

REACTION STEPS IN GAS SORPTION BY IMPREGNATED CARBON

by

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1. INTRODUCTION

The removal of a gas or vapor from a flowing stream by a bed of chemically impregnated activated carbon granules, in which both physical adsorption and chemical reaction occur, is represented as a series of seven consecutive steps. This sequence of seven steps in gas removal, initiated when the flowing gas-air stream approaches the first layer of carbon granules in the bed, is shown to be (1) mass transfer, (2) surface diffusion, (3) intragranular diffusion, (4) physical adsorption, (5) gas desorption (6) chemical reaction, and (7) surface renewal. The first four steps describe the sequence involved in the physical adsorption of a gas by an activated carbon. Since it is believed that physical adsorption occurs prior to any chemical reaction between the gas and the impregnants on the carbon steps (5) through (7) apply only to a chemically impregnated activated carbon. Some authors (1) have combined steps (2) and (3) into one, identifying it as an internal diffusion step. The overall rate of physical gas adsorption will be determined by which one of these steps, or combination of steps, is the slowest and therefore rate controlling.

Under dynamic flow conditions, wherein the mean residence time of a gas flowing through a carbon bed is a fraction of a second, gas removal from the flowing air stream by the activated carbon, due to physical adsorption processes alone, may not be efficient enough to produce the desired concentration attenuation. To increase the overall gas removal efficiency activated carbons may be impregnated with certain metals and/or metal salts which permit and induce chemical reaction between the impregnants and the initially adsorbed gas.

It is the intent of this paper to study the mechanism and kinetics of this dual approach to gas sorption by impregnated activated carbons and to devise a method of data analysis which will identify the rate controlling step.

2. EXPERIMENTAL

The activated carbon adsorbent was a 12-30 mesh BPL grade, lot 7502, from Pittsburgh Activated Carbon Company, Pittsburgh, Pennsylvania, having an internal surface area of 1000 m²/g. The weighted mean granule diameter was 0.104 cm. When pulverized to a 70-80 mesh fraction the mean diameter was 0.019 cm. The carbon when impregnated with an aqueous solution (12% NH₃) buffered by 10.9% carbonate ion and containing 8.5% copper, 4.1% chromate ion, and 0.3% silver nitrate was termed ASC whetlerite. The adsorbate vapor was 98% pure cyanogen chloride. Cyanogen chloride penetration of the bed was detected by the decolorization of a starch-iodine bubbler in a gas test apparatus similar in design to that described in detail by Jonas and Rehrmann (2).

3. THEORY

The general hypothesis on reaction steps taking place in gas removal by impregnated carbons is that

physical adsorption of the gas on the surface must precede any catalytic or reactive process. The proposed sequence of reaction steps in the removal of cyanogen chloride from an air mixture, flowing into a bed of impregnated carbon granules, is as follows:

1. Mass Transfer (bulk or external diffusion).

The gas molecules are transported from a vicinity of neighboring air molecules to a vicinity of the adsorbent granule outer surface. The transport is characterized by mass flow if a pressure gradient exists or by mass diffusion if a concentration gradient exists in the absence of a pressure gradient. For molecular diffusion the transfer can be quantified by Fick's 2nd Law of Diffusion which indicates that the rate of gas movement is a function of several parameters, most especially the concentration gradient. The simple form of Fick's Law for one-dimensional flow is shown as

$$-\frac{dm}{dt} = DA \frac{\partial C}{\partial X} \quad (1)$$

where dm/dt is the rate of mass decrease (g sec⁻¹) over a boundary of area A (cm²), $\partial C/\partial X$ the concentration gradient across the boundary thickness (g cm⁻⁴), and D the diffusivity or diffusion coefficient of the gas (cm² sec⁻¹).

The diffusivity D is normally dependent upon the 3/2 power of $T^\circ K$ and can be calculated using Gilliland's equation (3).

2. Surface Diffusion.

The rate of surface migration of gas molecules from their initial contact point on the surface of a sorbent granule to a pore opening is normally considered rapid when compared to the intragranular diffusion step, although a rigorous treatment of the mathematics has not been developed. However, if the surface migration step were the slowest step, and therefore rate controlling, the differential rate of gas adsorption would be independent of linear velocity, nearly independent of inlet gas concentration, and vary inversely with the square of the sorbent particle size (4).

3. Intragranular Diffusion.

Intragranular or Knudsen diffusion, also called pore or molecular diffusion, should prevail when the mean free path between intermolecular collisions is large compared to the pore diameter. In general, Knudsen diffusion occurs for gas phase reactions at one atmosphere pressure on surfaces whose pores are 20 nm in radius or smaller (5). Molecular flow due to Knudsen diffusion is independent of total pressure differences occurring in an adsorbent pellet as a result of reaction.

4. Physical Adsorption.

For the study of the adsorption kinetics of a bed of carbon granules exposed to an inlet gas concentration at a finite volumetric flowrate, and for which the breakthrough time represents the first trace of gas found in the bed exit stream, pseudo first order kinetics should pertain. The kinetic equation, applicable to the study of gas adsorption by a carbon bed, was originally

derived by Wheeler (6) from a continuity equation of mass balance between the gas entering an adsorbent bed and the sum of the gas adsorbed by plus that penetrating the bed. The equation can be shown in the form of

$$t_b = \frac{W_e}{C_o Q} \left[W - \frac{\rho_b Q}{k_v} \ln\left(\frac{C_o}{C_x}\right) \right] \quad (2)$$

where t_b is the gas breakthrough time in minutes at which the concentration C_x appears in the exit stream, C_o the inlet concentration in g/cm^3 , Q the volumetric flow rate in cm^3/min , ρ_b the bulk density of the packed bed in g/cm^3 , k_v the pseudo first order adsorption rate constant in min^{-1} , W the adsorbent weight in g , and W_e the kinetic saturation capacity in g/g at the arbitrarily chosen ratio of C_x/C_o . Values of t_b plotted as a function of W yield a straight line curve from whose slope and x-axis intercept the properties W_e and k_v can be respectively calculated.

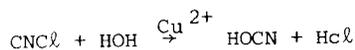
5. Gas Desorption. The study of gas desorption from a bed of carbon granules can be approached in terms of a regeneration of the bed, no desorption resulting in no regeneration and complete desorption resulting in 100% regeneration. The theoretical basis for the approximate solution of the desorption equations was accomplished by Wheeler (7) in the form

$$t_R = \frac{W_o - W_x}{Q(C_e - C_o)} \left[W + \frac{\rho_b Q}{k_d} \ln(1/f) \right] \quad (3)$$

where t_R is the time for regeneration to obtain the fractional regeneration f , k_d is the desorption (or regeneration) rate constant, and $W_o - W_x$ and $C_e - C_o$ are modified capacity and concentration terms. The form of equation (3) follows closely that of the adsorption equation (2), an important difference being that the terms within the brackets are added to rather than subtracted from one another.

Independent calculations by Jonas and Svirbely (8) have shown that the adsorption rate constant k_v for carbon tetrachloride was approximately 780 times larger than the desorption rate constant k_d , that for chloroform was 1285 larger.

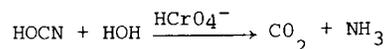
6. Chemical Reaction. A logical consequence of the fact that with activated carbons the adsorption rate constant was approximately 10^3 larger than the desorption constant is that the slower desorption step should permit a longer residence time for passage of the gas over those areas onto which the chemical impregnants were deposited. Thus, regardless of the actual reaction order of the gas with respect to the reacting chemical species a longer residence time indicates higher probabilities for reaction to occur. The postulated reaction of the cyanogen chloride with the chromate brochantite (believed to be the most active form of the chemical impregnants on the carbon) is catalyzed hydrolysis, shown as



and forming cyanic acid and hydrogen chloride.

7. Surface Renewal. The surfaces of the activated carbon, in the case of sorption of cyanogen chloride, are renewed by the further reaction or secondary hydrolysis step of the cyanogen chloride. For example, the cyanic acid is believed to react with

another mole of water



forming the volatile and poorly adsorbed carbon dioxide and ammonia, thus renewing the carbon surface and making it available for continuation of the reaction mechanism.

4. ANALYSIS

A series of gas tests has been devised using cyanogen chloride as the adsorbate and activated and impregnated carbons as the adsorbents. The tests will encompass the following conditions: invariant inlet concentration and temperature ($4 \times 10^{-6} g/cm^3$ at $25^\circ C$); variable carbon weight (1 to 9 g); variable flowrate corresponding to superficial linear velocities of 2, 10, and 60 cm/sec and covering the range 0.30 to 0.007 seconds residence time; variable mesh size (12-30 and 70-80); and three relative humidities (0, 50, and 80%). The values of W_e and k_v are calculated from a plot of t_b vs W in accord with equation (2). The calculated values are then tabulated in the following matrix shown below in generalized alphabetic row and column notation.

Rel Hum %	Sup Vel (cm/sec)	Ads Cap W_e (g/g)				Ads Rate Const k_v (sec $^{-1}$)			
		Act	Imp	Act	Imp	Act	Imp	Act	Imp
		12-30 Mesh	70-80 Mesh	12-30 Mesh	70-80 Mesh	12-30 Mesh	70-80 Mesh	12-30 Mesh	70-80 Mesh
0	2	AA	AB	AC	AD	AE	AF	AG	AH
	10	BA	BB	BC	BD	BE	BF	BG	BH
	60	CA	CB	CC	CD	CE	CF	CG	CH
50	2	DA	DB	DC	DD	DE	DF	DG	DH
	10	EA	EB	EC	ED	EE	EF	EG	EH
	60	FA	FB	FC	FD	FE	FF	FG	FH
80	2	GA	GB	GC	GD	GE	GF	GG	GH
	10	HA	HB	HC	HD	HE	HF	HG	HH
	60	IA	IB	IC	ID	IE	IF	IG	IH

A proper analysis of the data so charted should permit the determination of which of the seven consecutive reaction steps is rate controlling.

5. REFERENCES

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