower limit on the rate of mass transport. Unless the 0.100 layer film on Ar 1.0 fortuitously has the same mobility as the 0.800 layer film on bare copper, we can conclude that both of these films have such a small mobility that it is significantly less important than diffusion in bringing the film to equilibrium. The same is true of 0.300 layer on Ar 1.4 even at the higher pressures. For 0.025 and 0.050 layers on neon, however, equilibrium was reached much more rapidly at similar pressures, indicating that the film is even more mobile on neon than it is known to be on argon. This observation lends support to the notion that lateral mobility is in fact a general property of helium films at these temperatures and that the differences are merely quantitative.

The greatly increased mobility on neon made it possible to perform measuremements on the neon substrate down to very low coverages--aided of course, by the fact that the pressures corresponding to a given coverage were much higher on neon than on any of the other substrates; see figure (3-28). This figure also shows that any of the precoatings increases the pressure significantly over that on bare copper. Both of these results are reasonable and expected; somewhat more surprising is the sequence of the remaining isotherms. Although unexpected, this sequence probably does not represent anything really fundamental. Neither the pressure nor the isosteric heat of adsorption is a particularly good indicator of the true binding energy of an atom to the surface as the coverage is changed; but conversely both are still approximate indicators. Specifically, small changes in pressure as some parameter, such as the precoating, is changed may indicate changes in ordering or interactions as well as changes in binding energy. If the pressure change between Ar 1.0 and Ar 1.4 does reflect changes in binding, a possible explanation would be that of corner adsorption if the second half layer of argon has adsorbed as individual atoms on top of the first. This is an open question however.

The very large pressure changes which occur as the substrate is varied from bare copper to neon-coated copper almost certainly reflect changes in the binding energy, and the reason for expecting these isotherms to be arranged in order of descending atomic weight is that their mutual interaction strength with helium decreases in that order. However it must be remembered that the effective thickness of the one-monolayer precoating, while not susceptible to independent measurement, probably also decreases with decreasing atomic weight thus bringing the helium atoms into closer contact with the basic $1/Z^3$ field of the strongly attracting copper base. It is possible that the observed sequence of the isotherms represents the results of a competition between these two effects.

The bulk of these data were taken at temperatures between 3 °K and 4°K out of consideration of practicality. This represents a range of temperature, but one which is quite small in comparison to that used in calorimetric specific heat studies which have typically ranged over an order of magnitude in temperature. Basically, our study has been as a function of coverage rather than of temperature. This has the effect of severely limiting what we can say about those theories which relate primarily to the temperature-dependent properties of the film--the quantum mechanical tunneling band theory,(18,34) for example. However, in this connection it might be observed that the ~ 15°K studies of adsorbed submonolayer helium films by Ross and Steele(74) and by Barnes and Steele(43) on Ar-plated rutile and Xe-plated graphitized carbon black respectively were interpreted by their authors as being indicative of localized adsorption, consistent with their (apparently(34) inadequate) model of the system; this is in contrast to the mobility observed below 4.2°K on Ar-plated copper. These systems are obviously not identical to ours, and yet they are similar enough that it may be worth while to compare their results with ours in order to get some idea of the temperature-dependent properties. Ross and Steele include in their published data values for the isotherms and heats of adsorption at $\sim 15^{\circ}$K; from these we have derived $\partial S/\partial NR$ at coverages of $\sim$ 0.3, 0.7, and 1.0 layer for their system by the same method used for our own data. We find that $\partial S/\partial NR$ has approximately the constant value of $+3$ over this entire range whereas our own $\partial S/\partial NR$ curves vary markedly with coverage.

In summary, Ross and Steele found $\partial S/\partial NR$ to be constant at 15°K and hence $S \propto N$ whereas we find S to have extrema as a function of N; Ross and Steele also found that q_{st} decreased with N even at low coverage whereas we find a maximum in this function. Thus our lower temperature system is displaying more complicated behavior. This observation may have some relevance to the tunneling band theory if two more past works are referred to: Novaco and Milford(75) have calculated on a theoretical basis the band structure of He^4 adsorbed on a compressed argon substrate which supposedly simulates the argon-coated copper and they find that the tunneling band should extend up to about 5°K whereas the first thermally excited band does not begin until about 40°K. Furthermore, Dash(34) has stated that the effects of tunneling should not be noticeable in thermal measurements when kT is much greater than the top of the tunneling band. Dash apparently does not give an explanation for this statement but what he probably means is that, for example, 15°K is a low enough temperature that very few atoms would be excited into the thermal band but it is also a high enough temperature that the tunneling band is uniformly populated. Our temperature range of 3 - 4°K on the other hand is low enough that the levels of the tunneling band would not be uniformly occupied and furthermore it is lower than the bulk critical temperature (5.2°K) so that the effects of He-He interactions would be much more important than at 15°K.

4.4 Final comments

In keeping with the spirit of this study we shall devote the attention of this final section not to a restatement of the results of our experiments but rather to a summary of those questions which were raised and left unanswered. For example it appears that for a given temperature the nature of the film changes as the coverage is increased, but a satisfying model is lacking for either high or low coverage.

Our data have shown that there can be significant differences in the mobility of the film for different substrates, but the question remains: How does the mobility depend quantitatively on the substrate? This could be answered by systematic measurements of the diffusion rate on the various substrates, or possibly inferred from specific heat measurements. Information on the more fundamental question of tunneling itself would be obtainable by extending the temperatures of all these measurements up and down to cover a significant range.

If the conjecture is correct that the differences between the present data and that of Stewart and Dash stem from differences in the sponge fabrication process then this should be easily verified by repeating a typical run from each experiment utilizing a sponge prepared according to the opposing recipe. Furthermore if the adsorbed helium atoms do in fact tend to form large patches with significant cohesive energy then these might be readily observable by low energy electron diffraction or similar techniques.

We have in this chapter adopted the point of view, suggested by figure (3-25), that the film is a single well defined concept whose properties appear modulated differently by the different substrates in contrast to the point of view that each substrate with each coverage of adsorbed helium should be thought of as a separate system. However a precise description of this film and the principles it obeys, for example the mechanism of entropy removal at the higher coverages, await further experimental and theoretical consideration.

APPENDIX I

POSSIBLE IMPROVEMENTS IN THE EXPERIMENTAL EQUIPMENT

This research has been of an exploratory nature; collecting for the first time basic adsorption data for helium films over a wide range of coverage on many substrates under standard conditions. Since it is expected that other experimenters may wish to extend these results to even lower ranges of temperature or coverage than was possible in this research, or to carry out more detailed investigations in regions of particular interest; this section will be devoted to some suggestions for changes in apparatus and experimental method which might be useful.

First of all, the very wide range of pressures encountered in this work makes it appear that the idea of carrying out complete studies on a single sponge is impractical. Rather it appears that as many as three sponges might be required to cover the entire range of interest. The sponge described in this paper is very convenient for the range from ~ 10^{-5} Torr to 10^{-1} Torr since these pressures are sufficiently low that the dead volume does not affect the measurements. A sponge similar to the one used in this research but without such a large central hole would be useful in the range from 1 Torr upwards.

In order to work in the region below ~ 10^{-6} Torr the problems of background pressure and diffusion time must be met. Probably the best way to reduce the diffusion time is to abandon the sintered copper sponge altogether at these low pressures and go over to a system of copper foil. Foil systems are not satisfactory at higher pressures because of their unfavorable surface-to-dead volume ratio. But at extremely low pressures, the only problem is to make sure that the heat conductivity is good enough to make the same sponge usable for heat capacity measurements. (Of course if the microscopic structure of copper does affect the properties of the film, then the use of continuous foil rather than powder might add additional complications.) As a compromise between foil and powder from the standpoint of surface/volume, a porous foil is reportedly available commercially(76) which has a thickness on the order of mils and pore size on the order of microns.

The problems of background pressures can be attacked in two ways. First of all, more direct contact between the sponge and the gauges would increase the effective pumping speed of the bath, this might be accomplished as shown in figure (A-1). Secondly, the elimination of borosilicate glass from the high vacuum system would be very desirable because of its well known propensity to diffuse helium. If one did not desire to use an all-metal system it might be possible to substitute an aluminosilicate glass, such as Corning #1723 which has the low expansion coefficient and high working temperature of borosilicate glass, as well as the low helium diffusion constant of soda-lime glass(77,78).

There may also be ways of reducing problems associated with liquid helium level changes and re-transfers. If the filling tube were made with a vacuum-jacketed construction, then the experiment would be insensitive to changes in the liquid helium bath level. See figure (A-2).

Even this would not remove problems associated

Figure (A-1)

A short, direct filling tube
with a radiation baffle

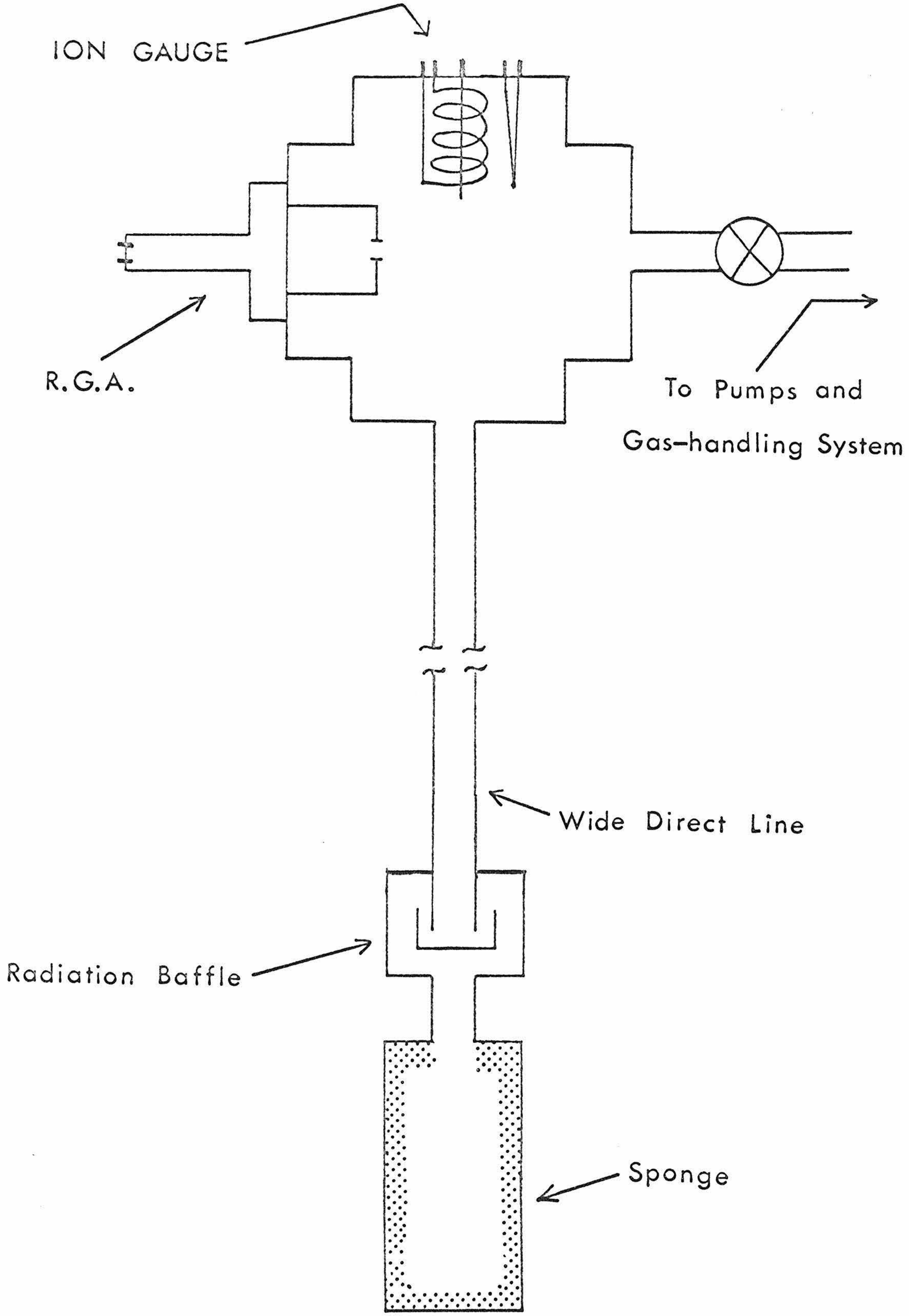
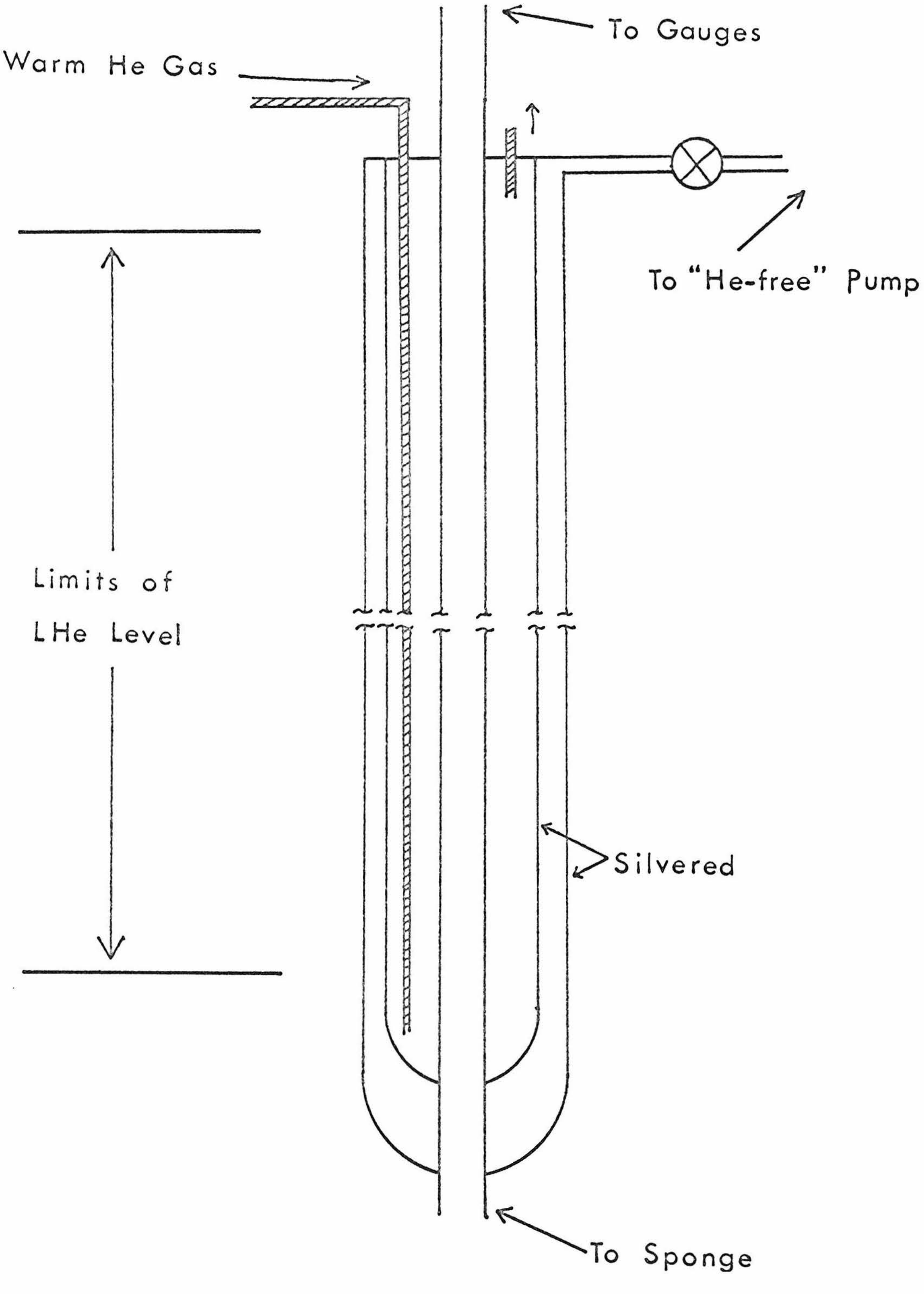

ION GAUGE
R.G.A.
To Pumps and Gas-handling System
Wide Direct Line
Radiation Baffle
Sponge

Figure (A-2)

A vacuum-jacketed filling tube

(Could easily be made consistently with Figure A-1)

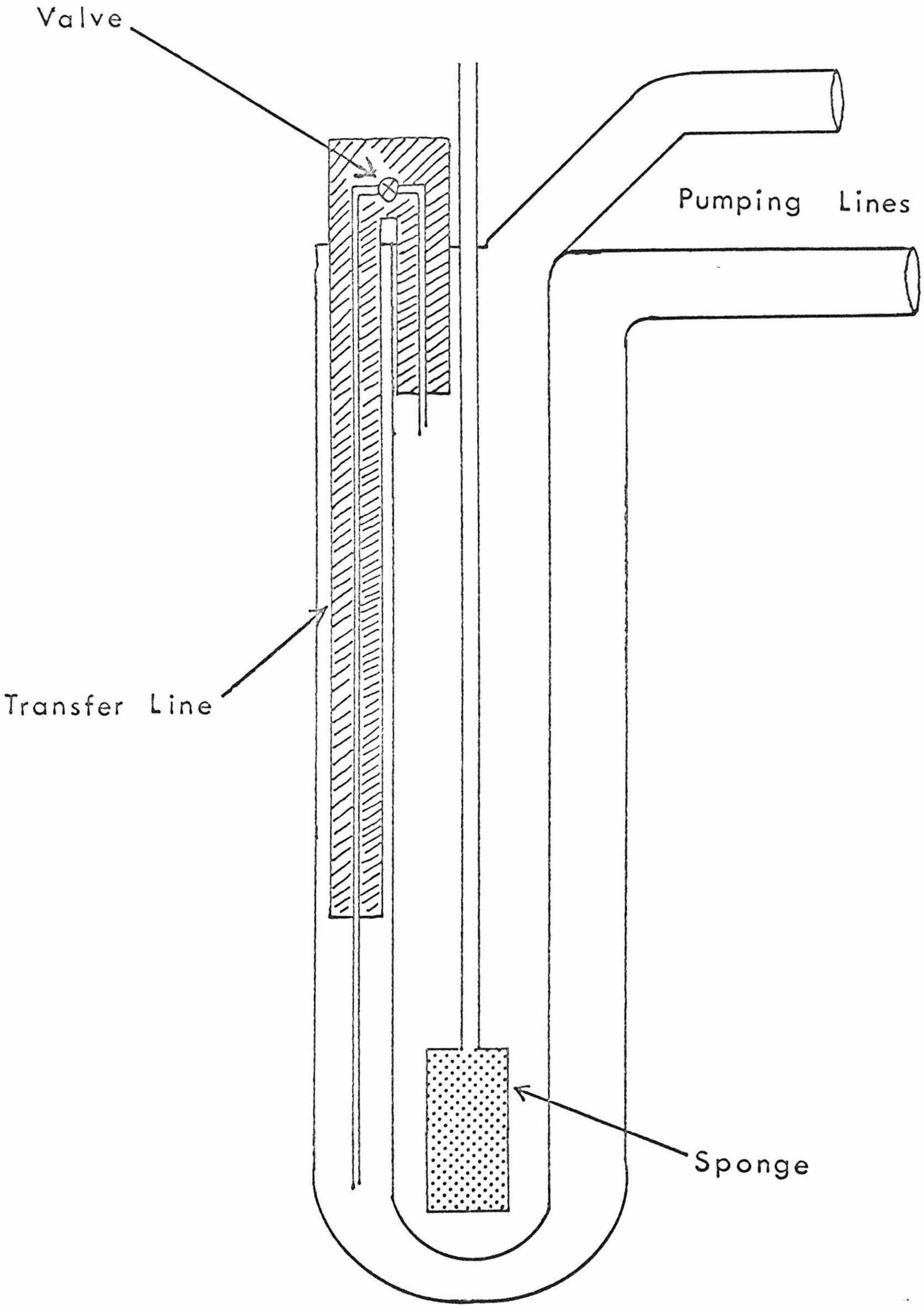

To Gauges
Warm He Gas
To "He-free" Pump
Limits of
LHe Level
Silvered
To Sponge

with warming the dewar up to $4.2^{\circ}K$ in order to retransfer, however devices have been described in the literature(79) for transferring liquid helium from a $4.2^{\circ}K$ storage dewar into a colder experimental dewar without significant warming of the experiment. Another approach might be to have three dewars rather than the usual two. The innermost dewar would contain the experiment and would be pumped and regulated in the usual manner. Changes in the temperature of the outer liquid helium dewar would not affect the inner dewar, and it could be warmed up to $4.2^{\circ}K$, refilled, and cooled again to the operating temperature. Then cold liquid helium could be transferred from the outer liquid helium dewar to the inner one at the operating temperature, see figure (A-3).

It is possible that the problem of the thermomolecular effect could be side-stepped altogether at least at the higher pressures ($\gtrsim 10^{-3}$ Torr) by the use of the relatively new techniques of measuring pressures with a gauge at liquid helium temperature. This has recently been discussed in the literature.(80)

Figure (A-3)

An arrangement for maintaining a helium dewar at temperatures below the normal boiling point indefinitely


Valve
Pumping Lines
Transfer Line
Sponge

APPENDIX II

GLOSSARY OF SPECIALIZED TERMS AND SYMBOLS

A: the area of the film.

C: the total heat capacity of the film.

C/N: the specific heat of the film.

dead volume: that part of the volume containing the sponge which is not occupied by the particles of powder.

g: the subscript "g" is used to identify the thermodynamic variables of the gas phase.

Ln: natural logarithm.

Log: common logarithm.

μ: the chemical potential.

N: the number of atoms in the film.

N_m: the monolayer capacity of the film.

N.B.P. normal boiling point.

OFHC: oxygen-free, high conductivity.

P_o: the vapor pressure of the bulk adsorbate.

ϕ: the two dimensional spreading pressure of the film.

q_{st}: the isosteric heat of adsorption.

R.G.A. residual gas analyzer.

S: the total entropy of the film.

S/N: the molar entropy of the film.

$\partial S/\partial N$: the partial molar entropy of the film.

STP cm^3: 22.4 STP cm^3 = 0.001 mole.

t: the thickness of the film, defined as one atomic diameter multiplied by θ.

θ: the reduced coverage, N/N_m.

V: the effective volume of the film, $A \cdot t$.

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