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TECHNICAL REPORT
R-51

ADSORPTION OF HALOGENATED FIRE-EXTINGUISHING AGENTS ON POWDERS

By ALLEN J. BARDUHN, BHAILAL S. PATEL, WALTER MEYER
and BRONISLAW B. SMURA

1960

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Syracuse University

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TECHNICAL REPORT R-51

ADSORPTION OF HALOGENATED FIRE-EXTINGUISHING AGENTS ON POWDERS

By Allen J. Barduhn, Bhailal S. Patel, Walter Meyer, and Bronislaw B. Smura

SUMMARY

Development of new and improved fire-extinguishing agents consisting of halogenated methanes adsorbed on fine powders has been initiated. The primary purpose of the investigation described herein was to determine the amounts of vapor adsorbed on a variety of adsorbents and to test some of these combinations for their effectiveness in extinguishing fires.

Adsorption data are presented for various combinations of four different Freons on carbon, silica gel, alumina, and molecular sieves at pressures up to 225 pounds per square inch gage. The carbons adsorbed 50 to 100 percent and the silica gels, 30 to 50 percent of their own weight of Freon.

Several adsorbed systems were tested in a standard dry-powder extinguisher on a 5-square-foot gasoline fire. The combination of bromotrifluoromethane (Freon 13B1) and carbon puts out fires about as well as commercial bicarbonate powder and nitrogen. Because the extinguishers used were not designed for use with adsorbed systems, the new agents were probably not applied to the test fire under optimum conditions. An extinguisher developed specifically for these agents would undoubtedly enhance their fire-fighting effectiveness.

INTRODUCTION

The state of the art and science of fire fighting is in continuous change. For many reasons it is desirable to improve the effectiveness of extinguishing agents with respect to the speed with which they put out a fire and to the weight of material required.

Agencies interested in military and commercial aircraft are especially concerned with this subject because aircraft are so susceptible to destruction by fire. Preventing a crashed military airplane from burning by using a few dollars worth of extinguishing agent can be of tremendous military significance during war time and of great economic significance at any time. The extinguishing agents must be effective because of the potent nature of aircraft gasoline fires and because the total weight of agent and application system must be low in order to reduce flight loads.

Extinguishing agents in common use today for aircraft fires are dry powders and halogenated hydrocarbons. Dry-powder agents consist of finely divided alkali metal salts (usually sodium bicarbonate) pressurized with nitrogen. The halogenated hydrocarbons now in common use are bromotrifluoromethane (Freon 13B1) and monochlorobromomethane (Dow CB). These materials are liquefied under pressure with inert gases added if necessary. They are vaporized by discharge through a nozzle directly into the fire zone.

The novel idea of combining powders and vapors into a single extinguishing agent was first proposed by Dr. C. S. Grove, Jr., of Syracuse University. Preliminary considerations of this idea revealed that it would be impossible to use powders and liquids together, since the slurry or mud formed is difficult to store and discharge. Also, the use of bicarbonate powder with gaseous extinguishing agents would be no better than the powder alone, since the amount of gas that could be stored would be a very small fraction of the amount of powder—on the order of 4 percent.

Grove thus proposed that the powders be materials that could adsorb large amounts of vapor. With this type system, the existence of a large quantity of vapor in the presence of fine powder stored under moderate pressure seemed very attractive. A further advantage of such a combination is apparent. The adsorbed vapor may desorb from the powder in the fire at such a rate that the time of exposure of the vapor to the fire will be materially prolonged. It is thus possible that a smaller quantity of extinguishing agent would be required.

To study the possibilities of adsorbed systems as fire-extinguishing agents, the amounts of various halogenated hydrocarbons adsorbed by various solids as a function of temperature and pressure must first be determined. Those combinations showing appreciable adsorption can then be tested for their extinguishing properties. This report and the experimental work were organized according to this plan.

The adsorption equilibrium work was undertaken in two separate phases because of the difference in the apparatus required. One phase involved low pressures from high vacuums to 1,000 millimeters of mercury, and the other involved high pressure from 1 atmosphere to 250 pounds per square inch absolute. The temperature range was from 30° to 75° C. The first part of this report covers the theory of adsorption, the results, and a discussion of the equilibrium data. Some thought is also given to the rates of adsorption and desorption.

The second part of this report covers the results of fire-extinguishing tests and a discussion of them. Also included is an analysis of the mechanism of desorption and some comments on the relative merits of adsorbed systems as compared with pure liquid systems as extinguishing agents.

This investigation was carried out at Syracuse University Research Institute under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

ADSORPTION

THEORY

ADSORPTION EQUILIBRIA

Adsorption is the phenomenon whereby gases or vapors are retained on the surface of a solid or liquid at a density greater than that in the ambient fluid. The attractive force that the surface exhibits for the gas is usually attributed to (a) unsatisfied physical forces that exist at all surfaces and are due to the unsymmetrical distribution of the surrounding mass, and (b) to unsatisfied or residual valence forces.

Heat of adsorption.—The adsorption phenomenon is a spontaneous one that results in a decrease in the free energy F of a gas molecule. Also, a molecule adsorbed on a mobile layer loses one or more of its three translational motions, while one adsorbed on a fixed spot loses all its translational motion. In either case, the result is a decrease in entropy S. (All symbols are defined in appendix A.)

The change in enthalpy ΔH of any system may be expressed as

$$\Delta H = \Delta F + T\Delta S \tag{1}$$

Because both F and S decrease during the adsorption process, ΔH must be negative. Therefore, when a gas or vapor is adsorbed isothermally, heat is evolved.

If only adsorption of gases by solids is considered, two general types may be described on the basis of the magnitude of the heat evolved during the adsorption process. The first type is referred to as chemisorption. As the term implies, the heat evolved is on the order of that of a chemical reaction. The second type of adsorption is referred to as physical adsorption. The heat evolved in this process is on the order of that encountered in condensation processes. Usually a dividing line of 10 kilocalories per gram-mole is used to distinguish the two types, but this figure is arbitrary and some investigators use 20 kilocalories per gram-mole.

To determine the heat of adsorption when calorimetric data are not available, Brunauer's equation (ref. 1, pp. 218–223) may be used:

$$q_d' + RT = RT^2\left(\frac{\partial \log_e p}{\partial T}\right)_a \tag{2a}$$

where q_d' is the differential heat of adsorption, R is the gas law constant, T is the absolute adsorption temperature, p is the equilibrium adsorption pressure, and $\left(\frac{\partial \log_e p}{\partial T}\right)_a$ is determined for a constant amount a of gas adsorbed.

The differential heat of adsorption has also been defined by

$$q_d = RT^2\left(\frac{\partial \log_e p}{\partial T}\right)_a \tag{2b}$$

These equations can be integrated for an average value of q_d over the temperature range T_1 to T_2 to give, respectively,

$$q_d' = \frac{RT_1T_2}{T_2-T_1}\log_e\left(\frac{p_2T_1}{p_1T_2}\right) \tag{3a}$$

and

$$q_d = \frac{RT_1T_2}{T_2-T_1}\log_e\left(\frac{p_2}{p_1}\right) \tag{3b}$$

Thus, to determine the heat of adsorption by equations (3), adsorption data at only two temperatures are required. In the results reported later, equation (3b) was used for all calculated values of q_d.

Adsorption isotherm theories.—The amount of a gas a adsorbed at equilibrium is a function of the final pressure and temperature:

$$a = f(p,T) \tag{4}$$

or at constant temperature

$$a = f(p)_T \tag{5}$$

Experimental adsorption data are usually presented in the form of equation (5) as adsorption isotherms.

In the interpretation of adsorption isotherms, theories of monolayer adsorption, multilayer adsorption, and capillary condensation have been developed (ref. 2). The classical isotherm equation, however, was presented originally by Freundlich as an empirical relation (ref. 3):

$$a = kp^{1/n} \text{ or } a = kp^m \tag{6}$$

where a is the amount of gas adsorbed per unit mass of adsorbent, k and n or m are empirical constants, and p is the equilibrium pressure. Halsey and Taylor (ref. 4) have subsequently derived equation (6) on a semitheoretical basis from the Langmuir equation.

Monolayer theories: The first equation based on a theoretical analysis of adsorption was published by Langmuir (ref. 5); similar expressions have been presented by Volmer (ref. 6) and Fowler (ref. 7). The Langmuir equation is

$$\frac{a}{a_m} = \frac{bp}{1+bp} \tag{7a}$$

or

$$\frac{p}{a} = \frac{1}{ba_m} + \frac{p}{a_m} \tag{7b}$$

where a_m is the amount of gas required to form a monomolecular layer of gas molecules and b is a temperature dependent constant. This equation assumes a completely accessible adsorbent surface that is saturated by the adsorption of a single layer of gas molecules. At very low pressures, equation (7a) becomes

$$a = a_m bp \tag{8}$$

Henry (ref. 1, pp. 84–89), Magnus (ref. 8), and Williams (ref. 9) have developed other isotherm equations based on the adsorption of a monolayer of gas.

Multilayer theories: Multilayer adsorption theories have been presented by Polanyi (ref. 1, pp. 95–120) and Brunauer, Emmett, and Teller (refs. 10 and 11). Polanyi postulated that an adsorbent exerts an attractive force on gas molecules within its vicinity. These forces are of such magnitude that they form adsorbed layers many molecules thick. Polanyi defined the work required to bring a molecule from the gas phase to the state of a saturated liquid on the surface of the adsorbent as the adsorption potential. Dubinin (ref. 12) suggested that similar types of compounds have equal adsorption potentials when equal volumes of gas are adsorbed on the same adsorbent. On this basis, Dubinin presents

$$\left[\frac{RT}{V'}\log_e\left(\frac{p_o}{p}\right)\right]_1 = \left[\frac{RT}{V'}\log_e\left(\frac{p_o}{p}\right)\right]_2 \tag{9}$$

where p and p_o are the equilibrium and saturation pressures, respectively, of the gas and V' is the molal volume of the gas as a saturated liquid at the adsorption temperature. Lewis et al. (ref. 12) modified equation (9) to the form

$$NV = \phi\left[\frac{T}{V}\log_e\left(\frac{f_o}{f}\right)\right] \tag{10}$$

where N is the moles of gas adsorbed, V is the molal volume of the saturated liquid at a vapor pressure equal to the adsorption pressure, f_o and f are the fugacity of the saturated gas and the gas at the adsorption pressure, respectively, and ϕ

indicates a function. Both equations (9) and (10) are referred to as modified Polanyi equations.

The BET (Brunauer, Emmett, Teller) equation was originally applied to multilayer adsorption on plane surfaces (ref. 10) and was later modified (ref. 11) to include adsorption in capillaries also. The original equation has two general forms. If the adsorption is not on a free surface, but on the walls of pores where the number of layers adsorbed on each pore wall is restricted to n, the adsorption equation is

$$a=\frac{a_m c(p/p_o)}{1-(p/p_o)}\left[\frac{1-(n+1)(p/p_o)^n+n(p/p_o)^{n+1}}{1+(c-1)(p/p_o)-c(p/p_o)^{n+1}}\right] \qquad (11)$$

where a_m is the amount of gas required to form a monolayer, c is a temperature-dependent constant, and p/p_o is the relative pressure (where p and p_o are, respectively, the equilibrium pressure and the saturation pressure of the gas at the adsorption temperature).

If the adsorption occurs on a free surface, $n=\infty$, and equation (11) reduces to

$$\frac{p}{a(p_o-p)}=\frac{1}{a_m c}+\frac{c-1}{a_m c}\,\frac{p}{p_o} \qquad (12)$$

For the case where $n=1$, equation (11) reduces to

$$a=\frac{a_m\,(c/p_o)p}{1+\,(c/p_o)p} \qquad (13)$$

which becomes the Langmuir equation when b is substituted for c/p_o.

Capillary condensation and hysteresis: Interpretation of adsorption data in the region of liquefaction and the phenomenon of hysteresis with respect to pressure were first related to capillary condensation by Zsigmondy (ref. 1, p. 394). Hysteresis is a variation of the desorption-data curve from the adsorption curve. In systems exhibiting the hysteresis effect, the adsorption curves correspond to smaller amounts of gas adsorbed than the desorption curves. Zsigmondy postulated that hysteresis was the result of foreign adsorbed gas molecules preventing the adsorbed vapor from wetting the capillary walls of the adsorbent. Zsigmondy applied the Kelvin equation (ref. 1, p. 120) for vapor pressure depression over a capillary to this reasoning. The resulting equation is

$$\log_e\frac{p_o}{p}=\frac{2\sigma V\cos\theta}{rRT} \qquad (14)$$

where r is the radius of the capillary in which condensation is taking place, σ is the surface tension of the adsorbate liquid, and θ is the wetting angle. Brunauer (ref. 1, p. 395) states that Zsigmondy's theory applies to the case of irreversible hysteresis where a different adsorption-desorption path is followed for each successive experiment.

For the case of reversible hysteresis where the same adsorption-desorption path is followed for successive adsorption cycles, Foster and Cohan (ref. 1, p. 137) suggested that the hysteresis effect is due to a delay in the formation of a meniscus in the capillary. The meniscus does not form until the adsorbed layers on opposite walls of a capillary are thick enough to touch and block the capillary opening at its narrowest point. The adsorption portion of the cycle, Foster (ref. 1, p. 401) states, represents a simultaneous process of adsorption and capillary condensation, while the desorption branch represents capillary condensation only and can be represented by the Kelvin equation.

McGavack and Patrick (ref. 13) and Kubelka (ref. 14) have also written expressions for correlating data in the region of capillary condensation.

RATE OF PHYSICAL ADSORPTION

Much less information is available on adsorption and desorption rates than on adsorption equilibria. The data that are available show that the time required to reach adsorption equilibrium varies from periods too short to measure to periods of several months. Many of the periods are measured in minutes, however.

In general, for physical adsorption it is reasonable to assume that gas molecules are adsorbed on a surface about as fast as they can reach the surface (ref. 1, pp. 7–11, 448–473). Thus, if a surface is completely available and exposed, the time required to reach equilibrium would be measured in milliseconds (molecular velocities over short distances). In cases where rates are slow enough to be measured easily, the retarding action is usually attributable to difficulties a molecule encounters in reaching a surface, for example, diffusion down long narrow pores or blocking of sites by foreign adsorbates. In chemisorption, rates are frequently quite slow because of high activation energies, but this is not of interest in this discussion.

When rates are measured for systems in which relatively large amounts of gas are adsorbed, the heat of adsorption raises the temperature of the solid, reducing the equilibrium amount of gas on the surface. Even if the true adsorption rate were instantaneous, the solid would gradually take on more adsorbate as the heat was dissipated to the constant-temperature surroundings. The apparent rate of adsorption would thus be really determined by the rate of heat transfer to the surroundings.

In the event that an inert (nonadsorbing) gas were present in the vapor phase along with the gas which does adsorb, the observed rates would be further retarded by diffusion effects in the bulk gas surrounding the solid. Experimentally it is simple to eliminate this effect by using pure gases, but the heat-transfer problem is not easily eliminated. The authors suspect that some adsorption rates reported in the literature are useless because the heat-transfer limitations were not recognized.

The difficulty in maintaining the solid at a constant temperature while making rate measurements is that the heat of adsorption is generated throughout the volume of the solid and it must be conducted out through the exposed surface. Solids such as silica gel and granular or powdered carbon are excellent insulators, and unless the conduction distance is extremely small, appreciable temperature gradients are bound to build up. The walls of the containing vessel and the fluid films bounding it may be important heat-transfer resistances also. Some experiments conducted in this laboratory using Freon 12 and Silica Gel 12 in a layer only 1 millimeter thick showed that immediately on admitting Freon into the gel about 90 percent of the gas adsorbed, the temperature rose 5° to 10° C above ambient, and several minutes were required for the gradient to disappear. Furthermore, it appeared that the gel and the gas were at adsorption equilibrium at every instant within the ability to measure time (± 2 sec) and temperature ($\pm 0.2°$ C). The rate at which the last 10 percent of the Freon was adsorbed from the gas phase was thus determined solely by the rate at which the solid temperature approached ambient.

Some investigators have correlated their rate data with the Langmuir rate equation (ref. 1, pp. 7-11, 448-473):

$$v=v_e(1-e^{-kt}) \tag{15}$$

where v and v_e are the amounts adsorbed at time t and at equilibrium, respectively, and k is a kinetic rate constant to be determined experimentally. It can easily be shown that if adsorption equilibrium is maintained continuously, and if heat transfer through the container walls controls the rate of adsorption, the rate expression will be

$$v=a+b(1-e^{-k't}) \tag{16}$$

where k' is now a function solely of the heat-transfer coefficient from the solid to the ambient and thermal properties of the system. Equation (16) also assumes that over the short temperature ranges involved the equilibrium amount of adsorption is linear with the temperature. The quantities a and b are constants. It will thus be very easy to confuse heat-transfer rates with true adsorptive rates if the pitfalls of such rate measurements are not recognized.

Langmuir's rate equation (15) is not useful for predicting true adsorption rates, since the constant k must be determined experimentally and is different for every system and temperature.

Damkohler (ref. 15) has pictured molecules of vapor diffusing in Knudsen flow down very narrow pores and also migrating in the condensed phase on the surface of these pores. The entire adsorption time required is consumed in diffusion or migration and the molecules are assumed to adsorb instantaneously once they arrive at an unoccupied site. With this theory, he shows that the differential equation describing the rate at which isothermal adsorption takes place is

$$\frac{\partial N}{\partial t}=D\frac{\partial^2 N}{\partial x^2} \tag{17}$$

where N is the number of molecules in the gas phase per unit pore length, D is a composite diffusion coefficient depending on individual gas and surface diffusion coefficients, and x is the coordinate measured along the pore axis. The solution to the equation is

$$\frac{v}{v_e}=1-\frac{8}{\pi^2}\sum^{m}\frac{exp[-\delta(2m+1)^2]}{(2m+1)^2} \tag{18}$$

where

$$\delta=(\pi/2L)^2Dt$$

and v/v_e is the fraction of the equilibrium amount adsorbed or desorbed in time t, and L is the pore length. This equation gives a relation between amount adsorbed (or desorbed) and time, which is quite similar to the Langmuir equation (15) for the latter half of the approach to equilibrium. It has the advantage, however, of allowing estimation of the time or rate of adsorption independent of experiment, provided something is known about the pore structure and particle size of the adsorbent.

For several similar silica gels desorbing Freon 12, such calculations have been made and the results are shown in the following table for which the effect of particle size on desorption rates was calculated from the Damkohler relations (ref. 15) (area, 832 sq m/g; pore volume, 0.45 cc/g; other properties calculated from Wheeler (ref. 16)):

Davison Silica Gel	Tyler screen size, mesh	Average particle diameter	Time required to desorb 99 percent of equilibrium amount
63	Through 325	0.02 mm	0.3 millisec
12	28 200	.20 mm	30 millisec
	6 10	2.0 mm	3 sec
		⅜ in.	1 min

These figures give only the order of magnitude of the adsorption or desorption time, since they are based on average pore lengths and diameters and average particle sizes. They are also based on estimated diffusivities. The important conclusion to draw, however, is that for small particle sizes (those that would be used in a fire extinguisher) the true desorption time would be measured in milliseconds or fractions thereof. Furthermore, the actual desorption times would be controlled entirely by the rates of hydrodynamic flow, heat transfer, and/or mass transfer in the bulk of the gas phase surrounding the particle. Such rates may in some cases be estimated from existing data on laminar and turbulent transport rates. In those cases where data are not available, the experimental techniques required to determine them are those of heat and mass transfer and not those of adsorption and desorption.

MATERIALS, APPARATUS, AND PROCEDURES

SUBATMOSPHERIC ADSORPTION

The apparatus used to measure subatmospheric adsorption was a McBain and Baker (ref. 17) multiple-type adsorption balance as used by Milligan et al. (ref. 18) and further modified by Josefowitz and Othmer (ref. 19). It was of Pyrex 774 suitable for measuring adsorption isotherms from 30° to 60° C at pressures from 10^{-3} to 1,000 millimeters of mercury. For assembling convenience, the apparatus consisted of interchangeable, ground glass, standard taper joints with mercury seals essential for high-vacuum work. All stopcocks were precision grade with mercury seal and hollow plug with oblique bore.

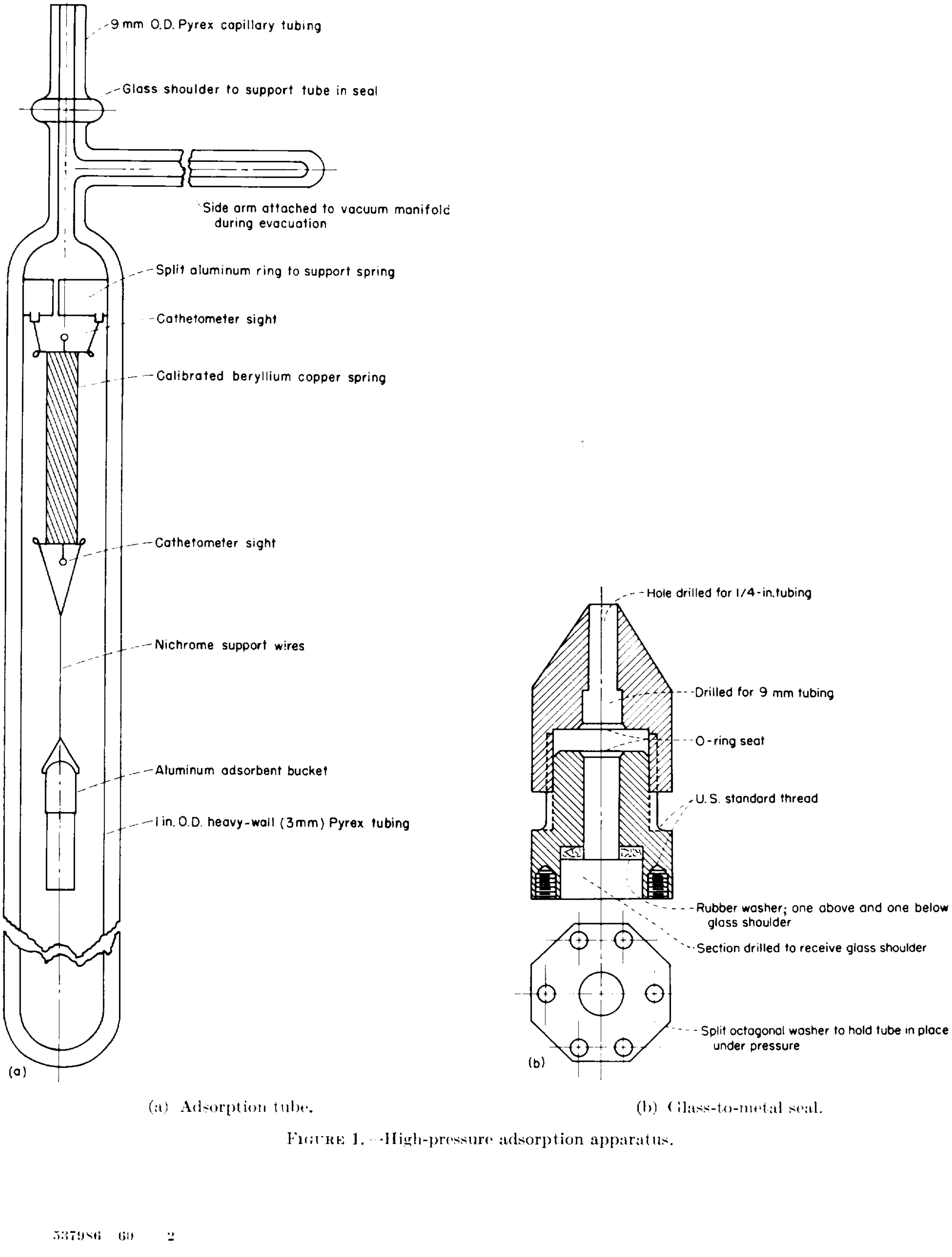
HIGH-PRESSURE ADSORPTION

The apparatus constructed to measure adsorption isotherms in the range from 1 atmosphere to 250 pounds per square inch absolute was of the McBain-Baker sorption balance (ref. 17) type. Adsorption was measured by a calibrated beryllium copper spring mounted in a heavy-wall Pyrex glass tube (fig. 1(a)).

The design of the glass adsorption tube was based on the work of Morris and Maass (ref. 20) who used Pyrex bomb tubing at a pressure of 46.2 atmospheres. Using a safe shearing stress for Pyrex glass as calculated from the data of Morris and Maass and a safe working pressure of 800 pounds per square inch, 1-inch-outside-diameter heavy-wall (3-mm) Pyrex brand glass tubing was selected for the adsorption tube. Three tubes of the design pictured in figure 1 (a) were blown, annealed, and tested outside the laboratory at pressures up to 1,000 pounds per square inch. Of the three, one failed. Under examination by a hand polariscope, the remaining tubes showed several points of high stress. The annealing time was subsequently lengthened to 1 hour at a controlled temperature of 575° C. Tubes treated in this manner were tested in the laboratory at pressures of 400 pounds per square inch for 5 to 10 hours and 500 pounds per square inch for ½ hour without failure.

The remaining components of the apparatus included a Heise 250 pounds per square inch gage for measuring pressures above 19 pounds per square inch, a 40-inch glass manometer for measuring pressures from 1 atmosphere to 19 pounds per square inch, a steel bulb to add capacity to the system, needle valves to isolate each component of the apparatus, a glass-to-metal coupling to connect the glass adsorption tube to the main sections of the apparatus, and a temperature-control system around the adsorption tube.

The basic design of the glass-to-metal seal or coupling is shown in figure 1(b). Testing in the



(a) Adsorption tube.

(b) Glass-to-metal seal.

FIGURE 1.—High-pressure adsorption apparatus.

laboratory of this seal at pressures up to 300 pounds per square inch using as the sealing element a $\frac{3}{8}$-inch-diameter Garlock O-ring showed no measurable leakage for a period of 2 weeks. Furthermore, the seal would hold a vacuum of 5×10^{-5} millimeter of mercury for 4 hours with no noticeable pressure change.

The temperature-control system around the adsorption tube consisted of a 32-inch-long, 4-inch-diameter glass cylinder with a side-arm level control opening at the top, a drain at the bottom, a water circulation pump, and a 36-inch-long, 1-inch-diameter copper tubing sealed at one end with its walls pierced by a series of orifices. A precision mercury thermoswitch, an electric relay, and a tubular 1,000-watt heater controlled the temperature. When the system was in operation, water was drawn from the bottom of the cylindrical bath by the circulation pump and then sprayed back into the cylinder along its entire length through the orifices in the copper tubing. A precision thermometer indicated that the bath temperature was maintained by this system within ±0.1° C of the control temperature during each experiment.

Briefly, the method of collecting the adsorption isotherm data was as follows. At the beginning of a run, the side arm tube of figure 1(a) was attached to a vacuum-system manifold. After heating the sample at 200° to 300° C for 1 hour by a circular furnace placed around the adsorption tube where the sample bucket was hung, the system was opened to high vacuum. Heating and evacuation were continued until a constant sample weight was obtained. In those cases where a sample was used for more than one isotherm, heating and evacuation were continued until the original sample weight was reproduced within 1 percent.

At this point, the furnace was removed and the temperature control bath was placed around the adsorption tube. The temperature control switch was set to the isotherm temperature. At thermal equilibrium, the free length of the spring was measured by a cathetometer, after which the vacuum was cut off by fusing the side arm closed while maintaining full vacuum.

Next, the adsorbate gas was admitted and its pressure adjusted to the desired level for the initial data point. In general, for pressures from 0 to 19 pounds per square inch, the system pressure was determined by the manometer as read by the cathetometer. With the manometer cut off from the system by a high-pressure valve, higher pressures were read directly from the Heise-Bourdon gage. The length of the balance spring was then measured several times until a constant value was achieved. Additional adsorption as well as desorption points were obtained in a similar manner.

PHYSICAL PROPERTIES OF GASES AND ADSORBENTS

Since the primary purpose of this study was to determine the fundamental adsorption data for those halogenated methane-adsorbent systems that might prove useful for fire-fighting purposes, the several adsorbents selected for study were chosen on the basis of probable fluorinated hydrocarbon adsorption capacity, availability, and ease of application to a fire.

The gases chosen were in general noninflammable, relatively nontoxic, and of such structure as to demonstrate the effect on adsorption of halogen substitution on the methane carbon atom.

Of the several gases selected for study, du Pont's experimental gas Freon 13B1 has been previously tested as a fire-extinguishing agent. A study of a collection of articles (ref. 21) published by the National Fire Protection Association indicated that Freon 13B1 would, on the basis of effectiveness, nontoxicity, and noncorrosiveness be a likely component of a gas-powder fire-extinguishing system.

Silica Gel 63 was used in fire-fighting tests, but no adsorption data were obtained with it. However, it is similar in all respects to Silica Gel 12 except for its particle size.

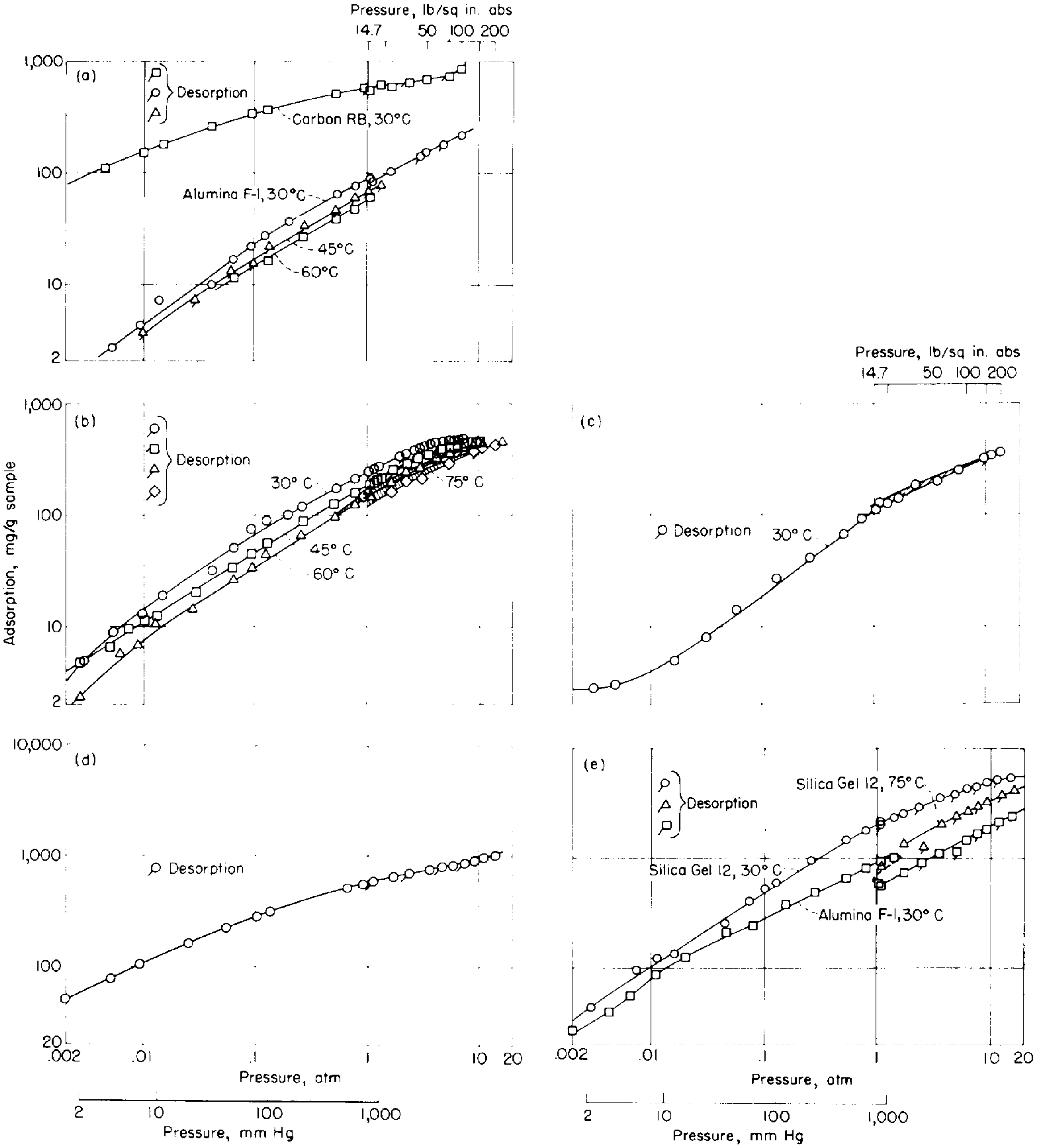
Table I presents the known physical properties of the gases. Table II presents the properties of the adsorbents.

PRESENTATION AND DISCUSSION OF RESULTS

GENERAL ADSORPTION SUMMARY

All reported adsorption data are presented graphically in figures 2 and 3 and are tabulated in tables VIII to XIX. Table III is a condensed summary of all the data and gives the amount adsorbed at only one temperature and two pressures for all the systems studied.

The weight of the adsorbent represents that of a dry degassed sample, while the amount adsorbed represents the gas held by the solid, assuming that all adsorbate is under the influence of adsorptive



(a) Adsorption of Freon 12 by Carbon RB and Alumina F-1.

(b) Adsorption of Freon 12 by Silica Gel 12.

(d) Adsorption of Freon 13B1 by Carbon RB; 30° C.

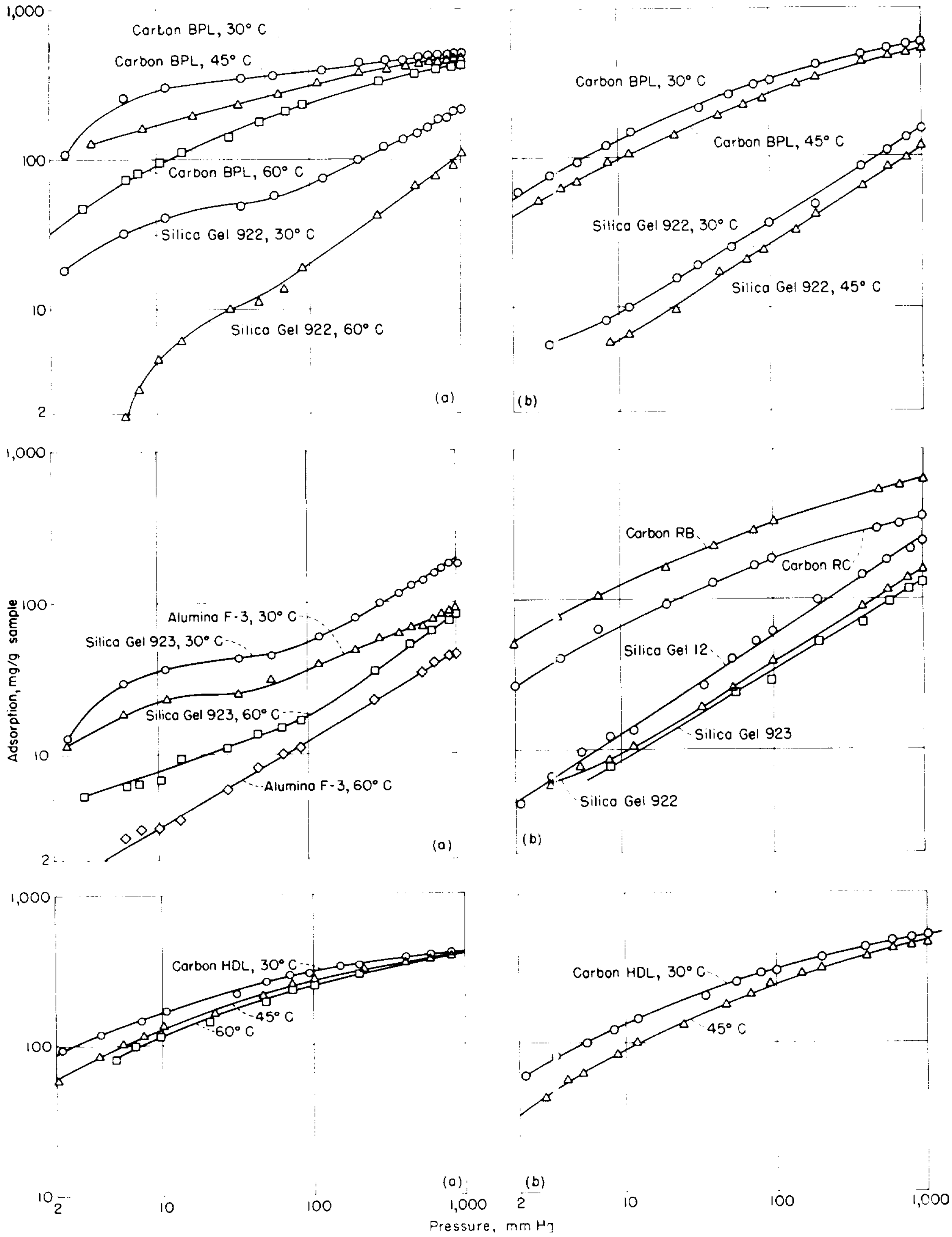
(c) Adsorption of Freon 13 by Silica Gel 12.

(e) Adsorption of Freon 13B1 by Silica Gel 12 and Alumina F-1.

FIGURE 2.—Adsorption data obtained with low- and high-pressure apparatus.

forces. It thus includes a volume of gas equal to the true volume of the adsorbed material but at a density equal to that of the bulk gas. This definition of the amount adsorbed requires a bouyancy correction not only for the volume of the adsorbent, etc., but also for the volume of the adsorbed phase. A discussion of buoyancy corrections is given in appendix B.

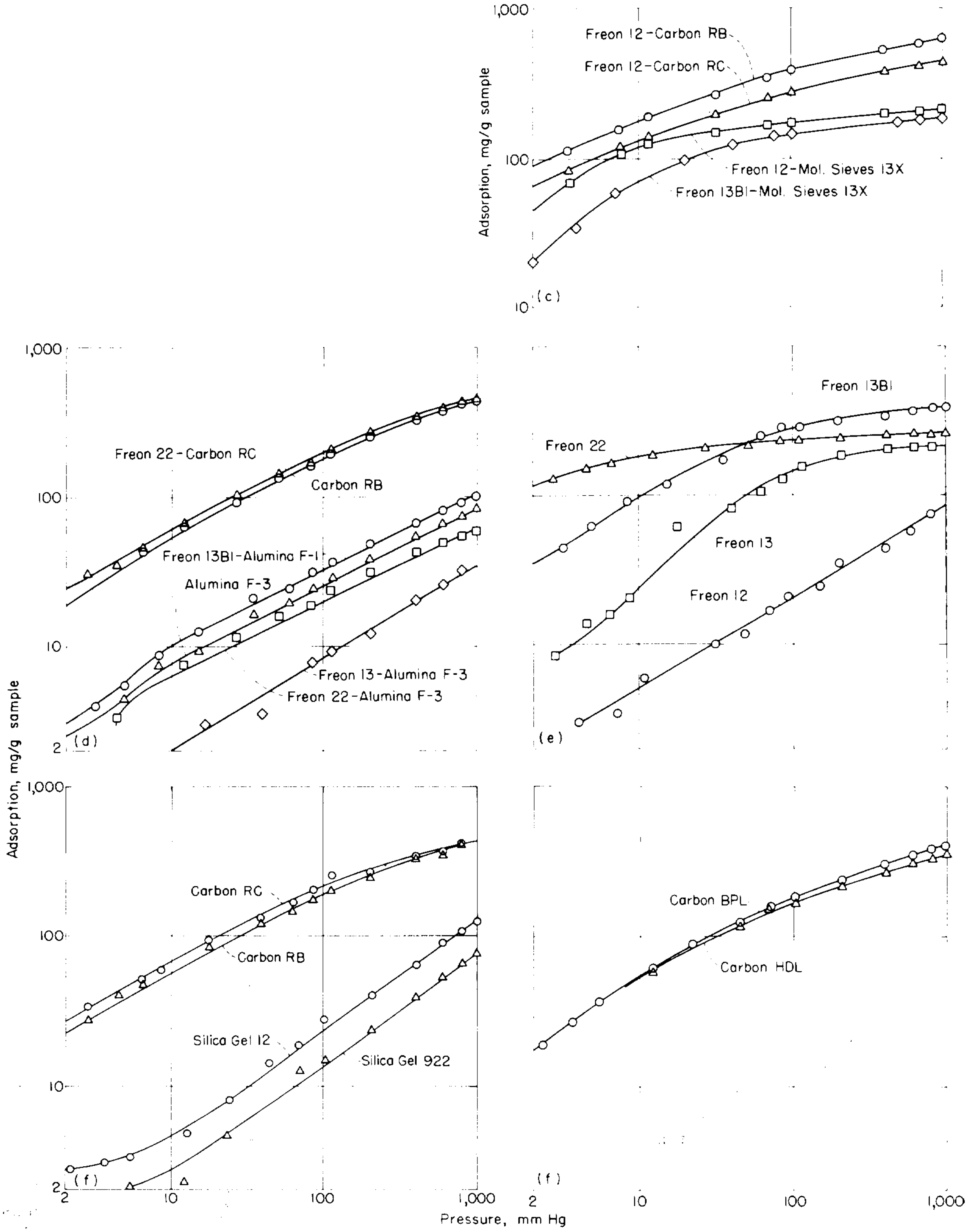
Figures 2 and 3 are plotted on logarithmic coordinates. This method of plotting gives straight



(a) Freon 12.

(b) Freon 13B1.

FIGURE 3.—Low-pressure adsorption data.



(c) Freon 12 and 13B1; 30° C.

(d) Freon 13, 13B1, 22; 30° C.

(e) Molecular Sieves 5A; 30° C.

(f) Freon 13; 30° C.

(f) Concluded. Freon 13; 30° C.

FIGURE 3 Concluded. Low-pressure adsorption data.

lines over the range for which the Freundlich equation applies. Figure 3 covers only low-pressure data (2 to 1,000 mm Hg), and figure 2 covers those data that were taken with both the low- and high-pressure apparatus, the overlapping range being 800 to 1,000 millimeters of mercury.

The results show the following trends:

(1) Among carbons, type RB is the most adsorptive. The next in order are Carbon RC, BPL, and HDL.

(2) Among silica gels, type 12 has the greatest capacity, then 922 and 923. Silica Gel 12 differs from 922 only in the particle size. The former is between 28 to 200 standard Tyler mesh, while the latter is through 200 mesh. In support of this, it may be reasoned that in the finer powder the pore structure is partly broken and more pore mouths are blocked at points of particle contact.

(3) Alumina F-1 is better than F-3.

(4) For Freon 12 adsorption, Molecular Sieves 13X (calcium alumino silicate) are better than 5A. For Freon 13B1 adsorption, Molecular Sieves 5A are better than 13X.

(5) Molecular Sieves 4A showed no adsorption of Freon 12, but if the maximum error introduced while measuring the length of the spring is taken into account, the adsorption could be 0.02 percent. The adsorption of Freon 13B1 on Molecular Sieves 4A is very small, 0.4 percent at 14.7 pounds per square inch absolute and 30° C. The diameter of all Freon molecules is greater than 4 angstroms, the pore diameter of Molecular Sieves 4A.

(6) Of the several adsorbents, carbon has the greatest capacity. Next in order are either silica gels or Molecular Sieves 13X. Aluminas have the lowest adsorption capacity.

(7) Compared on all adsorbents except Carbon RC, Freon 13B1 adsorbs to a greater extent than Freon 13, wherein the chlorine atom is replaced by a heavier bromine atom. The normal boiling point and the molecular cross-sectional area of Freon 13B1 as shown in table I are higher than those of Freon 13. From this it might be concluded that the higher the normal boiling point, molecular weight, and cross-sectional area of the adsorbate molecule, the greater is the adsorption, but a comparison of Freon 12 and 22 adsorption indicates that such a conclusion is unwarranted.

(8) It is evident that adsorption of Freons cannot be related to any physical property of the gases.

ACCURACY OF RESULTS

Adsorption data were collected on nine different systems over a pressure range from 2 millimeters of mercury to the approximate saturation pressure of the gas component at the temperature of the experiment. The data in the range of 2 to 1,000 millimeters of mercury were obtained with the low-pressure apparatus; data in the range from 800 millimeters of mercury to the saturation pressure were determined in the high-pressure apparatus. In seven of the nine cases mentioned, there was no noticeable break in the plot of the data at the point where the data from one apparatus joined the data of the second. Data in the overlapping pressure range for these seven cases agreed within 2 percent (maximum deviation).

In two cases, the adsorption of Freon 13B1 and Freon 12 by Alumina F-1, there was a definite break at the point of intersection of the two sets of data (figs. 2(a) and 2(e)). Although the data do not join, the slopes of the lines above and below 1 atmosphere are approximately the same. An analysis of what might cause such a break resulted in no definite conclusion other than that an unrepresentative sample may have been used in collecting the high-pressure data. Lack of time and the fact that alumina-gas systems seemed the least suited for fire-fighting purposes indicated that it was not worth spending time resolving the inconsistency.

The elongation of the beryllium copper springs used to measure the amounts of gas adsorbed and the weight of the samples were determined by a cathetometer of ±0.015 millimeter calibrated accuracy. However, experience showed that when the full range of this instrument was used, its accuracy was limited to ±0.05 millimeter. The springs used to measure the amounts adsorbed in the low-pressure and in the high-pressure apparatus had sensitivities of 41.6 and 60.5 milligrams per centimeter, respectively. Thus, the average accuracy of the adsorption measurements was ± 0.3 milligram in the case of the high-pressure apparatus, and ±0.2 milligram in the case of the low-pressure apparatus.

The temperature controls in both systems were sensitive to ±0.1° C. The gage used to measure pressures above 19 pounds per square inch in the high-pressure apparatus was calibrated in increments of 1/4 pound per square inch. After some experience with the gage, it was read to the nearest 1/100 pound in all cases. Pressures between atmospheric and 19 pounds per square inch were determined by the 40-inch mercury manometer as read by the cathetometer. The accuracy of these readings was, therefore, limited to the full range accuracy of the cathetometer or ±0.05 millimeter of mercury. The pressure measurements of the low-pressure apparatus were also determined by the cathetometer. In this case, however, the cathetometer was used over such a range that the accuracy of these readings was about ±0.02 millimeter of mercury.

In the case of the adsorption of Freon 12 at 30° C by Silica Gel 12, Alumina F-1, Carbon HDL, and Molecular Sieves 5A, the adsorption isotherms were determined twice using different sample weights, different sample buckets, and different springs. The reproducibility of the results of these two sets of experiments at a pressure range of 1 to 1,000 millimeters of mercury is presented in the following table:

Material	Average deviation, percent	Maximum deviation, percent	Nature of deviation
Carbon HDL	6.8	8.3	Second run consistently lower
Silica Gel 12	2.8	5.7	Random
Alumina F-1	1.5	6.5	Random
Molecular Sieves 5A	1	2	Random

No repetitive data were available to analyze the results of the data taken in the high-pressure range. Therefore, the Freundlich equation was selected to compare the results. Two plots of data were selected that followed this equation. Observed values of the amount adsorbed were compared with values calculated from the Freundlich equation using constants determined by the best straight line through the observed points. Such comparison gives a measure of the consistency of the data. The results of this analysis are presented in table IV.

FREUNDLICH RELATION

The logarithmic form of the Freundlich equation (6) is

$$\log a = \log k + \frac{1}{n} \log p$$

If a plot of log a against log p gives a straight line, the adsorption data obey the Freundlich equation. The slope of the straight line is $1/n$, and the intercept is log k. This equation, if obeyed, is useful for interpolating data. In figures 2 and 3, Freundlich plots have been shown for all the data taken with both the low-pressure and the high-pressure apparatus. In table V are given the values of k, $m=1/n$, and the pressure range for which the Freundlich equation is obeyed.

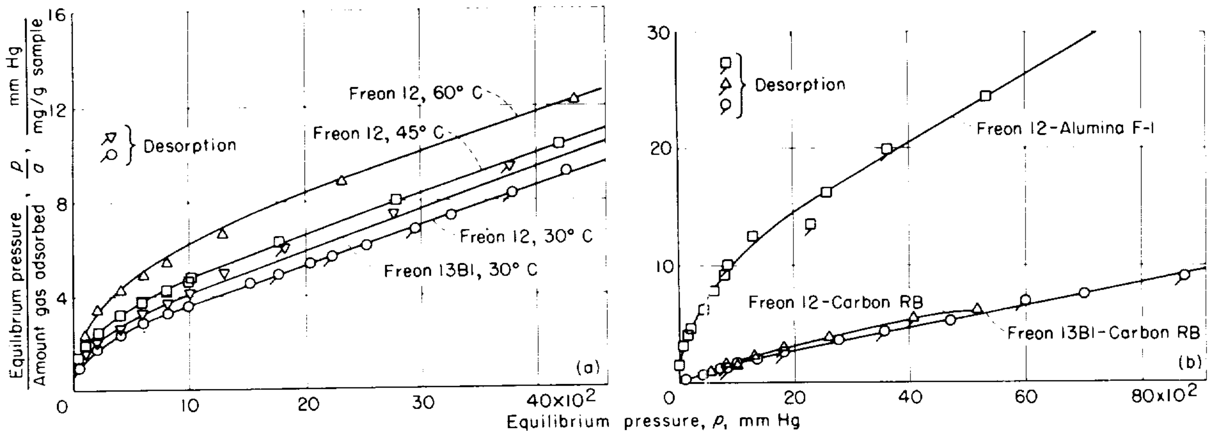
COMPARISON OF AMOUNTS REQUIRED TO FORM A MONOLAYER

The amounts required to form a monolayer have been found by (1) the Langmuir equation (7b), which is applicable for monolayer adsorption, (2) the BET equation (12) for adsorption on a free surface where the number of possible layers formed is infinite, and (3) the BET equation (11) for adsorption where the number of layers formed is finite. These experimental amounts required to form a monolayer have been compared with those estimated from the absolute surface area of the adsorbent and molecular size of the adsorbate.

Langmuir equation.—If p/a of equation (7b) is plotted against p on linear coordinates, the amount of adsorbate required to form a monolayer a_m is equal to the reciprocal of the slope of the straight part of the sigmoid curve. The temperature dependent constant b is equal to the ratio of the slope to the intercept. Langmuir isotherms for Freon 12 and 13B1 on some of the adsorbents are shown in figure 4. The values of a_m are presented in table VI.

BET equation.—If $p/[a(p_o-p)]$ is plotted against p/p_o (see eq. (12)) on linear coordinates, a_m is equal to the reciprocal of the sum of the slope and the intercept, using the straight portion of the sigmoid curve. Two typical plots are shown in figure 5, and for all the systems studied values of a_m are shown in table IV.

A comparison of the values of a_m shows that in all cases a_m values found by the Langmuir equation (7b) are larger than those found by the BET equation (12). For a finite number of layers adsorbed, Joyner, Weinberger, and Montgomery (ref. 22) showed that if n is really greater than 1, the use of the Langmuir equation ($n=1$) gives too large a value for a_m. The Langmuir equation (7b) is applicable only for isotherms which have n values very close to unity. If n is not greater than 3 or 4, the use of the infinite form of the BET



(a) Silica Gel 12 at various temperatures. (b) Carbon RB and Alumina F-1; 30° C.

FIGURE 4.—Langmuir isotherms for Freon 12 and 13B1 on various adsorbents.

equation (12) gives too small a value for the amounts adsorbed to form a monolayer. If it is obvious that the number of layers formed is finite, the full BET equation (11) must be used.

Full BET equation.—Joyner, Weinberger, and Montgomery (ref. 22) showed a comparatively easy and accurate method for using equation (11), which can be written as

$$a=\frac{a_m c\phi(n,p/p_o)}{1+c\theta(n,p/p_o)} \tag{19}$$

where

$$\phi(n,p/p_o)=\frac{(p/p_o)[1-(p/p_o)^n]-n(p/p_o)^n(1-p/p_o)}{[1-(p/p_o)]^2} \tag{20}$$

and

$$\theta(n,p/p_o)=\frac{p/p_o[1-(p/p_o)^n]}{1-(p/p_o)} \tag{21}$$

Equation (19) can be arranged in a linear form

$$\frac{\phi(n,p/p_o)}{a}=\frac{1}{a_m c}+\frac{\theta(n,p/p_o)}{a_m} \tag{22}$$

When equation (22) is used, the value of n is so selected that a plot of $\frac{\phi(n,p/p_o)}{a}$ against $\phi(n,p/p_o)$ on rectilinear coordinates gives the best straight line. These calculations were performed on the IBM 650 Digital Computer at the Syracuse University Computing Center. The values of n and a_m as computed from equation (19) are included in table VI. The computer program for solving equation (19) for the best values of n and a_m is available from the authors.

Area measurements.—In previous discussions, the amount of adsorbate required to form a monolayer has been found from experimental isotherms by using the Langmuir and the two forms of the BET equations. This amount may also be found by knowing the absolute surface area of the adsorbents and calculating the molecular cross-sectional area of the adsorbate molecule. Brunauer and Emmett (ref. 23) suggested that the area per adsorbate molecule

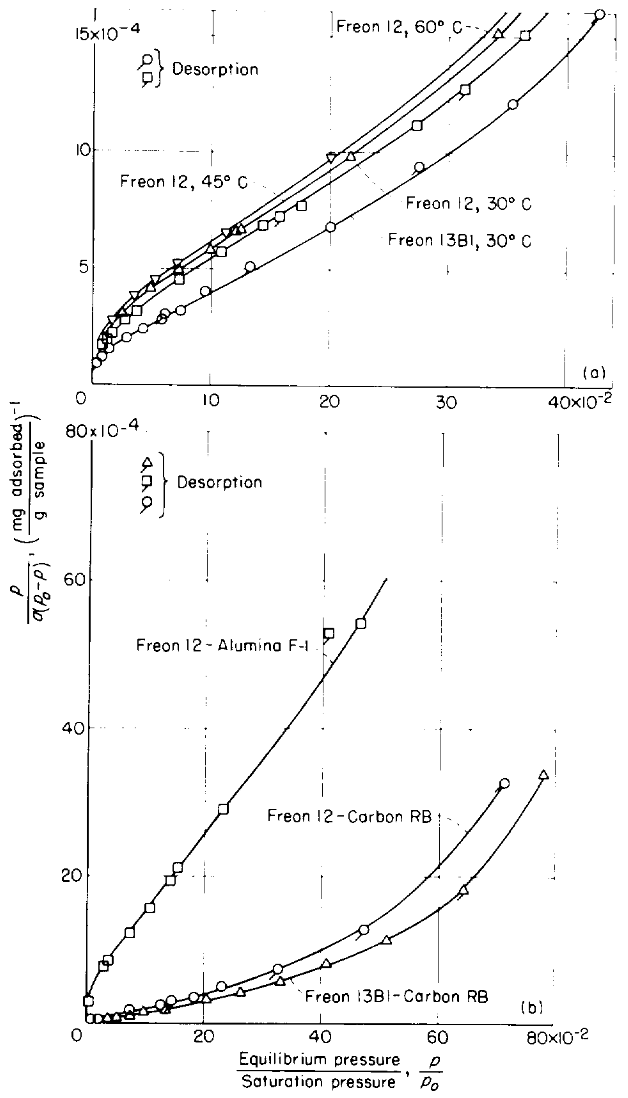
$$A_m=1.09\left(\frac{M}{Ad}\right)^{2/3} \tag{23}$$

where M is the molecular weight of the gas, A is Avogadro's number, and d is the density of solidified or liquefied adsorbate. Equation (23) is derived on the assumption that the adsorbate molecules are held in two-dimensional close packing on the surface, the area occupied by each molecule being the projected cross section of the molecular volume.

Knowing A_m, one may determine the amount of gas to form a monolayer by the relation

$$a_m=\frac{sM}{AA_m} \tag{24}$$

where s is the absolute surface area of the adsorbent. Surface-area data were supplied by the manufacturers and are shown in table II. The



(a) Silica Gel at various temperatures.
(b) Carbon RB and Alumina F-1; 30° C.

FIGURE 5.—BET (Brunauer, Emmett, Teller) isotherms for Freon 12 and 13B1 on various adsorbents.

density used in calculating a_m is that of the liquid adsorbate at the isotherm temperature, that is, 30° C, and is given in table I. Values of a_m are shown in table VI.

In all cases, the amount of adsorbate required to form a monolayer as calculated from the molecular cross-sectional area and the absolute surface area of the adsorbent is higher than that obtained from the BET equation (12). Absolute areas of adsorbents were those given by the manufacturer and were determined by nitrogen adsorption using the BET equation. The discrepancy must be due partly to lack of knowledge of properties of the adsorbed phase, for example, molecular spacing or density, and to the fact that small capillaries are available for nitrogen adsorption, but not for the adsorption of Freons. The latter cause accounts for the fact that areas determined by nitrogen adsorption are always larger than those determined with other molecules (ref. 24, pp. 36-40).

Also the area available for adsorption of different Freons on the same adsorbent is not the same. Emmett (ref. 24, p. 50) points out that the area depends on the relative dimensions of adsorbent pores and adsorbate molecules.

MODIFIED POLANYI CORRELATION

Typical plots of equation (10), NV on logarithmic ordinates and $T/V \log_e(f_o/f)$ on rectilinear abscissas are shown in figure 6. Excellent straight-line correlations in the pressure ranges shown were obtained for the following systems:

System	Temperature, ° C	Pressure range, mm
Freon 12—Silica Gel 12	30, 45, 60, 75	1—[a]218
—Silica Gel 922	30, 60	2—1,000
—Silica Gel 923	30, 60	50—1,000
—Alumina F-1	30, 45, 60	10—1,000
—Alumina F-3	30, 60	50—1,000
Freon 13B1—Silica Gel 12	30, 45, 75	1—[a]234
—Silica Gel 922	30, 45	10—1,000

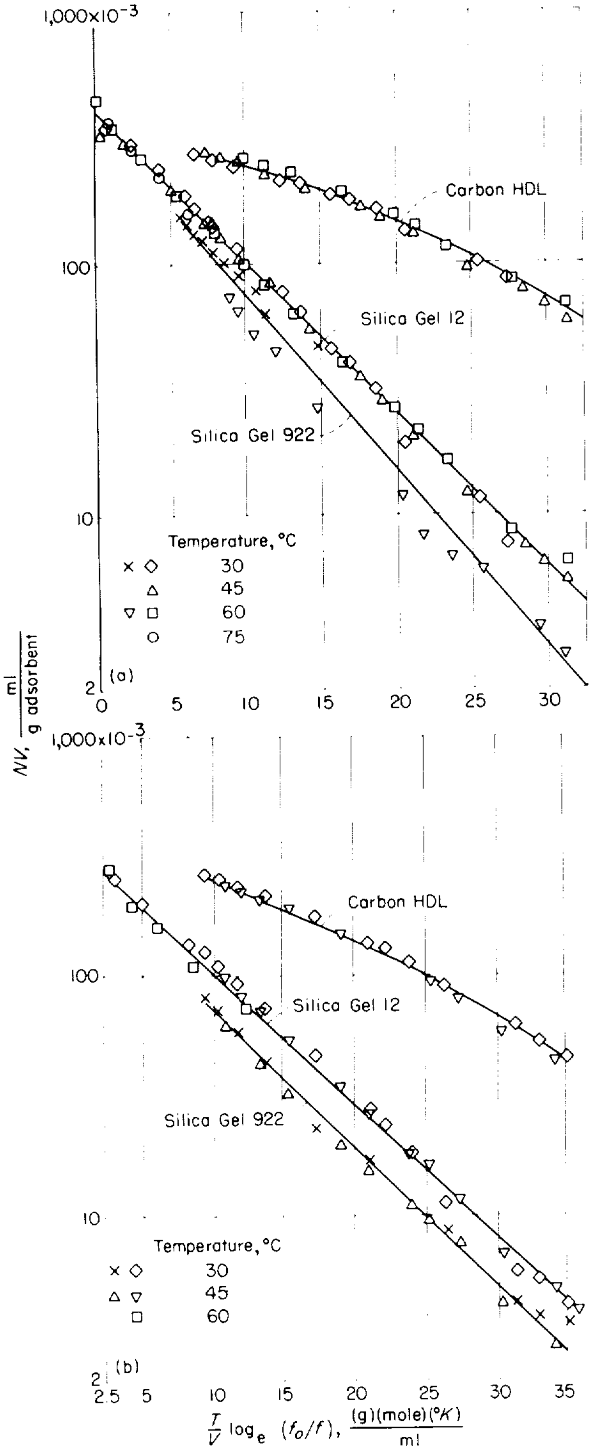
[a] lb/sq in. abs.

Those systems that gave a single curve for all temperatures studied but did not yield a straight line are listed in the following table.

These data are useful for interpolations to temperatures other than those used. No particular significance is to be attached to straight or curved lines; the important fact is that a single line represents data at several temperatures.

System	Temperature, ° C	Pressure range, mm
Freon 13 —Carbon HDL	30, 45, 60	2—1,000
Freon 13B—Carbon HDL	30, 45	2—1,000
—Carbon BPL	30, 45	2—1,000

The adsorption of Freon 12 on Carbon BPL at 30°, 45°, and 60° C gave three different curves



(a) Freon 12 systems.
(b) Freon 13B1 systems.

FIGURE 6.—Modified Polanyi correlation.

that converge to a single line at equilibrium pressures of between 500 and 1,000 millimeters of mercury.

HEAT OF ADSORPTION

Isosteric heats of adsorption are plotted in figure 7. The heats of adsorption for Freon 12 are at a mean temperature of 45° C and those for Freon 13B1 are at 37.5° C. The latent heats of liquefaction of Freon 12 at 45° C and Freon 13B1 at 37.5° C are 3.614 and 2.418 kilocalories per gram-mole, respectively.

For Freon 12 and 13B1 adsorption on both Carbon BPL and HDL, there are definite maximums in the heat of adsorption as more gas is adsorbed.

For Freon 12 on Silica Gels 12, 922, and 923, and Alumina F-1 and Freon 13B1 on Silica Gels 12 and 922, there is a sharp initial decrease in the heat of adsorption, which then falls off more gradually as the amount adsorbed increases.

Whatever may be the shape of the curve initially, the heat of adsorption asymptotically reaches a value close to the latent heat of liquefaction of the adsorbate concerned.

TYPE OF ADSORPTION

Conclusions derived from the following results show that in all cases at pressures higher than 760 millimeters of mercury there is physical adsorption:

(1) The heats of adsorption approach the heat of condensation of the adsorbate as discussed above.

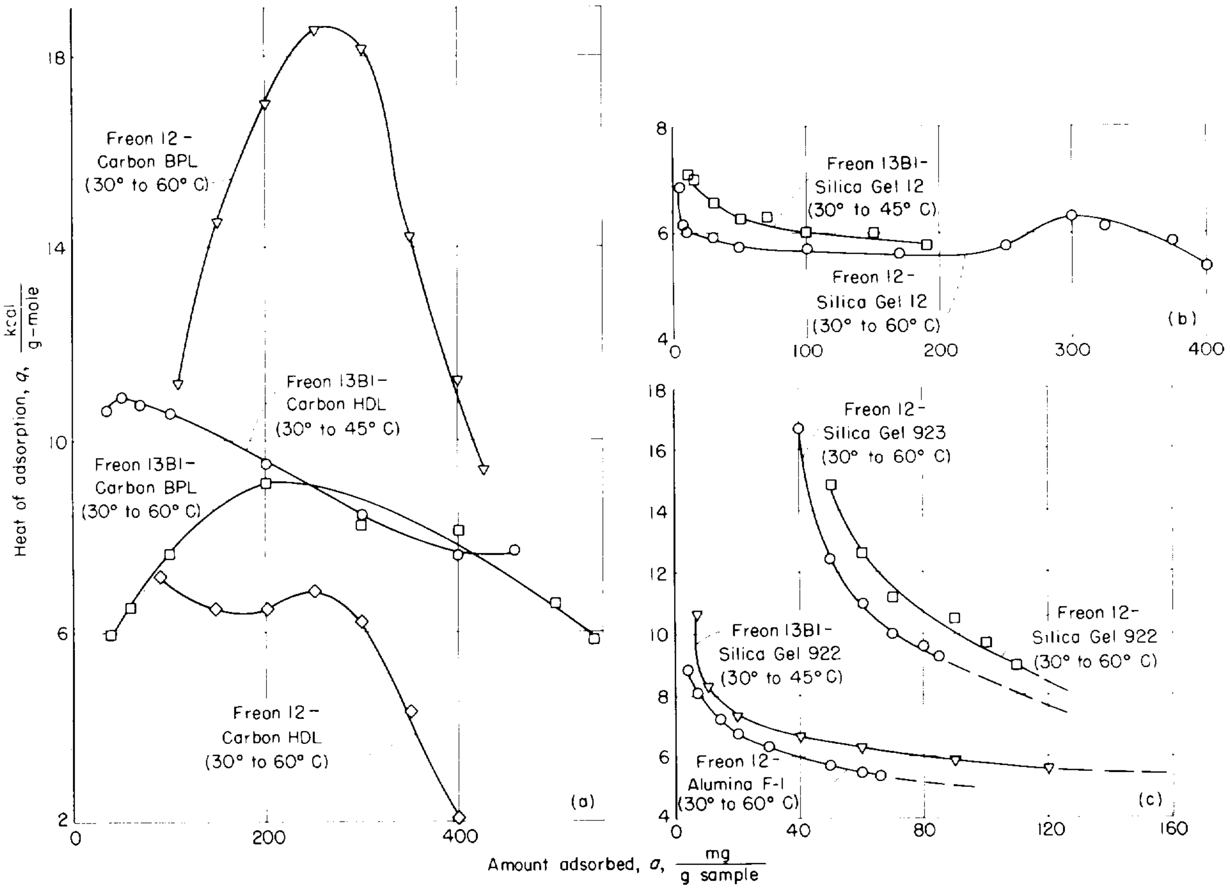
(2) The amount adsorbed per unit weight of adsorbent does not depend on any physical property of the adsorbate. It seems, however, that there is a certain specificity which, according to Brunauer (ref. 1, pp. 329–335), exists even in physical adsorption.

(3) While the adsorption data were being taken, it was noted that nearly all the adsorption takes place in less than 5 minutes.

(4) As the pressure is increased, the amount of adsorption is more than that required to form a monolayer.

HYSTERESIS

The phenomenon of hysteresis was noted in the adsorption of Freon 12 by Silica Gel 12 at 45°, 60°, and 75° C and in the adsorption of Freon 13 by Silica Gel 12 at 30° C. Based on the appearance



(a) Carbon BPL and HDL.

(b) Silica Gel 12.

(c) Silica Gel 922 and 923 and Alumina F-1.

FIGURE 7.—Heat of adsorption for Freon 12 and 13B1 on various adsorbents.

of the hysteresis effect only at higher pressures, it is believed the effect is of the reversible type. An attempt is made to correlate the Freon 12 desorption data points by the method of Foster (ref. 1, p. 137) using the Kelvin equation in the form

$$\pi = RT \log_e\left(\frac{p_o}{p}\right) = K\frac{\sigma}{\rho} \qquad (25)$$

where π is capillary condensation potential, K is a constant, σ is saturated liquid surface tension at T, and ρ is saturated liquid density.

This equation postulates that for equal volumes of liquid adsorbate at various temperatures, the value of $K=\pi\rho/\sigma$ should be constant. The values of K calculated for the isotherms at 45°, 60°, and 75° C did not prove to be constant.

The Polanyi equation as modified by Lewis, et al. (ref. 12) correlated the desorption data rather well, giving a straight line on the plot of log NV against $T/V\ \log_e(f_o/f)$. The modified Polanyi equation, however, is somewhat empirical in that V, the saturated molal volume at the adsorption pressure, had been substituted for the actual molal volume of the saturated adsorbate at the adsorption temperature. Therefore, to test further the type of adsorption on the desorption side of the hysteresis loop, the data were analyzed by comparing equal amounts adsorbed at different temperatures by the Kelvin equation in the form

$$\log_e\left(\frac{p_{o,1}}{p_1}\right) = \frac{\sigma_1 V_1 T_2}{\sigma_2 V_2 T_1}\log_e\left(\frac{p_{o,2}}{p_2}\right) \qquad (26)$$

and the Polanyi equation in the form

$$\log_e\left(\frac{p_{o,1}}{p_1}\right) = \frac{T_2}{T_1}\log_e\left(\frac{p_{o,2}}{p_2}\right) \qquad (27)$$

The following results were obtained from the Kelvin and Polanyi calculations:

Temperature, T_1, °C	Temperature, T_2, °C	Slope of line	Temperature ratio, T_2/T_1	$\frac{\sigma_1 V_1 T_2}{\sigma_2 V_2 T_1}$	Intercept
45	60	1. 000	1. 047	1. 394	−0. 050
45	75	1. 087	1. 094	2. 288	−. 220
60	75	1. 017	1. 045	1. 640	−. 145

The form of these equations indicates that if they correlate the data, a straight line passing through the origin will be obtained. Calculations were made for volumes of 0.3409, 0.3164, 0.2600, and 0.2044 cubic centimeters of Freon 12 adsorbed at 45°, 60°, and 75° C. Three straight lines were obtained for the temperature combinations in the above table.

The slopes of the lines obtained were approximately those predicted by the Polanyi equation; however, the intercept was not the origin. From the foregoing, it is concluded that the type of sorption encountered on both the desorption and adsorption loops was mainly of a multimolecular nature expressible by the Polanyi equation with capillary condensation occurring only to such an extent as to lift the desorption curve slightly above the adsorption line.

FIRE EXTINGUISHING WITH ADSORBED SYSTEMS

THEORY

There are many theories concerning why certain powders and gases inhibit combustion and put out fires. Much of what is known about this subject is summarized by Friedman and Levy (ref. 25). The subject is broad; there is no one explanation to cover many cases; much is yet unknown.

It has been postulated that liquid or gaseous agents may extinguish fires by cutting out air supply (blanketing), cooling the combustible below its ignition temperature, or by the chemical action of chain breaking and thus stopping the combustion reactions. Some of the actions by which powders may be effective extinguishers are cooling, radiation blocking, and specific chemical effect on the flame reactions. The explanation of specific chemical effect is the most widely accepted but is not well understood.

In this investigation, interest is in the possible mechanism of flame extinguishment by a powder on which is adsorbed large quantities of a gas known to be a good fire-fighting agent. The action might be exceptionally good simply because both a vapor and a powder are being applied simultaneously. This should not be heavily counted on, however, because the powder is not likely to contribute much since the type of solid needed to adsorb large amounts of vapor (e.g., carbon or silica gels) is not the type found to suppress flames (i.e., salts of alkali metals).

The following discussion does not pursue the theories of flame extinguishment any further since this investigation was not undertaken for that purpose. Rather the differences that exist between a pure vapor extinguisher and an adsorbed system are discussed.

Consider what may happen when a vapor adsorbed on a powder in a closed pressure vessel is suddenly released through a nozzle and directed on a fire. If all the vapor desorbs instantaneously on pressure release, the fire will experience only the separate actions of vapor and powder. If the fire dies, it probably would have done so even if the same amount of vapor were applied to it without the powder. It shall be assumed for the moment that the powder has no action. Then, the only possibility for the adsorbed system to appear more effective than the pure vapor is that the desorption step be slow enough to keep a concentration of the vapor in the fire zone long enough to be more effective than it otherwise would be.

Thus inquiry about the rates of desorption is important. It was shown previously that these rates are most likely controlled by the flow of heat and mass away from the particle surface. Therefore, the desorption time may be divided into two periods: (1) that time required for the equilibrium pressure above the solid particle to drop from the initial pressure to 1 atmosphere, and (2) that time required for it to drop from 1 atmosphere to some low value at which most of the gas is desorbed.

The first period will take place within a few milliseconds, since the controlling processes will be pore diffusion and hydrodynamic flow away from the particle. The latter part of this first process will take place at sonic velocities, since the desorbed vapor will simply push back the atmosphere. It was shown previously that pore diffusion is also extremely fast. If the jet leaves the nozzle at velocities on the order of 700 feet per second, the first period will be complete by the time the powder is a few inches from the nozzle. How much gas desorbs in this period depends on the shape of the adsorption equilibrium curve and the temperature coefficient of the quantity adsorbed. For the systems studied in this investigation, 30 to 50 percent of the gas will be desorbed in this period and the powder will cool about 50° F.

The action taking place in this first desorption period is entirely analogous to the flashing of a high-pressure saturated liquid when the pressure is released. Vapor is formed practically instantaneously. The heat required for vaporization or desorption comes from cooling of the unvaporized remainder, since no time is available for heat to transfer from the surroundings. This period will be referred to as the flash period.

When the pressure exerted by the adsorbed vapor is less than 1 atmosphere (or whatever the ambient pressure may be), the desorbed vapor can no longer push back the atmosphere by force and must leave the vicinity of the particle by diffusion through the boundary layer of air or combustion products. The rate at which this will occur will be much slower than flashing. The temperature of the particle will be determined by the relative rates of heat transfer to the particle and mass transfer away from it. This is analogous to a wetted wick assuming a wet-bulb temperature. This period will be called the diffusion period.

The desorption rate in this second period will thus be variable, but it will depend on the velocity of the particle, the temperature of the flame, and the instantaneous extent of desorption. Heat will be transferred to the particle both by radiation and convection. It may be possible to make rough estimates of the rate of diffusional desorption by using existing correlations on drag and heat and mass transfer to single particles or to clouds of them.

The other possibility for an adsorbed system to show better action in a fire than in a pure vapor is the contribution of the powder itself to the action. Friedman and Levy (ref. 25) report that McCamy and coworkers state (in a private communication) that one effect of a powder is to form a radiant-energy barrier between the hot flame and the burning liquid. This barrier reduces the rate of vaporization of the liquid and presumably makes it easier to put out the fire. It is difficult to see, however, how this effect can extinguish a fire entirely by its own action, especially if the flash point of the liquid is below room temperature.

In any case, some action may be expected from the powder because it adsorbs radiant heat. There is the screening action mentioned and also the slight increase in the desorption rate due to this mechanism of heat transfer.

It is not certain what rates of diffusional desorption would be most effective in fire extinguishing. If it were possible to estimate such rates, they would have to be related to actual extinguishing tests in order to interpret them properly.

SITE DESCRIPTION AND FIRE TEST PROCEDURES

Numerous methods are used to evaluate fire-extinguishing agents. W. G. Sylvester of Walter Kidde & Company, Inc. stated in a personal talk that the method which gives the most reliable results consists in evaluating the agent under normal use circumstances. The experience of this company in the fire-extinguishing field formed the basis of the test program.

Four basic elements are required for this type evaluation: a fire, an extinguishing agent, an extinguisher, and an operator to apply the agent to the fire. The fire consisted of a 1-inch layer of unleaded gasoline burning above a 7-inch layer of water. Both liquids were placed in a 12-inch-deep, square container giving a total liquid depth of 8 inches and a tank freeboard of 4 inches. The sides of the tank were 26⅞ inches, giving an exposed gasoline surface of 5 square feet. Normally, a 16-square-foot fire is used for evaluations with a standard "5-pound" extinguisher, but for reasons of economy and safety, a 5-square-foot fire was used.

The extinguishing agent consisted of commercial "dry powder" (sodium bicarbonate, $NaHCO_3$) or other powders with adsorbed Freon gas. These agents were placed in the extinguishers and were then pressurized with nitrogen or Freon or both. Because of the different powder densities, the weight capacity of the "5-pound" extinguishers (volume, 150 cu in.) varied as follows:

Powder	Amount in filled extinguisher, lb
Carbon	1.4
Silica gel	2.5
Alumina	3.8
Dry chemical ($NaHCO_3$)	6.0

No initial degassing of the powder was necessary for the adsorption of Freon. One person was trained in the method of extinguishing a fire with the powder.

There are numerous variables connected with this type of test, for example, weather conditions, operator experience, type of powder and Freon, powder flow characteristics, and gasoline properties. Wind velocity was the most important weather variable. A roofless windbreak barricade, 8 feet high and 8 by 12 feet in area, was constructed at the test site, but such turbulence of airstreams existed within this barricade while the test fire was burning that it was difficult to extinguish the fire. Therefore, the barricade was abandoned and all tests after 10 were conducted in the open. Another important variable was the consistency of the operator. This consistency was obtained by permitting a single individual to practice putting out gasoline fires using the 5-pound extinguisher. A total of 100 pounds of dry chemical was used during this practice phase. Because of the smaller fire size (i.e., 5 rather than the standard 16 sq ft), a lower rate of powder application was desirable for certain fire tests. Therefore, a 0.107-inch-diameter extinguisher orifice instead of the normal 0.193-inch diameter was used, giving an area ratio of 5:16. The last variable considered of importance was the particle size of the powder. Literature sources indicated that the smaller the particle size, the better are the extinguishing properties. Thus, all of the powders tested, with the exception of the commercial dry chemical (sodium bicarbonate), were the smallest size available in large quantities, this being 100 percent through 325 mesh.

The procedure for testing the powders was first to ignite the gasoline and permit it to burn for a period of 1 minute. During this time, the operator observed the best direction from which to attack the fire this direction was always from the windward side of the tank. With the dry chemical it was found that the best initial position of the extinguisher nozzle was about 1 foot above and 1 foot horizontally away from the top edge of the tank. The nozzle was pointed toward one of the near corners of the tank initially. Upon discharge of the powder, the flame in this corner would be extinguished, and by sweeping the powder stream across the front edge of the burning gasoline and then back again, gradually progressing to the rear of the tank, this initially extinguished zone would be enlarged and eventually spread completely over the tank. Obtaining an initial extinguished zone on the surface of the gasoline is known as "getting a bite on the fire." With some powders, it was possible to obtain a bite but it could not be enlarged because of the reignition of the once extinguished zone when the powder stream was swept across the tank. With other powders, especially carbon and Freon 13B1 and occasionally with dry chemical (sodium bicarbonate), it was possible to enlarge the bite over the complete surface of the tank with the exception of a small flame zone located about 1 foot above the gasoline surface at a rear corner of the tank. This flame could, and often would, cause a complete reignition (i.e., flashback) of the gasoline surface, necessitating repetition of the extinguishing procedure. Thus, although some materials were not capable of extinguishing the fire completely, there was a definite action that could be observed. Likewise, there were materials that showed no extinguishing effects whatsoever; these materials were described as "no action."

Since it was not known whether the optimum procedure using dry chemical would also be optimum for the powder-Freon systems, many variations in the latter procedure were made. The initial extinguisher pressure and the location and size of the nozzle with respect to the tank and the speed of the sweeping motion during extinguishing apparently have significant effects on the test results. However, no definite conclusions can be made concerning these variables of procedure because of the limited number of tests performed. Problems of powder flow were not present in the adsorbed system and no spacing agents or particle lubricants were necessary; commercial dry chemical contains both spacing agents and lubricants.

To obtain a good comparison between the dry chemical and the powder-Freon system would require the determinations of optimum performance characteristics of the latter systems. Determining these characteristics would require not only a study of procedure but also a study of equipment, especially the size and shape of the extinguisher nozzle. It may be stated that the evaluation program has given a rough basis of comparison among the agents tested.

DISCUSSION AND ANALYSIS

GENERAL

Using the procedures described previously, 42 fire tests were made: 21 using commercial sodium bicarbonate pressurized with nitrogen to about 170 pounds per square inch, 19 using various adsorbed systems, and 2 miscellaneous tests. A tabulated summary of these tests appears in table VII.

Since these new systems contain powders, they have to be discharged from extinguishers similar to conventional dry-powder extinguishers. It seems expedient, therefore, to compare the test results with those obtained using dry powders on the same fires. Kidde bicarbonate powders were used for this purpose. The 22 tests made thus were to familiarize the operator with fire-fighting techniques and to compare results with those obtained with the adsorbed systems.

Under the best fire-fighting conditions where all possible variables are held within strict limits, the results are often somewhat erratic because they depend on the personal skill of the operator. A statistical analysis of such results is very useful if the results are numerous. The tests made in this study were not numerous and one important variable, the wind, was left uncontrolled. The structure built to protect the fire from wind proved useless and was not used for any of the important tests. Much of the indefinite nature of the fire-test results can be attributed to erratic winds.

BICARBONATE TESTS

By the time the operator had used the bicarbonate powder in about 20 tests, he was able fairly consistently to put out the standard fire. The average time required for successful results was 0.18 minute (11 sec) and the average amount of bicarbonate used was 1.7 pounds. The actual times and weights required varied over a range, the extremes of which were in the ratio of 2.5:1 and 4:1, respectively. These tests were most useful not for their quantitative results but for the experience they gave the operator in knowing how to fight a fire and how a good extinguishing agent should behave under the conditions to be used on adsorbed systems.

ADSORBED SYSTEMS

Tests of adsorbed systems were made using Freon 12 and 13B1 on Silica Gel 63, Carbon RB, and Alumina F–1. Freon 12 was used because it was cheap and nonflammable, it produced a dense vapor, and adsorption data were available. Freon 13B1 was chosen because it was known to be a superior fire-extinguishing agent when used by itself. One solid from each of the three types on which many adsorption data had been obtained was chosen. In each case, the grade that adsorbed the most Freon was used.

Two tests (20 and 36) were made using silica gel and carbon powders with no Freon adsorbed. Nitrogen was used as the propellent. Applying these systems to the fire made it burn much hotter and brighter, and there was no noticeable extinguishing action. When a jet of any gas and powder was directed into the fire, an initial increase in intensity always occurred. This is undoubtedly due to the jet's entraining large volumes of air and bringing them into the flame in a high state of turbulence. Any extinguishing agent must put out this more intense fire and not just the normal fire. Since the physical properties of the bicarbonate and the adsorbent powders are not radically different, the very superior action of the bicarbonate must be due to chemical action in this case. Furthermore, silica gel and carbon powders appear to have little intrinsic ability to extinguish fires.

None of the tests in which Freon 12 was adsorbed on carbon or silica (21, 23, 24, and 37) showed any promise. The action was very similar to that occurring with adsorbents plus nitrogen only. The density of gaseous Freon 12 is 4.3 times that of nitrogen and 2.7 times that of carbon dioxide, and yet no smothering or blanketing action is noticeable. Two explanations of this are possible. Probably the Freon 12 would show better smothering if it were discharged in a stream similar to that of a standard carbon dioxide extinguisher, that is, a low-velocity, large-area stream. The high-velocity, narrow cone of the stream from a powder-type extinguisher gives such good mixing of the gas and flame that no blanketing occurs. The other explanation is that perhaps blanketing is not an effective means of putting out a 5-square-foot gasoline fire under windy conditions and thus carbon dioxide would not be effective either. In test 34, a 5-pound standard carbon dioxide extinguisher was tried and found to be ineffective even in a light wind.

Four tests were made using Freon 13B1 adsorbed on silica gel or alumina (27, 28, 30, and 31) with no success. The wind was brisk, but a fire was put out with bicarbonate in 0.17 minute (10 sec) under the same conditions. The alumina does not adsorb enough Freon to appear useful (9 g/100 g adsorbent at 1 atm and 30° C).

Seven tests were made using Freon 13B1 adsorbed on carbon (26, 29, 33, 38, 40, 41, and 42) with interesting results. The action in the last four tests was good. In test 33, the fire was put out in the record time of 6 seconds. It was easy to get a bite on the fire and to enlarge this bite, but it was often difficult to extinguish the last small corner of flame. In test 42, the fire was 95 percent out at five different times and each time the small corner left reignited the entire area. This test and test 38 were counted as successes since the action was so definite. Much of the difficulty with the last corner of flame was due to the inexperience of the operator with this particular system. The bicarbonate behaves quite differently from the carbon powder although both are effective in putting out fires. It is apparently necessary for the operator to become familiar with each different combination of gas and powder in order to get optimum results.

During the seven tests on carbon and Freon 13B1, the nozzle size was changed to study its effect. The large size gave better results whether the total propelling pressure was high (150 lb/sq in. and above) or low (85 to 125 lb/sq in.). With the low total pressure, the action was much improved, probably because the jet action of air entrainment was reduced. This increased the effectiveness although the operator also had more experience by this time. Simultaneously with the nozzle and pressure changes, the operator changed the angle of attack of the jet from nearly vertical to nearly horizontal. There was some difference in effectiveness depending on this angle but the results are inconsistent.

Two tests (32 and 35) were made with Freon 13B1 adsorbed on a 50:50 mixture by bulk volume of bicarbonate and carbon powders. This combination appeared less effective than either the bicarbonate plus nitrogen or the carbon plus Freon alone.

Why does carbon appear so much more effective than silica gel when combined with Freon 13B1? The carbon, of course, adsorbs more vapor (60 compared with 22 g/100 g at 1 atm and 30° C), and this may be the principal reason. Other possibilities exist, however. It may be that the desorption rate on the gel is too low to be effective in the flame zone. The carbon, being black, absorbs more radiant heat from the flame and will thus have a higher rate of diffusional desorption than the gel. The magnitude of this effect is not known at present, but one useful observation was made during the fire tests. The carbon particles were once observed to be burning in the flame cloud, and it is thus probable that most of the Freon had desorbed. One other fact may have influenced these disparate results and that is that more runs were made with carbon than with silica gel (seven against two), and this gave the operator more familiarity with the carbon system.

CARBON-FREON 13B1 COMBINATION

The system of carbon plus Freon 13B1 appears to have good possibilities of being a new and useful fire-extinguishing agent. It shows good action in a gasoline fire and appears to be about as good an extinguishing agent as is bicarbonate powder. The last five tests made on the new system were considered good and the third test put out the fire in record time. The first two tests did not put out the fire, but neither did the first 12 out of 13 bicarbonate tests. The extinguisher used for all tests was designed specifically for use with bicarbonate. Lowering the total pressure of the Freon improved the action considerably. Very likely a different nozzle design, the addition of a large horn to the nozzle, and better operating conditions would further improve this action. It is felt, in general, that the extinguisher itself and the lack of extinguishing experience limited the performance of these new systems. With an extinguisher designed to suit adsorbed systems, it is entirely possible that adsorbed systems will be superior extinguishing agents.

Also, the type of fire used may not have been best suited to adsorbed systems. A fire having solid surfaces present, for example, tire and brake fires, or gasoline soaked waste, might give the powder a better chance to desorb its vapors and be effective in extinguishing.

CONCLUSIONS

The following conclusions were drawn from data obtained on the adsorption of four different halogenated methanes on four different types of adsorbent and from fire-extinguishing tests made on a 5-square-foot gasoline fire using a slightly modified dry-chemical fire extinguisher charged with various combinations of Freon 12 and 13B1 adsorbed on carbon and silica gel:

1. The type of adsorption noted was physical adsorption generally, although the heats of adsorption in some cases were as high as 18 kilocalories per gram-mole. The large amounts adsorbed and the speed of adsorption make it unlikely that chemisorption occurred to any extent.
2. The modified Polanyi equation correlated many of the data very well and is thus useful for predicting data at temperatures other than those studied.
3. The phenomenon of hysteresis noted in the adsorption of Freon 12 and 13 on silica gel was a result of capillary condensation.
4. The quantitative results show that carbon and silica gels adsorb sufficient amounts of Freon to warrant studying these combinations as fire-fighting agents.
5. Comparison of the results of the tests using the modified dry-chemical fire extinguisher charged with Freon 12 and with 13B1 with the results using dry chemical (sodium bicarbonate) show that the Freon 13B1 carbon system extinguished fires as well as the dry chemical.
6. Too few fire tests were made to draw definite conclusions regarding the usefulness of adsorbed systems as superior fire extinguishing agents.
7. The fact that one of these new systems appeared as good as existing extinguishing agents strongly indicates the need for a development program to improve the characteristics of the new systems.
8. The adsorbed systems were tested under conditions and in apparatus designed for dry powders. This undoubtedly limited the effectiveness of the adsorbed combinations. Better nozzle design and the addition of a large horn to the nozzle could improve their relative performance. The horn would cut down on air entrainment and retard diffusional desorption until the powder was nearer the fire.
9. A much larger number of fire tests would allow comparison of adsorbed systems with straight vapor systems. For example, Freon 13B1 alone should be compared with Freon 13B1 adsorbed on powders.
10. It is possible that a different type of fire should be used for evaluation, for example, one containing burning solid surfaces. The adsorbed systems may be especially useful in such cases since the powder could lie on this surface while desorbing its vapor. It has been suggested that adsorbed systems would be quite successful for putting out brake fires on jet aircraft.

Syracuse University
Syracuse, N. Y., *August 14, 1957*

APPENDIX A

SYMBOLS

A	Avogadro's number
A_m	area of adsorbate molecule
a	amount adsorbed, mg/g adsorbent
a	constant in adsorption-rate equations
a_m	amount of adsorbate required to form a monolayer
b	constant in adsorption-rate equations
b	temperature dependent constant in Langmuir equation
c	constant in BET equation
D	composite diffusion coefficient
d	density
F	free energy
f	fugacity of gas
f_o	fugacity of saturated gas
g/g_c	ratio of acceleration due to gravity to gravitational constant. Units are force/mass. Numerical values near 1.00 at earth's surface.
H	enthalpy
K or k	constant in Freundlich equation
k	kinetic rate constant in Langmuir equation (15)
k'	function proportional to heat-transfer coefficient, hA/mc_p
L	pore length
M	molecular weight
m	constant in Freundlich equation, $1/n$
N	moles adsorbed per unit weight of adsorbent
N	number of molecules in gas phase per unit pore length
n	constant in Freundlich equation (15
n	number of layers of adsorbate
p	equilibrium pressure
p_o	saturation pressure
q	heat of adsorption
q_d	differential heat of adsorption
R	gas constant
r	radius of pore
S	entropy
s	absolute surface area
T	absolute temperature, °K
t	time
V	molal volume of saturated liquid at vapor pressure equal to adsorption pressure
V'	molal volume of adsorbate measured as a saturated liquid at adsorption temperature
v	amount absorbed at time t
v_e	amount absorbed at equilibrium
x	coordinate measured along pore axis
θ	wetting angle
θ	function denotation
π	capillary condensation potential
ρ	saturated liquid density
σ	surface tension
ϕ	a function denotation

Subscripts:

a	constant amount adsorbed
o	saturation condition

APPENDIX B

DERIVATION OF BUOYANCY-CORRECTION RELATIONS

When the amount of vapor adsorbed on a solid at high pressures is measured by the spring-balance method, the results depend on the definition of the amount adsorbed. There are two commonly used definitions, and which one is used determines how the buoyancy corrections are made:

(1) The amount adsorbed is the material on the surfaces of the adsorbent in excess of that which would be there if the vapor were entirely at its normal bulk density at the pressure and temperature of the experiment.

(2) The amount adsorbed is all the material on the surfaces and in the pores of the adsorbent.

As pointed out previously, definition (2) was used in this work. In this case, a buoyancy correction must be made for the volume displaced by the adsorbed material. When definition (1) is used, no such correction is made and buoyancy is attributed only to the solid adsorbent, bucket, springs, etc. At pressures below 1 atmosphere, there is no appreciable difference in the results for either method. At high pressures, the total buoyancy corrections may amount to 25 to 50 percent of the weight of the adsorbed material; hence, such corrections should be made accurately.

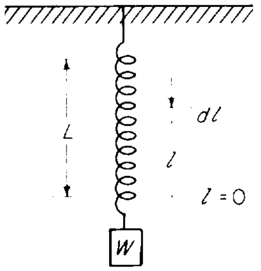
The general method used is to calculate the volume of all the material weighed by the spring and then determine the mass of vapor displaced by this volume. The buoyant force is equal to this mass multiplied by g/g_c, which is assumed numerically equal to unity.

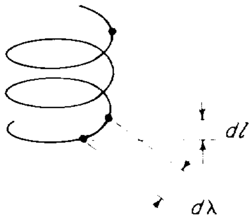
Three problems occur in applying this principle. The first problem is knowing what powder density should be used. The fused density for these samples has been taken from handbooks, which give properties of pure compounds. The following values were used:

Material	Density, g/ml
Silica	2.1
Alumina	4.0
Carbon	2.1
Molecular Sieves	2.76 (Calcium alumino silicate)

The second problem concerns the volume displaced by the adsorbed material. The mass of this material can be determined, but its density must be assumed to equal that of the saturated liquid at the temperature of the determination. In cases where the temperature was above critical, the critical density was used.

The third problem concerns the spring itself. These springs are very flexible and their own weight is an appreciable fraction of the total load imposed on them. Furthermore, the buoyancy correction will be greatest on the bottom coil and will be least on the top coil. Thus, the effective volume displaced by the spring will be some fraction of its total volume. An analysis of this problem could not be found in the mechanical engineering literature. Therefore, the following analysis is presented. The results show that the fraction of the spring volume to be used in buoyancy corrections is exactly one-half.





In the following derivation, the spring length and mass refer to a section included between any two fixed points on the spring itself.

F_b	buoyant force in length l of spring only
F_{sl}	force due to weight of spring in length l
F_w	net force due to applied weight corrected for its own buoyancy (includes everything that does not elongate)
F_l	total force in spring at any point l
k	spring constant, elongation per unit force times g/g_c (calibrated in air)
L	observed spring length

m	mass of spring wire per unit length measured along wire
V	volume of bucket, support, wires, sample, adsorbate (everything but spring)
V_s	volume of spring
W	mass of applied load in vacuum
W'	$W-V\rho_v$
W_s	mass of spring in vacuum
W_{sl}	mass of spring in length l
λ	length of spring wire
ρ_{air}	air density at spring-calibration conditions
ρ_s	spring metal density (assumed same as bucket and wire density)
ρ_v	ambient vapor density

Then

$$F_l=F_w+F_{sl}-F_b$$

$$F_w=W'(g/g_c)\cong W'$$

$$F_{sl}=W_{sl}(g/g_c)\cong W_{sl}$$

$$F_b=W_{sl}(\rho_v/\rho_s)$$

Therefore

$$F_l=W'+W_{sl}(1-\rho_v/\rho_s)$$

Now

$$m\,d\lambda=dW_{sl}$$

$$dl=k'F_l\,d\lambda$$

where k' is a constant related to k.

Therefore

$$dW_{sl}=m\,dl/k'F_l$$

and

$$[W'+(1-\rho_v/\rho_s)W_{sl}]dW_{sl}=(m/k')dl$$

Integrate from $W_{sl}=0$ to W_s and from $l=0$ to L:

$$W'W_s+(1/2)(1-\rho_v/\rho_s)W_s^2=(m/k')L$$

or

$$L=(k'/m)WW_s+(1-\rho_v/\rho_s)(k'/2m)W_s^2$$

but

$$W_s/m=\lambda$$

$$k'\lambda=k$$

and

$$W'=W-V\rho_v$$

Thus

$$L=k[W+(1/2)W_s]-k\rho_v[V+(1/2)V_s] \tag{28}$$

Equation (28) is the basic spring equation. The first term on the right gives the spring length in vacuum and the second gives the decrease in length due to buoyancy. It may be written as

$$L=L_{\text{vac}}-\Delta L$$

If ΔW is weight to be *added* to the observed weight due to buoyancy corrections, then

$$k\Delta W=\Delta L$$

and

$$\Delta W=\rho_v[V+(1/2)V_s]$$

A small additional correction can be made that accounts for the fact that the springs were calibrated in air instead of vacuum. This correction gives the final relation for buoyancy correction:

$$\Delta W=\rho_v[V+(1/2)V_s]-(\rho_{\text{air}}/k\rho_s)L \tag{29}$$

The second term on the right is negligible under all conditions used in this work.

APPENDIX C

SPRING-CALIBRATION METHODS

The beryllium copper springs supplied for this work by the Instrument Specialties Company, Inc., Little Falls, N.J. have the following specifications:

Coil diameter, in.	5/16
Wire diameter, in.	0.0070
Spring constant per coil (approx.), cm/mg	0.83×10^{-4}
Coils per spring (as supplied)	300

The number of coils used in each spring was determined by using the approximate spring constant per coil and the estimated required spring sensitivity. The low-pressure adsorption work used springs of approximately 40 milligrams per centimeter sensitivity, while springs of 60 milligrams per centimeter sensitivity were used in the high-pressure work.

Once the springs had been cut to the calculated number of coils, they were weighed to the nearest milligram and then assembled in a manner similar to that pictured in figure 1(a). The spring and all subassemblies supported by the spring were carefully weighed in order to compute the buoyancy correction.

The spring was next calibrated by replacing the adsorbent bucket with a weight-carrying basket and mounting the spring in a glass tube in a controlled temperature bath. Various weights were added to the basket, and the spring length determined as a function of the weight applied. The springs used in this work were usually calibrated at 30°, 45°, 60°, and 75° C.

The plots of spring elongation against applied weight were generally linear over the range of utilization of the spring. The spring constant, however, was found to be a function of temperature.

In the following table is presented a tabulation of the weight applied against the spring sensitivity for two representative springs, one each from the low-pressure and the high-pressure apparatus:

Applied weight, mg	Spring sensitivity, mg/cm	
	Spring 2, 30° C (high pressure)	Spring 2′, 25° C (low pressure)
200	60.75	
400	60.29	41.99
600	60.44	41.84
800	60.36	42.02
1000	60.31	

The spring-sensitivity determinations in several cases were rechecked for constancy. The results of this check for spring 2 of the high-pressure apparatus at 30° C for an applied weight of 230.5 milligrams are as follows:

Determination	Sensitivity
1	60.785
2	60.753

The accuracy of the cathetometer used to measure the spring elongation was demonstrated to be ±0.05 millimeter over the range used. Thus, the values reported above are accurate within the experimental error involved in their determinations.

Data collected to determine the variation in the spring constant with time and use are reported in the following table. These data are reported for low-pressure spring 2′ with the same weight applied.

Date of determination	Sensitivity, mg/cm
Jan. 9, 1957	41.49
Mar. 18, 1957	41.88

The variation in sensitivity in this case exceeds the magnitude of the variation that one might expect from experimental error. Therefore, to maintain the accuracy of the results within the experimental error, repeated calibrations are necessary.

When computing the amount of gas adsorbed as reported in the high-pressure results, the calibration curves were used rather than a sensitivity value calculated over the range of the calibration curve. The low-pressure spring-calibration curves were sufficiently linear over the range used that the results could be calculated accurately and more conveniently by using a sensitivity factor directly.

The following results indicate the variation in spring sensitivity with temperature:

Temperature, °C	Spring sensitivity, mg/cm	
	Spring 2 (high pressure)	Spring 2′ (low pressure)
30	60.29	41.99 (25° C)
45	60.02	
60	59.45	41.32
75	58.82	

REFERENCES

1. Brunauer, S.: Physical Adsorption. Vol. I of the Adsorption of Gases and Vapors, Princeton Univ. Press, 1943, pp. 7–11; 448–473.
2. Ries, Herman E., Jr.: Physical Adsorption. Vol. I of Catalysis, pt. 1, ch. 1, Paul Emmett, ed., Reinhold Pub. Corp., 1954, pp. 1–30.
3. Freundlich, H.: Kapillarchemie. Vol. I. Berlin, 1930, pp. 153–172.
4. Halsey, George, and Taylor, Hugh S.: The Adsorption of Hydrogen on Tungsten Powders. Jour. Chem. Phys., vol. 15, no. 9, Sept. 1947, pp. 624–630.
5. Langmuir, Irving: The Constitution and Fundamental Properties of Solids and Liquids. Jour. Am. Chem. Soc., vol. 38, Nov. 1916, pp. 2221–2295.
6. Volmer, M.: Thermodynamische Folgerungen aus der Zustandsgleichung für adsorbierte stoffe. Zs. Phys. Chem., Bd. 115, 1925, pp. 253–260.
7. Fowler, R. H.: A Statistical Derivation of Langmuir's Adsorption Isotherm. Proc. Cambridge Phil. Soc., vol. 31, pt. 1, Jan. 1935, pp. 260–264.
8. Magnus, A.: Theorie der Gasadsorption. Zs. Phys. Chem., Bd. 142, 1929, pp. 401–430.
9. Williams, A. M.: Thermodynamics of Adsorption. Proc. Roy. Soc. (Edinburgh), vol. 38, 1918, pp. 23–39.
10. Brunauer, Stephen, Emmett, P. H., and Teller, Edward: Adsorption of Gases in Multimolecular Layers. Jour. Am. Chem. Soc., vol. 60, no. 2, Feb. 8, 1938, pp. 309–319.
11. Brunauer, Stephen, Deming, Lola S., Deming, W. Edwards, and Teller, Edward: On a Theory of the van der Waals Adsorption of Gases. Jour. Am. Chem. Soc., vol. 62, no. 7, July 6, 1940, pp. 1723–1732.
12. Lewis, W. K., Gilliland, E. R., Chertow, B., and Cadogan, W. P.: Pure Gas Isotherms. Ind. and Eng. Chem., vol. 42, no. 7, July 1950, pp. 1326–1332.
13. McGavack, John, Jr., and Patrick, W. A.: The Adsorption of Sulfur Dioxide by the Gel of Silicic Acid. Jour. Am. Chem. Soc., vol. 42, May 1920, pp. 946–978.
14. Kubelka, P.: Adsorption und Kapillarkondensation. Zs. Electrochem., vol. 37, 1951, pp. 637–642.
15. Damköhler, G.: Über die Adsorptionsgeschwindigkeit von Gasen an porosen Adsorbentien. Zs. Phys. Chem., Bd. A174, 1935, pp. 222–238.
16. Wheeler, Ahlborn: Reaction Rates and Selectivity in Catalyst Pores. Advances in Catalysis. Vol. III. Academic Press, Inc., 1951, pp. 250–327.
17. McBain, J. W., and Baker, A. M.: A New Sorption Balance. Jour. Am. Chem. Soc., vol. 48, 1926, pp. 690–695.
18. Milligan, W. O., et al.: Precision Multiple Sorption-Desorption Apparatus. Anal. Chem., vol. 23, no. 5, May 1951, pp. 739–741.
19. Josefowitz, Samuel, and Othmer, Donald F.: Adsorption of Vapors. A New Apparatus and Data for the Lower Ketones, Benzene, and Hexane on Activated Carbon. Ind. and Eng. Chem., vol. 6, no. 4, Apr. 1948, pp. 739–743.
20. Morris, H. E., and Maass, O.: Discontinuity in the Adsorption of Gases, Vapors and Liquids of Solid Surfaces at the Critical Temperature under Critical Pressure: Systems Propylene-Alumina. Canadian Jour. Res., vol. 9, 1933, pp. 240–251.
21. Downing, R. C., Eiseman, B. J., and Malcolm, J. E.: Halogenated Extinguishing Agents. National Fire Protection Assoc., 1951.
22. Joyner, Leslie G., Weinberger, Edward B., and Montgomery, C. W.: Surface Area Measurements of Activated Carbons, Silica Gel and Other Adsorbents. Jour. Am. Chem. Soc., vol. 67, no. 12, Dec. 1945, pp. 2182–2188.
23. Emmett, P. H., and Brunauer, S.: The Use of Low Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron Synthetic Ammonia Catalysts. Jour. Am. Chem. Soc. vol. 59, no. 8, Aug. 5, 1937, pp. 1553–1564.

24. Emmett, Paul H.: Measurement of the Surface Area of Solid Catalysis. Vol. I of Catalysis, pt. 1, ch. 2, Paul H. Emmett, ed., Reinhold Pub. Corp., 1954, pp. 31–74.

25. Friedman, Raymond, and Levy, Joseph B.: Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents. Tech. Rep. 56-568, WADC, Jan. 1957.

26. Anon.: "Freon" Compounds. Kinetic Tech. Bull. B-2, E. I. du Pont de Nemours & Co., Inc., 1954.

27. Anon.: "Freon" Fluorinated Hydrocarbon Fire-Extinguishing Agents. Kinetic Tech. Bull. B-4, E. I. du Pont de Nemours & Co., Inc., 1954.

28. Anon.: Thermodynamic Properties of Freon 12. E. I. du Pont de Nemours & Co., Inc., 1956.

TABLE I. PHYSICAL PROPERTIES OF GASES

[Data taken or calculated from refs. 26 to 28.]

	Freon 12 [a]	Freon 13B1 [a]	Freon 13 [a]	Freon 22 [a]
Chemical formula	CCl_2F_2	$CBrF_3$	$CClF_3$	$CHClF_2$
Manufacturer's purity, percent	97.0	99.8	99.0	97.0
Molecular weight	120.9	148.9	104.5	86.5
Boiling point at 1 atm, °C	−29.8	−57.8	−81.4	−40.8
Freezing point, °C	−158	−168	−181	−160
Critical pressure, lb/sq in. abs	600	575	561	716
Critical temperature, °C	112	67	28.9	96
Critical density g/cc	0.558	0.747	0.578	0.525
Saturated liquid density at 30° C, g/cc	1.293	1.46	1.298	1.175
Viscosity at 30° C, centipoises				
Vapor	0.0127	0.0121	----	0.0131
Liquid	0.251	0.25	----	0.220
Latent heat of vaporization at 1 atm, cal/g-mole	4820	3940	3705	4836
Cross-sectional area of molecule (sat. liq., 30° C), sq A/molecule	31.38	32.66	28.44	26.78

[a] Copyright E. I. du Pont de Nemours & Co.

TABLE II.—PROPERTIES OF ADSORBENTS

Material	Manufacturer	Pore volume, cc/g	Assumed fused density, g/cc	Pore diam., A	Surface area, sq m/g	Nominal mesh size	Purity, percent
Carbon	Pittsburgh Coke and Chemical Co., Pittsburgh, Pa.						
HDL		0. 8	2. 1	32	1, 000		7 Max. ash
BPL			2. 1		1, 050–1, 150		8 Max. ash
RC			2. 1		1, 050–1, 150	80% Through 325	21 Max. ash
RB			2. 1		1, 200–1, 300	80% Through 325	23 Max. ash
Silica Gel	Davison Chemical Corp., Baltimore, Md.						
12		0. 45	2. 1	22	832	28–200	99.71 SiO_2
922		. 45	2. 1	22	832	Through 200	99.71
923		. 40	2. 1	22	500	100–200	99.85
63		. 45	2. 1	22	832	Through 325	99.71
Alumina	Aluminum Company of America.						
F-1			4. 0		210	Granular	92 Al_2O_3
F-3			4. 0		200	Granular	
Molecular Sieves	Linde Air Products Co., Tonawanda, N.Y.						
4A			2. 76	4	750		
5A			2. 76	5	750		
13X			2. 76	13	750		

TABLE III.—FREON ADSORBED PER 100 GRAMS DRY ADSORBENT AT 14.7 AND 100 POUNDS PER SQUARE INCH ABSOLUTE AND 30° C

Material	Freon adsorbed, g						
	Freon 22 ($CHClF_2$)	Freon 12 (CCl_2F_2)		Freon 13 ($CClF_3$)		Freon 13B1 ($CBrF_3$)	
	Pressure, lb/sq in. abs						
	14.7	14.7	100	14.7	100	14.7	100
Carbon							
HDL		40. 0		32. 5		49. 5	
BPL		49. 5		37. 5		57. 0	
RC	43. 0	41. 0		41. 7		33. 0	
RB	41. 0	59. 0	86. 0	41. 0		59. 0	88. 0
Silica Gel							
12		23. 7	47. 0	10. 5	26. 5	21. 5	44. 5
922		18. 8		6. 4		13. 3	
923		16. 0				11. 2	
Alumina							
F-1		8. 7	21. 5			9. 2	16. 0
F-3	5. 4	7. 9		3. 0		7. 3	
Molecular Sieves							
4A		<0. 02				0. 4	
5A	26. 2	7. 2		21. 4		39. 0	
13X		20. 5				17. 8	

TABLE IV. REPRODUCIBILITY OF DATA

(a) Adsorption of Freon 13B1 by carbon RB. Pressure range, 700 to 11,000 millimeters of mercury.

[Probable error, 6.57 mg/g; percent difference range, 1.1 to 0.7.]

Equilibrium pressure, p, mm Hg	Gas adsorbed (observed), a, mg/g	Gas adsorbed (calc.), a, mg/g	Difference, mg/g
701	579. 2	577. 5	−1. 7
1004	633. 3	630. 5	−2. 8
1354	666. 2	670. 5	+3. 2
2789	767. 6	777. 7	+10. 1
4499	844. 5	857. 5	+13. 0
7007	923. 6	939. 5	+15. 9
			Total 46. 7

(b) Adsorption of Freon 13B1 by Silica Gel 12. Pressure range, 2,600 to 10,000 millimeters of mercury.

[Probable error, 6.56 mg/g; percent difference range, 2.2 to 1.2.]

Equilibrium pressure, p, mm Hg	Gas adsorbed (observed), a, mg/g	Gas adsorbed (calc.), a, mg/g	Difference, mg/g
1984	297. 8	307. 4	−9. 6
2759	368. 2	348. 8	+19. 4
3808	398. 3	394. 6	+3. 7
4834	449. 0	432. 4	+16. 6
5958	462. 7	468. 4	−5. 7
7136	503. 1	501. 9	+1. 2
			Total 56. 2

TABLE V.—CONSTANTS IN FREUNDLICH EQUATION $a=kp^m$

[0 indicates that the Freundlich equation was not applicable over a useful range.]

Material	Freon 12			Freon 13B1		Freon 13	Freon 22
	Temperature, ° C						
(a)	30	45	60	30	45	30	30
Carbon							
HDL	0	0	0	0	0	0	—
BPL							
k	220	0	0	0	0	0	—
m	0. 122						
p	10–1, 000						
RC	0	—	—	0	—	0	0
RB							
k	0	—	—	153	—	0	0
m				0. 208			
p				700–11, 000			
Silica Gel							
12							
k	4. 1	3. 1	2. 34	3. 4	2. 22	0. 78	—
m	0. 611	0. 613	0. 619	0. 645	0. 738	0. 745	
p	2–4, 000	2–3, 000	2–3, 000	3–1, 000	8–1, 000	10–1, 000	
922							
k	6. 7		0. 77	2. 1	1. 3	0. 45	
m	0. 502	—	0. 713	0. 627	0. 654	0. 744	
p	70–1, 000		45–1, 000	8–1, 000	8–1, 000	10–1, 000	
923							
k	378	—	0. 68	2. 1			—
m	0. 563		0. 674	0. 603			
p	100–1, 000		100–1, 000	8–1, 000			
Alumina							
F-1							
k	2. 5	1. 32	1. 1	3. 2	—	—	—
m	0. 534	0. 587	0. 592	0. 505			
p	10–1, 000	5–1, 000	20–1, 000	8–1, 000			
F-3							
k	5. 6	—	0. 84	2. 29	—	0. 49	1. 98
m	0. 399		0. 579	0. 523		0. 62	0. 499
p	30–1, 000		2–1, 000	8–1, 000		10–1, 000	10–1, 000
Molecular Sieves							
5A							
k	1. 27	—	—	0	—	0	170
m	0. 61						0. 066
p	4–1, 000						20–1, 000
13X							
k	106	—	—	80	—	—	—
m	0. 099			0. 121			
p	10–1, 000			40–1, 000			

[a] Pressure range, *p*, mm Hg for which the constants *k* and *m* are applicable.

TABLE VI.—COMPARISON OF AMOUNTS OF ADSORBATE REQUIRED TO FORM A MONOLAYER CALCULATED FROM LANGMUIR EQUATION, BET (BRUNAUER, EMMETT, TELLER) EQUATION, AND AREA, ESTIMATED FROM AREA AND MOLECULAR SIZE AT 30° C

[Amount in millimoles of adsorbate/g of adsorbent.]

Material	Freon 12				Freon 13B1				Freon 13			Freon 22		
	Langmuir	BET		Area	Langmuir	BET		Area	Langmuir	BET	Area	Langmuir	BET	Area
		$n=\infty$	$n=n$			$n=\infty$	$n=n$			$n=\infty$			$n=\infty$	
Carbon														
HDL	3. 612	2. 950	---	5. 289	3. 976	3. 478	---	5. 084	4. 108	3. 723	5. 836			
BPL	4. 400	3. 355	---	5. 817	4. 509	4. 043	---	5. 593	4. 934	4. 422	6. 423			
RC	4. 074	2. 843	---	5. 817	2. 797	2. 414	---	5. 593	5. 038	4. 662	6. 423	6. 723	5. 446	6. 818
RB	5. 785	4. 106	---	6. 611	5. 209	4. 526	$n=2.50$ $a_m=4.22$	6. 355	5. 408	5. 207	7. 295	6. 607	5. 192	7. 747
Silica Gel														
12	3. 411	2. 231	$n=0.50$ $a_m=7.77$	4. 400	3. 140	2. 365	$n=0.50$ $a_m=6.93$	4. 230	2. 776	2. 240	4. 853			
922	2. 954	1. 942	---	4. 400	2. 100	1. 782	---	4. 230	2. 058	1. 589	4. 853			
923	2. 545	1. 512	---	2. 644	2. 267	1. 847	---	2. 540						
Alumina														
F-1	1. 133	0. 793	---	1. 111	1. 066	0. 922	---	1. 068						
F-3	1. 009	. 690	---	1. 058	. 884	. 743	---	1. 017	0. 921	0. 856	1. 168	0. 948	0. 749	1. 237
Molecular Sieves														
5A	4. 241	---	---	3. 966	2. 960	2. 533	---	3. 813	2. 369	2. 310	4. 374	3. 125	2. 787	4. 648
13X	1. 762	1. 464	---	3. 966	1. 330	1. 183	---	3. 813						

TABLE VII.—RESULTS OF FIRE TESTS

[Standard conditions: Fire area, 5 sq ft; water depth, 7 in.; gasoline depth, 1 in.; freeboard, 4 in.; preburn, 60 sec; R.V.P. of gasoline, 10.4 lb/sq in.; extinguisher, Kidde 5-lb dry-powder type.]

Charging conditions									Conditions that extinguish fire				Notes
Date 1957	Run (a)	Powder (b)	Gas partial pressure, lb/sq in. abs (c)	Total pressure gases and air, lb/sq in. abs	Weight of powder		Weight of gas		Gas and powder used		Time, min	Nozzle size (d)	
					lb	oz	lb	oz	lb	oz			
4-24 p.m.	1-4	Bicarbonate e	N_2=155-175	170-190								S	Unsuccessful.
	5	Bicarbonate	N_2=150	65	5	0	—	—	2	4	0.22	S	Successful. Atmosphere fair, slight wind. ¾-in. gas layer.
	6-13	Bicarbonate	N_2=140-180	155-195								S except 12	Unsuccessful.
4-30 a.m.	14	Bicarbonate	N_2=170	185					1	13	.15	S S	½ In. old gasoline and ½ in. new gasoline.
4-30	15	Bicarbonate	N_2=170	185					—	—	—	S	Too windy.
5-13	16	Bicarbonate	N_2=170	185					—	—	—	S	Too windy.
5-13	17	Bicarbonate	N_2=170	185					2	10	.25	S	½ In. old and ½ in. new gasoline.
5-13	18	Bicarbonate	N_2=170	185					2	3	.22	S	½ In. old and ½ in. new gasoline. Preburn time, 0.88 min.
5-13	19	Bicarbonate	N_2=170	185					0	11	.10	S	Preburn time, 0.83 min. ½ In. old and ½ in. new gasoline.
5-14 a.m.	20	Silica	N_2=180	195	2	9	—	—	—		—	S	Not effective.
5-14 a.m.	21	Silica	F 12=60	195	21	0	—	—	—		—	S	Not effective.
5-14 p.m.	22	Bicarbonate	N_2=160	175	5	1	—	—	0	14	.18	S	No wind at all. Flames were vertical.
5-14 p.m.	23	Silica	F 12=160	175	2	6	0	15	—	—	—	S	Unsuccessful.
5-14 p.m.	24	Silica	F 12=160	175	2	9	1	0	—	—	—	S	Unsuccessful.
5-16 a.m.	25	Bicarbonate	N_2=180	195	5	0	—	—	1	11	.17	S	Successful in spite of wind.
5-16 a.m.	26	Carbon	F 13B1=180	195	1	6	1	9	—	—	—	S	Carbon adsorbs about 60 percent of Freon 13B1, yet this is not successful.
5-16 a.m.	27	Alumina	F 13B1=180	195	3	13	1	0	—	—	—	S	Not effective.
5-16 a.m.	28	Silica	F 13B1=180	195	2	11	1	6	—		—	S	No success. Large nozzle should be tried.
5-16 p.m.	29	Carbon	F 13B1=150	165	1	6	1	3	—	—		L	No success. Windy.
5-16 p.m.	30	Alumina	F 13B1=180	195	3	11	0	14		—	—	L	No success. Windy.
5-16 p.m.	31	Silica	F 13B1=140	155	2	3	1	8		—	—	L	No success. Windy.

5-24 a.m.	32	Carbon plus bicarbonate	F 13B1 = 180	195	2	13	0	12			—	S	Good bite. Light wind. Carbon, 50 percent by volume. Freeboard, 4 in. Not as good as bicarbonate alone.
5-24 a.m.	33	Carbon	F 13B1 = 110	125	1	7	1	5	2	7	.10	L	Success. Put out fast. Low pressure. Low angle of application.
5-24	34	No Powder. Standard CO_2 extinguisher	CO_2	—		—	4	8	—		—		No success.
5-24 a.m.	35	Carbon plus bicarbonate	F 13B1 = 180	195	2	9	0	12		—		—	Similar to No. 32. Pure carbon is better. Freeboard, 2 in.
5-24 p.m.	36	Carbon	N_2 = 110	125	1	11	0	2	—		—	L	Poor action.
5-24 p.m.	37	Carbon	F 12 = 50 N_2 = 50	115	1	7	0	13	—	—		L	No better than using pure N_2.
5-24 p.m.	38	Carbon	F 13B1 = 75	90	1	9	1	4	2	9	.3	L	Good action. Fire really only 99 percent out. Reignited last instant.
5-24 p.m.	39	None	Liquid	—		—	1	3	—		—	L	Using CO_2 extinguisher. Some action. Too low discharge rate.
6-5	40	Carbon	F 13B1 = 100	115	1	8	1	7		—		L	Good bite. Spray, 60° from horizontal.
6-5	41	Carbon	F 13B1 = 70	85	1	6	1	6		—		L	Good bite. Spray, horizontal.
6-5	42	Carbon	F 13B1 = 80	95	1	7	1	9	2	12	.35	S	Good action. Fire reignited at the last instant. Spray, near vertical.

[a] Runs 1 to 10 made inside enclosure; runs 11 to 39 made outside enclosure.

[b] Particle size: Bicarbonate, 65 to 90 percent through 325 mesh
Carbon RB, 80 percent through 325 mesh
Silica Gel 63, 100 percent through 325 mesh
Alumina F-1, 100 percent through 325 mesh.

[c] Freon is designated by F.

[d] Nozzle size: Large, L, 0.193 in.
Small, S, 0.109 in.

[e] Walter Kidde & Company, Inc.

TABLE VIII. FREON 12 ADSORPTION ISOTHERM DATA

(a) Temperature, 30° ±0.1° C; Silica Gel 923 and 922, Alumina F-3, and Carbon BPL

Pressure, mm Hg	Adsorption, mg/g sample			
	Silica Gel 923	Silica Gel 922	Alumina F-3	Carbon BPL
2.5	12.8	18.3	11.5	106.4
6.0	29.1	31.5	18.6	255.8
11.4	35.7	40.8	23.6	297.0
34.8	42.5	49.3	24.6	341.3
58.4	44.8	56.6	31.5	361.3
121.0	58.5	75.5	39.6	395.5
211.9	77.9	99.2	48.1	439.8
310.7	97.5	120.5	57.7	452.9
413.2	112.9	136.5	62.5	461.6
509.4	129.3	151.6	67.9	476.8
610.1	139.9	166.3	72.4	490.7
709.9	155.3	188.0	79.0	496.2
816.5	169.0	192.6	82.6	499.8
911.6	179.6	212.3	87.6	504.5
1012.9	181.8	218.4	88.3	517.2

(b) Temperature, 60° ±0.1° C; Silica Gel 923 and 922, Alumina F-3, and Carbon BPL

Pressure, mm Hg	Adsorption, mg/g sample			
	Silica Gel 923	Silica Gel 922	Alumina F-3	Carbon BPL
1.47	----	0.4	-----	24.6
3.2	5.3	.95	1.8	46.2
6.2	6.2	1.9	2.8	72.5
7.6	6.4	2.8	3.2	81.3
10.4	6.8	4.6	3.2	94.3
14.5	9.4	5.9	3.7	109.4
28.5	11.2	10.0	5.9	138.5
45.9	13.7	11.0	8.0	174.2
68.0	14.9	13.4	10.4	208.8
90.2	16.7	18.6	10.9	231.6
286.6	34.9	42.7	23.2	328.3
496.5	51.9	68.3	33.7	747.2
693.6	63.6	77.0	39.9	401.0
893.8	76.8	94.5	43.0	416.1
997.0	83.7	105.9	45.1	429.4

(c) Temperature, 30° ±0.1° C; Carbon HDL, Silica Gel 12, Alumina F-1, and Molecular Sieves 5A

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon HDL	Silica Gel 12	Alumina F-1	Molecular Sieves 5A
2.20	92.8	4.9	---	-----
4.00	115.5	8.7	2.7	3.0
7.17	144.7	12.8	4.3	3.4
10.73	169.4	19.1	7.0	5.9
31.3	217.3	31.9	9.9	10.1
48.5	261.6	50.9	16.8	11.8
69.8	284.0	64.7	22.1	17.0
94.1	297.7	76.3	27.3	21.3
151.5	326.7	100.3	36.6	24.8
203.4	337.4	119.3	43.5	35.0
407.1	374.9	173.7	64.0	43.9
603.2	396.2	211.5	77.0	58.6
803.8	406.4	243.7	87.3	75.4

TABLE VIII.—FREON 12 ADSORPTION ISOTHERM DATA—Concluded

(d) Temperature, 45° ± 0.1° C; Carbon HDL, Alumina F–1, Silica Gel 12, and Molecular Sieves 5A

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon HDL	Alumina F–1	Silica Gel 12	Molecular Sieves 5A
2.0	58.9	2.6	4.7	5.0
3.8	85.0	-----	6.5	5.9
5.5	97.7	3.6	9.3	5.9
7.6	114.4	3.7	10.9	5.9
10.2	129.9	5.3	12.7	5.9
22.3	161.5	7.2	20.0	6.9
46.6	211.5	13.0	33.4	7.4
73.7	247.2	15.4	44.8	9.3
101.6	267.9	21.8	55.7	10.1
212.5	311.9	33.4	86.5	-----
400.0	350.8	46.0	124.9	24.6
594.6	377.6	59.2	158.8	27.2
800.0	391.7	68.2	188.7	28.6
1011.6	403.0	76.5	212.8	33.3

(e) Temperature, 30° ± 0.1° C; Carbon RC and RB and Molecular Sieves 13X and 4A

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon RC	Carbon RB	Molecular Sieves 13X	Molecular Sieves 4A
1.03	46.5	62.3	22.2	Nil
3.46	81.8	110.6	68.1	
7.55	115.8	155.0	108.0	
11.40	136.1	182.8	121.7	
31.7	191.0	261.4	144.6	
71.3	246.0	345.7	160.9	
102.6	272.4	380.5	168.6	
406.9	365.3	519.6	192.5	
703.8	403.3	578.5	202.6	
1000.0	429.8	619.7	208.7	

(f) Temperature, 45° ± 0.1° C; Carbon BPL

Pressure, mm Hg	Adsorption, mg/g sample
0.38	80.3
1.82	103.8
3.64	128.0
7.98	159.3
17.1	191.8
32.8	228.0
60.9	274.8
112.1	329.2
212.7	381.9
317.9	405.1
416.9	422.4
519.2	439.6
611.1	452.8
711.4	462.4
813.0	472.5
919.5	478.3
1010.0	487.3

(g) Temperature, 60° ± 0.1° C; Carbon HDL, Alumina F–1, and Silica Gel 12

Pressure, mm Hg	Adsorption, mg/g sample		
	Carbon HDL	Alumina F–1	Silica Gel 12
1.0	35.2	--------	0.4
2.0	55.6	2.5	2.4
4.7	80.9	4.1	5.7
6.7	96.2	4.7	6.7
9.8	114.6	6.5	10.8
20.7	142.2	7.4	14.2
48.4	189.4	12.1	26.7
71.3	225.4	15.6	34.4
98.6	248.6	16.3	42.3
198.5	300.9	26.7	62.7
403.1	345.3	39.3	96.0
604.1	369.8	48.6	123.0
804.8	387.4	56.9	147.9

TABLE IX.—FREON 13B1 ADSORPTION ISOTHERM DATA

(a) Temperature, 30° ± 0.1° C; Carbon BPL, Silica Gel 12 and 922, and Carbon HDL

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon BPL	Silica Gel 12	Silica Gel 922	Carbon HDL
1.0	23.8	3.8	0.8	36.6
2.2	60.4	4.4	2.3	59.7
3.5	74.9	6.5	5.7	81.3
5.5	94.9	9.8	8.1	103.1
8.4	119.4	12.4	8.5	123.2
12.0	147.1	13.3	9.9	143.2
33.8	212.8	25.6	19.2	205.4
55.5	267.3	40.9	25.1	256.5
78.0	309.7	53.5		291.5
99.7	332.8	60.9	37.4	310.3
199.3	414.9	98.0	49.2	374.5
398.6	500.4	149.1	89.4	438.5
597.0	544.1	184.2	113.7	472.1
805.8	581.1	219.6	139.9	499.2
1008.4	598.5	247.4	157.8	516.5

(b) Temperature, 45° ± 0.1° C; Carbon BPL, Silica Gel 12 and 922, and Carbon HDL

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon BPL	Silica Gel 12	Silica Gel 922	Carbon HDL
[illegible].53	34.1			25.7
2.98	51.2	3.4		42.5
4.15	63.7	7.4	5.4	56.1
5.35	70.3	8.0		63.2
8.71	93.2	9.1	6.0	84.4
1[illegible].96	107.9	11.2	6.5	100.4
24.5	140.2	15.7	9.6	132.2
46.6	191.0	26.2	17.1	180.9
69.1	227.6	35.4	21.4	213.4
9[illegible].1	252.6	42.5	24.1	240.8
15[illegible].2	312.0	57.7	33.0	291.2
202.9	351.4	72.1	42.1	319.6
401.7	433.7	110.8	66.6	384.8
601.3	483.0	140.9	86.6	421.8
804.1	516.0	169.2	102.6	445.6
1004.8	554.2	191.6	120.4	467.1

(c) Temperature, 30° ± 0.1° C; Carbon RC and RB and Molecular Sieves 13X and 4A

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon RC	Carbon RB	Molecular Sieves 13X	Molecular Sieves 4A
1.97	26.4	51.0	19.6	
3.87	41.1	77.3	34.4	
6.98	61.9	104.2	58.6	
19.94	91.7	164.3	93.0	
41.4	128.4	227.5	120.2	2.55
77.2	165.2	289.7	135.7	3.31
102.4	186.2	326.4	142.2	4.21
500.0	299.4	533.2	171.8	4.21
701.0	321.4	579.2	179.4	4.21
1004.0	349.9	633.3	183.9	4.21

(d) Temperature, 30° ± 0.1° C; Alumina F–1, Silica Gel 923, Alumina F–3, and Molecular Sieves 5A

Pressure, mm Hg	Adsorption, mg/g sample			
	Alumina F–1	Silica Gel 923	Alumina F–3	Molecular Sieves 5A
0.95		0.7	2.0	9.8
1.5	2.7	3.7	2.2	31.9
3.2	4.0	4.5	3.9	44.5
4.9	5.6		4.4	62.4
8.3	8.9	6.6	7.5	92.5
15.3	12.7	8.0	9.3	120.4
34.7	21.3	11.9	16.5	175.5
59.7	24.7	18.9	19.7	264.7
85.5	31.7	24.4	24.7	284.2
114.5	37.4	29.6	29.1	296.8
203.0	49.2	44.3	39.2	317.2
403.6	67.2	70.3	54.7	342.7
603.8	81.9	95.6	66.1	362.8
808.2	93.5	118.1	76.7	388.6
1007.9	103.2	137.3	84.3	394.4

TABLE X. FREON 13 ADSORPTION ISOTHERM DATA

(a) Temperature, 30° ± 0.1° C; Carbon RC and RB, Alumina F–3, and Molecular Sieves 5A

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon RC	Carbon RB	Alumina F–3	Molecular Sieves 5A
1. 3	17. 3	17. 7		7. 3
2. 8	34. 1	26. 7	0. 5	8. 4
4. 5		40. 4	. 6	13. 8
6. 4	51. 8	49. 0	1. 1	16. 3
8. 5	60. 1	60. 7	1. 5	20. 8
17. 2	94. 8	86. 0	3. 0	63. 2
38. 7	134. 7	122. 4	3. 5	81. 8
62. 2	169. 5	149. 3	4. 0	108. 0
85. 6	203. 7	179. 8	7. 8	129. 2
113. 5	255. 2	206. 5	9. 3	160. 4
199. 6	271. 4	255. 5	12. 3	179. 7
404. 5	343. 9	328. 7	20. 4	206. 1
600. 6	383. 1	375. 3	26. 1	217. 2
805. 8	417. 7	418. 3	33. 6	227. 7

(b) Temperature, 30° ± 0.1° C; Carbon BPL and HDL and Silica Gel 12 and 922

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon BPL	Silica Gel 12	Silica Gel 922	Carbon HDL
1. 1	11. 9	2. 1		10. 9
2. 3	19. 2	2. 9		19. 3
3. 6	27. 1	3. 1	0. 3	30. 3
5. 4	36. 4	3. 4	2. 3	37. 0
12. 4	59. 3	4. 9	2. 4	60. 5
23. 8	87. 4	7. 9	4. 7	87. 1
44. 4	122. 1	14. 3	10. 3	118. 5
69. 3	152. 7	18. 7	12. 9	148. 5
102. 7	179. 3	26. 9	15. 2	171. 1
206. 1	236. 9	41. 5	24. 7	215. 6
400. 9	299. 8	66. 2	39. 1	266. 6
599. 4	348. 1	91. 5	54. 5	303. 5
803. 4	378. 9	110. 5	66. 5	327. 9
1001. 5	400. 8	125. 1	76. 6	346. 3

TABLE XI. FREON 22 ADSORPTION ISOTHERM DATA; TEMPERATURE, 30° ± 0.1° C

Pressure, mm Hg	Adsorption, mg/g sample			
	Carbon RC	Carbon RB	Alumina F–3	Molecular Sieves 5A
0. 22	5. 7	1. 9	0. 9	41. 8
. 73	9. 6	8. 2	1. 1	76. 0
1. 4	15. 7	17. 6	1. 1	100. 8
2. 7	31. 0	24. 5	3. 2	131. 4
4. 4	36. 0	33. 3	3. 5	151. 2
6. 5	45. 6	44. 6	5. 9	164. 6
12. 4	67. 7	69. 4	7. 8	186. 1
26. 9	105. 6	95. 0	11. 7	208. 5
50. 9	142. 4	133. 0	16. 4	218. 7
82. 7	169. 6	163. 9	18. 7	227. 4
109. 4	208. 6	198. 4	24. 4	235. 3
200. 5	269. 8	260. 5	32. 1	241. 9
403. 0	347. 4	338. 4	42. 7	254. 3
602. 7	396. 9	391. 7	50. 6	259. 7
801. 5	433. 5	423. 1	55. 4	262. 8
1001. 5	459. 4	448. 7	60. 2	265. 5

TABLE XII. FREON 13B1 ON ALUMINA F–1 ADSORPTION ISOTHERM DATA; TEMPERATURE, 30° ± 0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
25. 77	74. 9
50. 19	106. 3
90. 13	147. 4
134. 86	193. 8
222. 90	242. 3
Pressure decreasing	
176. 08	219. 3
114. 73	170. 5
70. 53	114. 5
36. 95	92. 0
16. 00	57. 9

TABLE XIII.—FREON 13B1 ON CARBON RB ADSORPTION ISOTHERM DATA; TEMPERATURE, 30°±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
25. 99	667. 2
53. 91	767. 6
86. 98	844. 5
135. 45	923. 6
204. 98	1030. 0
Pressure decreasing	
169. 20	971. 6
110. 60	889. 4
69. 20	814. 3
35. 16	710. 5
15. 84	597. 7

TABLE XIV.—FREON 13B1 ON SILICA GEL 12 ADSORPTION ISOTHERM DATA

(a) Temperature, 30°±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
25. 10	260. 7
53. 33	368. 2
93. 40	449. 0
138. 05	503. 1
224. 35	543. 7
Pressure decreasing	
171. 38	521. 2
112. 53	462. 7
72. 65	398. 3
35. 02	297. 8
15. 80	204. 7

TABLE XIV.—FREON 13B1 ON SILICA GEL 12 ADSORTION ISOTHERM DATA—Concluded

(b) Temperature, 75°±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
25. 99	138. 9
54. 06	203. 0
93. 37	273. 5
138. 34	330. 9
234. 27	420. 9
Pressure decreasing	
187. 80	379. 8
115. 28	306. 2
73. 61	247. 4
38. 31	127. 1
16. 20	86. 6

TABLE XV.—FREON 12 ON SILICA GEL 12 ADSORPTION ISOTHERM DATA

(a) Temperature, 30.5°±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
18. 98	276. 3
29. 32	334. 6
39. 21	378. 5
43. 81	413. 4
62. 90	442. 5
82. 18	459. 7
107. 88	473. 0
Pressure decreasing	
101. 53	468. 8
89. 90	465. 4
73. 04	458. 0
56. 92	432. 3
43. 49	395. 0
33. 87	358. 2
17. 05	259. 7

(b) Temperature, 45.0°±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
19. 12	211. 1
34. 12	282. 2
53. 50	343. 8
81. 06	406. 8
132. 14	444. 2
154. 50	456. 4
Pressure decreasing	
139. 29	447. 6
110. 08	436. 0
97. 41	426. 3
70. 66	387. 5
43. 06	320. 7
25. 67	252. 1
116. 20	196. 6

TABLE XVI.—FREON 12 ON SILICA GEL 12 ADSORPTION ISOTHERM DATA

(a) Temperature, 60.0° ±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
24. 89	193. 2
44. 51	257. 7
82. 46	347. 5
153. 30	426. 8
214. 07	445. 9
Pressure decreasing	
170. 61	435. 8
118. 29	404. 4
63. 61	315. 5
34. 05	245. 6
15. 14	158. 6

(b) Temperature, 75.0° ±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
25. 15	160. 9
47. 26	221. 6
83. 06	299. 8
136. 02	370. 5
218. 23	429. 2
Pressure decreasing	
165. 29	403. 2
62. 73	276. 3
34. 32	208. 4
15. 58	146. 5
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TABLE XVII.—FREON 12 ON ALUMINA F-1 ADSORPTION ISOTHERM DATA; TEMPERATURE, 30° ±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
24. 82	103. 2
49. 96	158. 4
102. 76	218. 5
Pressure decreasing	
70. 18	183. 3
44. 30	131. 0
16. 39	84. 6

TABLE XVIII.—FREON 12 ON CARBON RB ADSORPTION ISOTHERM DATA; TEMPERATURE, 30° ±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
29. 94	598. 2
50. 49	582. 3
100. 17	860. 6
Pressure decreasing	
78. 80	752. 2
35. 05	643. 8
15. 62	558. 3

TABLE XIX.—FREON 13 ON SILICA GEL 12 ADSORPTION ISOTHERM DATA; TEMPERATURE, 30° ±0.1° C

Pressure, lb/sq in. abs	Adsorption, mg/g sample
Pressure increasing	
24. 88	138. 2
54. 49	201. 0
82. 38	253. 9
141. 98	314. 5
194. 16	351. 5
Pressure decreasing	
163. 46	337. 0
34. 90	182. 7
16. 86	128. 5

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