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HEATS OF ADSORPTION OF AMMONIA AND CARBON DIOXIDE ON TOOTH COMPONENTS

by

William V. Loebenstein

Chemist, Dental Research Section, National Bureau of Standards,
Washington, D. C. 20234

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The study demonstrates how heats of adsorption and area of coverage can be used as criteria for comparing the ultimate strength of chemically reactive groups for incorporation in potential dental adhesives. Carbon dioxide and ammonia were chosen as the reactive gases because they typified acidic and basic groups, respectively, as possible candidates for bonding linkages in an adhesive. The presence of collagen exerted a profound influence on the BET area depending upon the gas used when compared with nitrogen. Ammonia exhibited a higher surface area as well as a higher heat of adsorption on dentin than did carbon dioxide. It would therefore qualify as a better adhesive under the conditions of comparison. The surface area of dentin available to ammonia, however, was no greater than the surface area of anorganic dentin. It appears, therefore, that the extent of swelling of the collagen in dentin was restricted by the pore boundaries of the apatite mineral. The average heat of adsorption of ammonia on anorganic dentin based on the anorganic whole is estimated to be at least as large as it is for whole dentin. Thus, it would appear that the presence of collagen did not contribute to the adhesive strength of ammonia.

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I-Introduction

A study has been made of the heats of adsorption of two chemically reactive gases on the surfaces of tooth components. The purpose was to provide a criterion for the selection of chemical structures to be incorporated in potential adhesives. The choice of ammonia and carbon dioxide was made to typify relatively simple molecules possessing alkaline and acid forming groups, respectively.

Some investigators ^[1,2] have resorted to thermal desorption techniques for determining the strength of chemisorbed bonds. Such methods would be impractical in the present application where the integrity of the collagenous component must be preserved. It would be destroyed if subjected to the extreme temperatures that would be indicated by such methods. The possibility of measuring the adsorption of the reactive gases at ambient temperatures was considered and had, in fact, ^[3] been done for CO₂ on hydroxyapatite ^[4] and NH₃ on other solids at temperatures of zero degrees and higher. The inability to cleaning the surface without going to temperatures high enough to destroy the sample was, again, a reason for not choosing this direction. Furthermore, a relatively small fraction of

the surface would be involved with forces strong enough to be measured and therefore would not be as representative of the sites involved in adhesion for a potential dental adhesive as would be the case where the less active sites, as well, were included. Accordingly, it was decided to measure the isotherms in the vicinity of the respective boiling points of the gases employed. This would have the additional advantage of permitting a comparison of the specific surface available to each gas with that for nitrogen under comparable conditions. Finally, sufficient resolution of several adsorption isotherms over a 20-degree range in temperature could be expected to permit isosteric heats of adsorption to be readily obtainable.

It would be extremely useful to be able to correlate the relative strength of adhesive forces with the different components of tooth structure. The contribution of collagen to the adsorption studies can best be understood by a comparison of the adsorptive properties of collagen-containing tooth components with specimens from which the organic matter had been selectively extracted (i.e., anorganic).

A consideration equally as important as the strength of an adhesive bond is the concentration or number of such bonds per unit area of tooth material. Inasmuch as adsorption measurements afford a means of determining surface area accessible to the particular adsorbate used, they provide a measure of the maximum number of adhesive links at the molecular level.

The ultimate strength of an adhesive should be the resultant of the bond strength per unit linkage summed over the number of such bonds per unit cross section.

II-Materials *

Caries-free human teeth were ground in a diamond mortar until the particles passed a 120 mesh sieve. The enamel was not separated from the dentin. The mixture was repeatedly extracted with ethylenediamine^[4] and washed with water until no trace of organic matter remained. This constituted the anorganic whole tooth samples used in this work. The dentin samples were prepared as described^[5] in an earlier publication. Water-pumped nitrogen, helium, and carbon dioxide were obtained from Air Products Corp. The ammonia was supplied by J.T. Baker Chemical Co. The nitrogen purification train consisted of heated copper turnings for removal of oxygen followed by "Ascarite" and "Anhydrone". The carbon dioxide was merely dried over "Anhydrone", as was the helium. Drying of the ammonia was accomplished by passing the gas through a column of pelletized KOH.

* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the material or equipment identified is necessarily the best available for the purpose.

III-Experimental

A simplified surface area apparatus [6] was used for the adsorption measurements, although conventional volumetric gas-adsorption equipment would have sufficed as long as the sample tube was equipped with an entrance and exit at the top and bottom for scrubbing with an inert gas. The cryostat used to maintain the sample at the desired temperature is shown in Fig. 1. It was similar to one first described by Scott and Mellors [7]. It consisted of a $\frac{1}{2}$ -inch copper bar bent into an inverted U. Copper plates were brazed on to one leg to form radial fins, yet sufficiently compact to allow that leg to be lowered into a dewar flask containing liquid nitrogen. Attached to the other leg was a cylinder fashioned out of copper plate open top and bottom so it could be raised to enclose the sample tube and slotted to enhance circulation. When in place it, in turn, was contained in a dewar flask filled with a liquid which would not freeze at the temperature of the experiment. Trichlorethylene or toluene were the liquids used for this purpose. The top of the inverted copper U bar was covered with a thick layer of polystyrene foam for heat insulation. Heat was supplied on demand through a hand-wound glass-enclosed immersion heater at about 25 watts. The temperature sensing probes were thermistors attached as plug-in elements for ease of substitution. Fenwal thermistors KB22J1 and KB23J1 were used for the ammonia adsorption experiments while JD12J4 and JD21J1 were used for carbon dioxide. (The high sensitivity of the thermistors restricted the temperature range of each.)

The thermoregulator shown in Fig. 2 was constructed of parts readily obtainable. The secondary windings of the transformer, T_1 , besides providing the source of e.m.f., comprised the two inductive arms of the AC bridge. Stability of the amplifier was accomplished by negative current feedback brought about by the unbypassed cathode resistors. Decoupling was obtained by the cathode-follower stage. The thermo-regulator-amplifier was so sensitive, that even a 5000 ohm carbon resistor could be used in place of the thermistor in an emergency (with somewhat more sluggish response) by using the highest setting of potentiometer, P_1 . However, it is important that resistor R_{16} and potentiometers P_2 and P_3 (by composition or compensation) have virtually no temperature coefficient of resistance in order for the bridge to ignore changes in room temperature. The apparatus, using thermistors, held the temperature within $\pm 1/4$ degree even though a glass well was used to isolate the thermistor from direct contact with the liquid coolant.

Agitation of the liquid was provided by bubbling dry air into the bottom of the dewar. Temperatures were measured by a chromel-alumel thermocouple connected to a Rubicon Precision potentiometer (Cat. no. 2745) and were monitored by a Honeywell chart recorder.

Corrections^[8] were made for the non-ideal behavior of the adsorbates at their respective isotherm temperatures and equilibrium pressures.

IV-Pretreatment

In any adsorption work, seemingly insignificant variations in the preparation of the surface can have a devastating effect upon the reproducibility of the measurement. Accordingly, it was necessary to establish a procedure for pretreatment of the sample. Beebe [9] has pointed out in the adsorption of methanol on hydroxyapatite that the adsorption on a freshly outgassed surface was always greater than subsequent adsorptions in which the sample was pumped free of the adsorbing gas at room temperature prior to repeating the run. The former represented chemisorption as well as physisorption, while the latter only physisorption. This observation was equally valid for the gases used in the present investigation.

For the anorganic whole teeth, the sample was purged of impurities by heating overnight in a stream of purified helium at 110 C. The heating was accomplished by a thermostatically controlled sleeve furnace. Upon cooling to room temperature, the helium was replaced with the gas to be adsorbed. This was then removed by evacuating the sample for 15 minutes while still at room temperature. The sample was then cooled to the temperature of the experiment before the adsorbing gas^{was} introduced.

When dentin was used as the adsorbent, two separate sets of experiments were performed. In one set the purging in helium was accomplished at 50 C because of the possibility that higher temperatures might cause denaturation of the collagen.

The remaining steps in the pretreatment were the same as those described for the anorganic whole teeth. In the second set of experiments, the temperature of purging was brought back up to 110 C. It was reasoned that the desirability of having the same maximum temperature as the anorganic whole teeth was of compelling importance in case denaturation of the collagen was either absent or minimal.

It is significant that following the second set of experiments, it was possible to reproduce the improved low temperature adsorptive characteristics which followed the 50 C pretreatment providing the sample was first equilibrated with room air (50 percent relative humidity) then again pretreated at 50 C. While this does not preclude denaturation, it indicates that the adsorptive characteristics were reversible.

The order of experiments consisted of the first and last isotherms carried out at the same temperature: -33.4 C (the boiling point) for NH_3 and -78.4 C (the sublimation point) for CO_2 to insure that no poisoning of the surface had taken place during the intervening runs. The other isotherms were displaced by five and ten degrees on each side of these fixed points. Except for the initial and final runs, the order in which the experiments were performed was randomized.

V-Results and Discussion

In all sets of experiments, families of adsorption isotherms were obtained corresponding to the five different temperatures as typified by the curves for NH_3 on dentin pretreated at 50 C as shown in Fig. 3. They were type II (sigmoid) in each case although in the higher temperature isotherms the inflection points were usually beyond atmospheric pressure - the upper limit attainable with the apparatus.

Surface areas were calculated using the experimental points between 0.1 and 0.3 relative pressure of the corresponding boiling point and sublimation point isotherms in the usual BET linear transformation:

$$x/[v(1-x)] = [(C-1)/(v_m C)]x + 1/(v_m C) \quad - - - - (1)$$

where x = relative pressure; v = volume of gas adsorbed (ml/g); while v_m and C are the characteristic parameters representing, respectively, the gas volume needed to cover a monolayer and a function of the heat of adsorption which will be discussed later.

The resultant surface areas are shown in Table 1 using the molecular cross sections^[10] as indicated for each gas. Values of surface areas available to N_2 adsorbed at liquid nitrogen temperatures are shown in the bottom row.

The values for anorganic whole teeth are in substantial agreement for each of the three adsorbents. This becomes more apparent when it is realized that CO_2 , because of its larger size, is denied access to pores readily accessible to NH_3 and

even to N_2 .

It has long been known that the surface of dentin available to N_2 is of the order of $10 \text{ m}^2/\text{g}$.^[11] This is consistent with the value of 7.5 and 6.5 obtained in this work (depending upon the conditions of pretreatment). The surprising result is that the same sample when measured by NH_3 disclosed an area of $160 \text{ m}^2/\text{g}$, far greater than could be accounted for based on differences in molecular size. Indeed, it agrees well with the value that N_2 gave ($149 \text{ m}^2/\text{g}$) when the collagen had been selectively removed from the dentin.

In attempting to reconcile these observations with an hypothesis of what is actually happening, one might postulate that collagen inhibits access of nitrogen to the smaller pores of the dentin. This would satisfactorily explain the low ($7.5 \text{ m}^2/\text{g}$) value for N_2 on dentin and the large value ($149 \text{ m}^2/\text{g}$) for N_2 on anorganic dentin. It would also explain the essential agreement among all these adsorbates on anorganic whole teeth. The present paper does not include adsorption on collagen alone although Marshall and Moore^[1 2] found appreciable adsorption of NH_3 on another protein, silk fibroin, accompanied by swelling. If NH_3 caused the collagen to expand, this might unblock the pores allowing the NH_3 free access to the entire surface of the mineral component ($160 \text{ m}^2/\text{g}$). This would also be consistent with experiments now taking place (but as yet unpublished) on the adsorption of water vapor on dentin where again the collagen would swell to allow the water to reach the mineral pores for an area of about $150 \text{ m}^2/\text{g}$.

The above picture does not account for the intermediate behavior of CO_2 on dentin. If the collagen does not allow access of CO_2 to any but the larger pores, one would expect a smaller area than for N_2 because

CO_2 has a larger cross section and would be denied some access to pores available to N_2 , yet the area available to it was much greater, ($50 \text{ m}^2/\text{g}$). The role played by CO_2 is, however, complicated according to Spencer, et al^[13]. These authors point out that although the CO_2 molecules have no permanent dipole, they are highly polarizable and, in addition, have a permanent electric quadrupole which is quite strong. These factors are bound to exert a significant influence on the adsorption characteristics such as that observed here.

No appreciable adsorption of N_2 on collagen takes place at liquid N_2 temperatures,^[14, 15] although adsorption by water at room temperature is equivalent to about $400 \text{ m}^2/\text{g}$ ^[16] again accompanied by swelling.

It would appear that the actual adsorption of NH_3 and H_2O on dentin (which by weight is about 1/3 collagen) is less than would be anticipated in the light of these considerations unless the mineral component restricts the degree of swelling of the collagen to such an extent that full advantage of its adsorptive capacity cannot be realized.

It has recently been reported by Hagymassy, Brunauer, and Mikhail^[17] from other considerations that perhaps H_2O rather than N_2 should be used as the standard adsorbate for

surface area and pore size determination, especially in biological systems.

The difference between the surface areas available to NH₃ for the 50 C and 110 C pretreatment temperatures for dentin is probably attributable to the ^{three percent} difference in the amounts of residual water present in each case.

Insofar as the present work is concerned, the NH₃ molecule (at 160 m²/g for dentin) indicates far more points of attachment than does CO₂.

From each of the family of curves such as that shown in Fig. 3 it was possible to apply the Clausius-Clapeyron relationship:

$$\frac{\partial (\ln p)}{\partial (1/T)} \Big|_v = - \frac{Q_{ST}}{R} \quad \text{--- --- --- --- ---} \quad (2)$$

which defines the Isosteric Heat of Adsorption, Q_{ST}, in terms of the pressure, absolute temperature and gas constant while the amount adsorbed, v, is held constant. This was accomplished by plotting ln p against 1/T for various ordinates of the families of isotherms such as that shown in Fig. 3 according to the integrated linear form of Eq. (2):

$$\ln p = - (Q_{ST}/R)(1/T) + \text{const.} \quad \text{--- --- --- ---} \quad (3)$$

which is valid providing the change in Q_{ST} over the temperature

interval used is negligible. This assumption was reinforced by good linearity obtained from the plots of Eq. (3).

Fig. 4 compares the resultant isosteric heat as a function of the amount of gas adsorbed for each of the systems studied. The value of v_m on each abscissa was calculated from Eq. (1) and represents the point at which a monolayer was completed. Values corresponding to the smallest amounts adsorbed could not be calculated because of the poor resolution of the families of isotherms in this region. Typical curves are represented by both NH_3 and CO_2 adsorption on anorganic whole teeth and by NH_3 on dentin pretreated at 110 C. In these systems the isosteric heat fell off rapidly until the monolayer was formed. Beyond here it became almost flat. Somewhat less common but often observed [13,18] in the investigations of others is the shape of the curves for both NH_3 and CO_2 on dentin pretreated at 50 C. Definite maxima were found in both instances. It occurred in each case beyond the amount adsorbed that was required to fill a monolayer. It is extremely likely that at coverages below the resolution of these isotherms, the heats of adsorption were much higher. Since the temperature of pretreatment is the only condition which was different, the existence of the maximum (at least in these experiments) appears to be related to the residual gases which were less completely removed at the lower pretreatment temperature and this would suggest adsorbed water. Despite their difference in shape, the isosteric heats of adsorption at higher coverages

for NH₃ on both preparations of dentin was reasonably constant at about 6 kcal/mol.

On comparing the isosteric heats of NH₃ and CO₂ for corresponding surfaces at the completion of a monolayer, it is seen that the values for NH₃ are greater as would be expected based upon their known heats of liquifaction and sublimation, respectively.

The heat of adsorption over the first layer is, of course, dependent upon the distribution function. The present method can be employed to obtain these heats at successively smaller fractions of the surface by going to higher temperatures. It has been shown, for example, [3] that the isosteric heat of adsorption of CO₂ on synthetic hydroxyapatite when measured at zero degrees, dropped from 13.5 to about 9 kcal/mol when measured up to 1/4 of a monolayer.

The ultimate strength of an adhesive might be considered as proportional to the integral, U, where

$$U = \int_0^A Q_{ST} dA \text{ - - - - - (4)}$$

and A is the surface area. However, the average isosteric heat, \bar{Q}_{ST} , over the entire surface would be defined as

$$\bar{Q}_{ST} = (1/A) \int_0^A Q_{ST} dA \text{ - - - - - (5)}$$

so by combining equations (4) and (5), it is seen that

$$U = A \bar{Q}_{ST} \text{ - - - - - (6)}$$

Unfortunately, the present results do not extend to low enough fractions of the surface to evaluate \bar{Q}_{ST} with any degree of precision. However, an independent estimate is available from the c parameter evaluated from the BET equation. Brunauer^[19] defined E_1 as " - - the average heat of adsorption on the less active part of the adsorbing surface." in terms of the heat of liquefaction E_L according to Eq. (7):

$$E_1 = E_L - RT \ln c \text{ - - - - - (7)}$$

Values of E_1 computed in this manner are also shown in Table 1. Assuming, therefore, that $E_1 \approx \bar{Q}_{ST}$ and using the surface areas of Table 1, it can be estimated from Eq. (6) that NH_3 ($U=1136$) at -33°C would be about five times as strong an adhesive for dentin pretreated at 50°C as would CO_2 ($U=215$) at -78°C .

It is appreciated that this study is of a preliminary nature and is intended merely to point the direction. If these results are substantiated by additional experiments, (see Sec. VII), it would show that the presence of collagen was not especially

beneficial either to NH_3 as an adhesive or to CO_2 . Estimates can be made of U-values from Eq. (6) of 523 and 230 $\text{kcal}\cdot\text{mol}^{-1}\cdot\text{m}^2\cdot\text{g}^{-1}$ for NH_3 and CO_2 , respectively, adsorbed on anorganic whole teeth. Whole teeth, however, include enamel which has a much lower surface area than dentin. If the values of U obtained for anorganic whole teeth were extrapolated to anorganic dentin, assuming the same heats of adsorption corresponding adhesive strengths would probably be increased by a factor sufficient to nullify any apparent advantage of dentin over anorganic whole teeth. Thus, the surface area expected for anorganic dentin when measured by NH_3 would be $149 \times 67/64 = 156 \text{ m}^2\cdot\text{g}^{-1}$ and $U = 156 \times 7.8 = 1217$ as compared with a U-value of 1136 for dentin, itself.

VI-Conclusions

Subject to the limitations of the method, gas adsorption can be used as a tool in the search for better dental adhesives. It provides quantitative information relating to the strength per unit adhesive linkage as well as the maximum concentration of such linkages. Ammonia appeared to score better than carbon dioxide on both of these counts under the conditions selected for these experiments. The presence of collagen, while not completely understood, seemed to contribute no profound influence upon the theoretical ultimate strength of the bonding.

Among the limitations of the method are:

(1) The possibility that the relative adsorptive properties of the gases would be seriously modified when chemically combined as reactive appendages in a practical adhesive.

(2) The fact that there may be no gas representative of some chemical groups whose adhesive properties may be of interest.

VII-Suggestions for Future Work

Reinforcement of some of the points brought out in this paper could be attained by:

- (1) The adsorption of methylamine on dentin.
- (2) The adsorption of ammonia on collagen.
- (3) Solvent exchange of swollen collagen and dentin to attempt to show larger surface areas accessible to nitrogen.

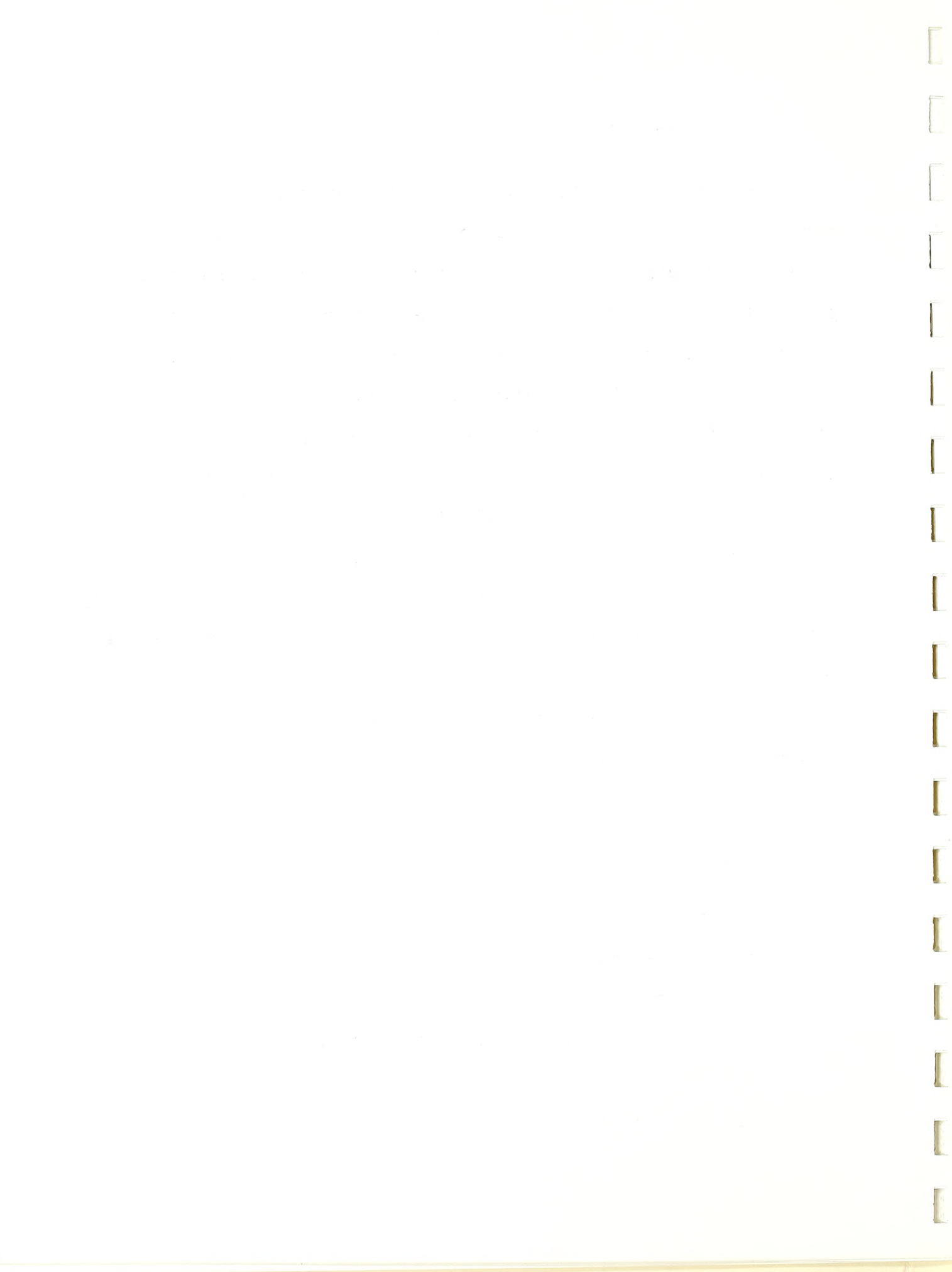


Table 1

BET Surface Area Accessible to Each Adsorbate

	Anorganic Whole Teeth (m ² /g)	Dentin (50 C Prep) (m ² /g)	Dentin (110 C Prep) (m ² /g)	Anorganic Dentin (m ² /g)
NH ₃ (14.6 A ²)	67 (E ₁ =7.8)	160 (E ₁ =7.1)	138 (E ₁ =6.9)	--
CO ₂ (21.0 A ²)	48 (E ₁ =4.8)	50 (E ₁ =4.3)	--	--
N ₂ (16.2 A ²)	64	7.5	6.5	149

E₁ values (kcal/mol) were determined from the BET c-parameters

Caption for Figures

Figure 1: Cryostat Used in Gas Adsorption Measurements

Figure 2: Schematic Diagram of Thermistor-Sensed Thermo-Regulator

R_1, R_2 : 10,000 ohms; R_3, R_4, R_5, R_{11} : 0.12 megohms; R_6, R_7 : 1,500 ohms; R_8, R_9, R_{12} : 1,200 ohms; R_{10}, R_{13}, R_{15} : 0.47 megohms; R_{14} : 220 ohms; R_{16} : (W.W.) 1,500 ohms; P_1 : 0.5 megohms; P_2 : (W.W.) 5,000 ohms; P_3 : (W.W.) 50 ohms; C_1, C_2 : (Electrolytic) 8 microfarads; C_3, C_4 : (Electrolytic) 4 microfarads; C_5, C_6, C_7, C_8 : 0.1 microfarads; C_9 : (Paper) 4 microfarads; C_{10} : 0.05 microfarads; V_1 : 6H6; V_2, V_3 : 6SL7; V_4 : 6SN7; T_1 : 6.3 volts (C.T.), 3 amperes, Filament Transformer; Ry_1 : 5000 ohm Plate Circuit Relay; Thermistor: (see text)

Figure 3: Typical Family of Adsorption Isotherms at the Boiling Point and at Temperatures Displaced Five and Ten Degrees Above and Below it.

Figure 4: Isosteric Heats as Functions of the Amounts of Gas Adsorbed.

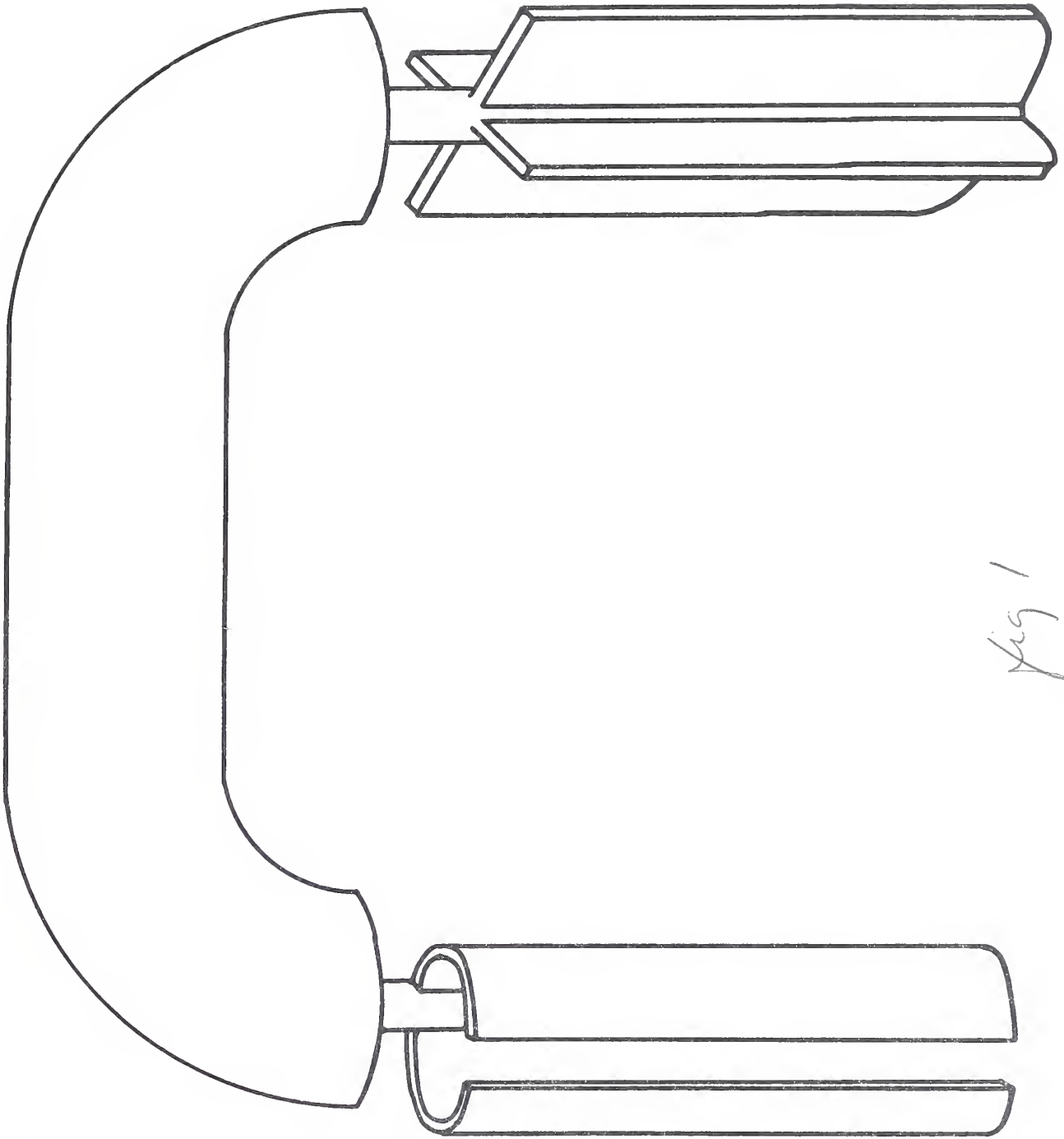


Fig 1

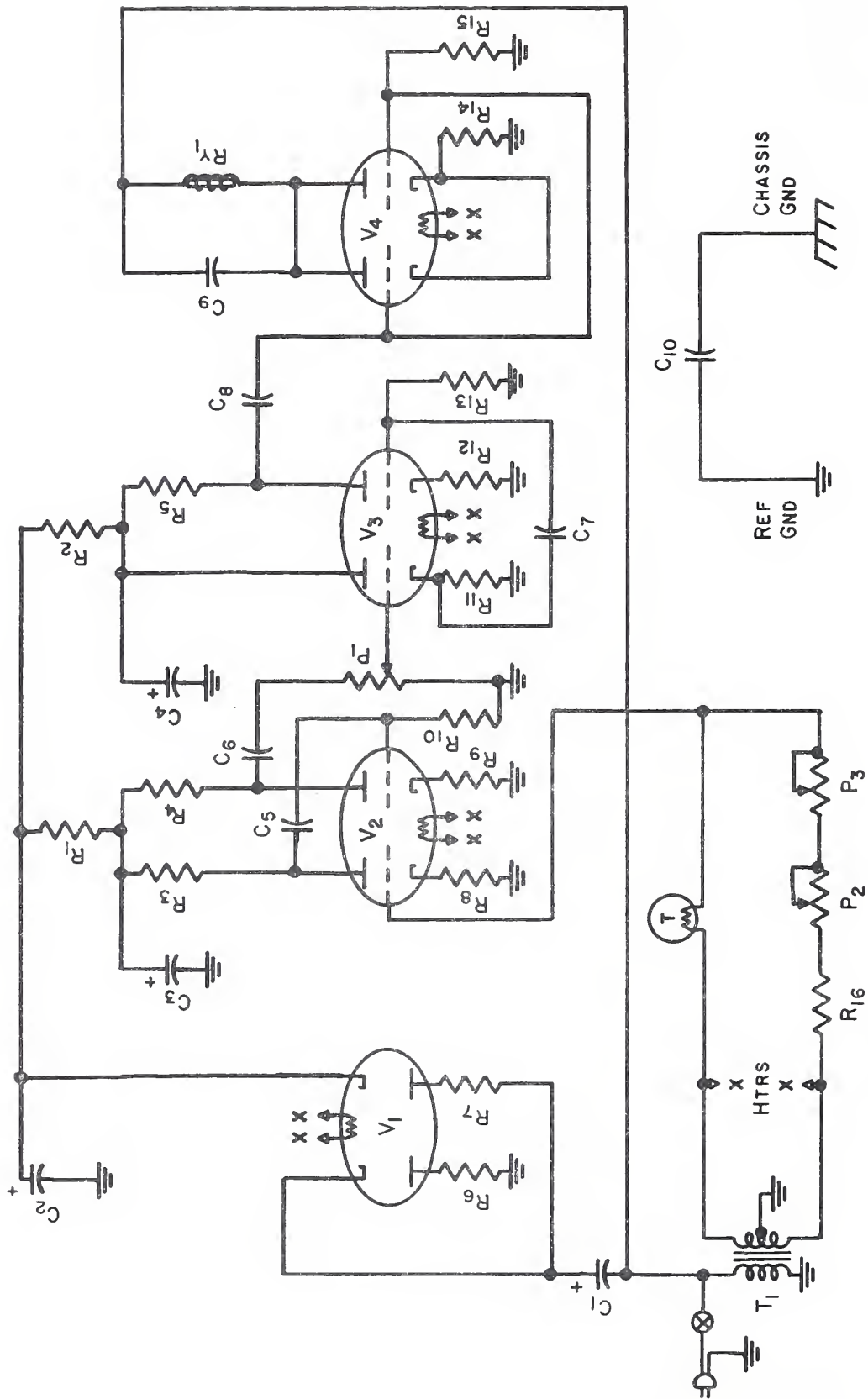


fig 2

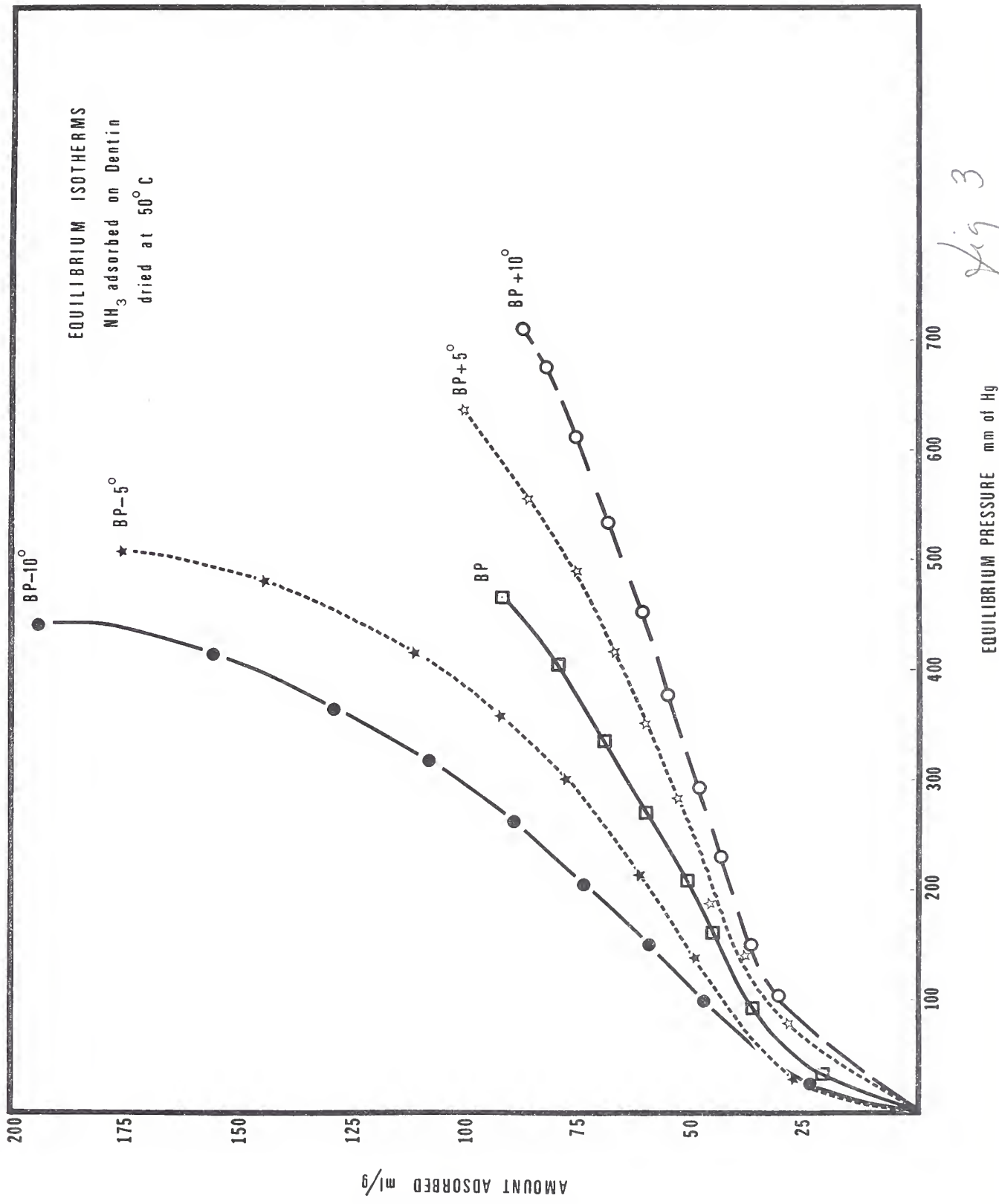
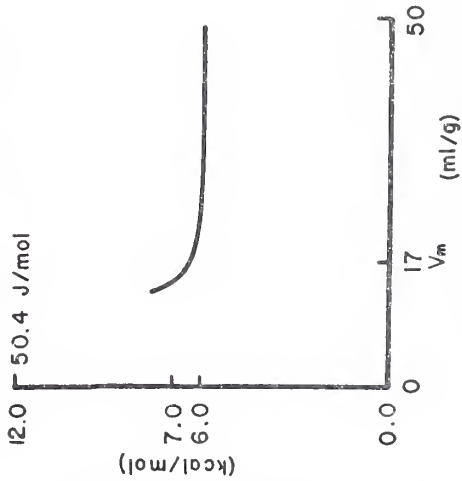


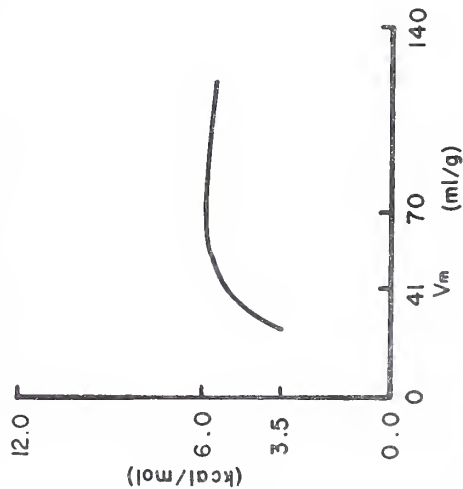
Fig 3

AMMONIA

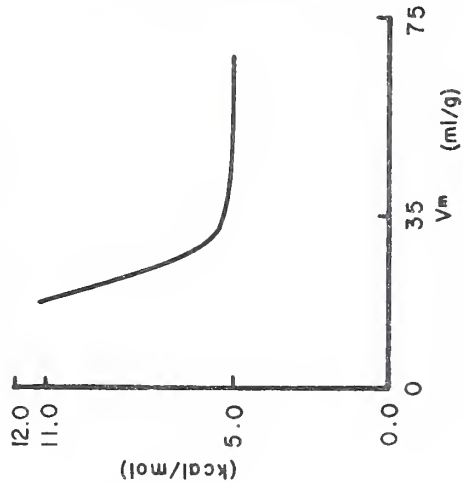
ANORGANIC WHOLE TEETH



DENTIN (50 C PREP.)

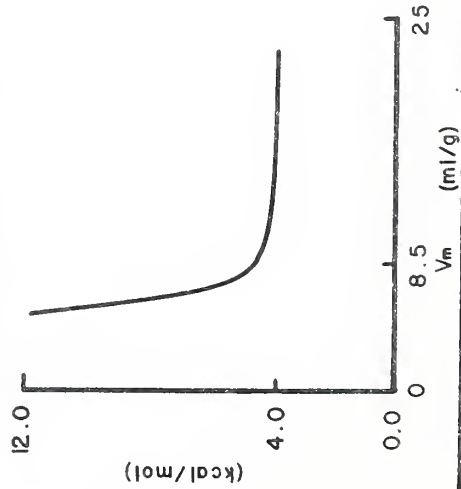


DENTIN (110 C PREP.)

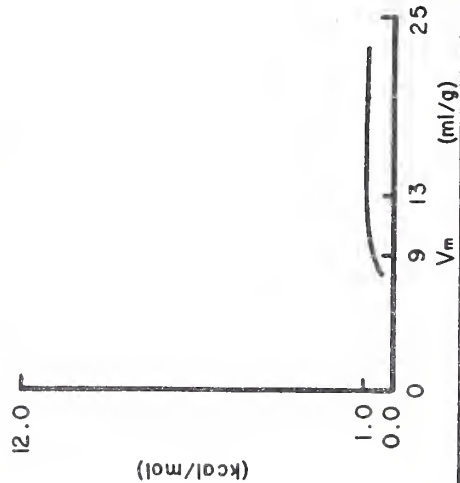


CARBON DIOXIDE

ANORGANIC WHOLE TEETH



DENTIN (50 C PREP.)



ISOSTERIC HEATS
OF ADSORPTION

VS

AMOUNTS ADSORBED
PER G OF SUBSTRATE

Fig 4

Bibliography

- [1] A. C. Zettlemoyer and J. J. Chessick Jour of Phys Chem 64 1131 (1960)
- [2] M. S. Goldstein EXPERIMENTAL METHODS IN CATALYTIC RESEARCH - Chapter 9, Academic Press, N.Y. and London (1968)
- [3] V. R. Deitz, F. G. Carpenter and R. G. Arnold CARBON 1 245 (1964)
- [4] S. C. Peckman, F. L. Losee and I. Ettleman Jour Dent Res 35 1947 (1956)
- [5] E. F. Huget, G. M. Brauer and W. V. Loebenstein Ibid 47 291 (1968)
- [6] W. V. Loebenstein and V. R. Deitz Jour of Res. NBS 46 51 (1951)
- [7] R. B. Scott and J. W. Mellors Ibid 34 243 (1945)
- [8] W. V. Loebenstein "Calculations and Comparisons of Non-Ideal Gas Corrections for Use in Gas Adsorption" (to be published)
- [9] R. A. Beebe Proc of the First Workshop on Adhesive Restorative Dental Materials, NIDR - HEW 75 (1961)
- [10] A. L. McLellan and H. F. Harnsberger Jour of Colloid and Interface Sci 23 577 (1967)
- [11] G. M. Brauer. Adhesive Restorative Dental Materials-II. Public Health Service
- [12] P. A. Marshall and W. J. Moore Jour Am Chem Soc 74 4779 (1952) | Pub. No. 1494,
| p. 203 (1965).
- [13] W. B. Spencer, C. H. Amberg and R. A. Beebe Jour Phys Chem 62 719 (1958)
- [14] A. C. Zettlemoyer, A. Chand and E. Gamble Jour Am Chem Soc 72 2752 (1950)
- [15] R. G. Mitton and R. J. Mawhimney Jour Soc Leather Trades' Chemists 39 172 (1955)
- [16] J. R. Kanagy Jour of the Am Leather Chemists Assn 45 12 (1950)
- [17] J. Hagymassy, Jr., S. Brunauer and R. SH. Mikhail Jour of Colloid and Interface Sci 29 485 (1969)
- [18] H. Cochrane, P. L. Walker, Jr., W. S. Diethorn and H. C. Friedman Ibid 24 405 (1967)
- [19] S. Brunauer THE ADSORPTION OF GASES AND VAPORS p-158 Princeton Univ. Press, Princeton, N. J. (1943)

