Elution Equations for Adsorption and Ion Exchange in Flow Systems

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Letters to the Editor

*T*HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

The Vapor Pressure and Heat of Sublimation of Graphite

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IN a recent communication under the above title, Brewer, Gilles, and Jenkins[1] describe an equilibrium effusion method for measuring the vapor pressure of graphite. From the results of experiments below 3000°K they conclude that the vapor reaches a pressure of one atmosphere at 4630°K, and that the heat of sublimation is 170 kcal./g-atom.

However, apart from the fact that several indirect lines of evidence discussed elsewhere[2] will not admit of the latter value, these figures encounter a number of serious difficulties when compared with much evidence of a more direct nature, as pointed out below:

(i) Setting aside experiments involving the temperature of the positive crater in the carbon arc, which do not give consistent results, there are only three other sets of experiments in which equilibrium temperatures and pressures are measured for graphite. The results of two of these, namely, those of Thiel and Ritter[3] (first two of the three methods described) and Basset,[4] provide temperature-pressure data closely supporting the figure 125 kcal./g-atom for the heat of sublimation (the lowest alternative considered by Brewer et al.). The third, due to Ribaud and Bégué,[5] is in poor agreement with the other two and indicates a lower vapor pressure; but in all three cases the vapor-pressure data are higher than those of Brewer et al. by several powers of ten.

(ii) Basset[4] found the coordinates of the triple point of carbon to be 4000°K and 100 atmospheres, below which pressure the carbon sublimed without melting. Even if, as Brewer et al. suppose, the temperature measurements of Basset are seriously in error, the same is not likely to be true of his pressure measurements. Further, the pressure at the triple point has been independently determined by Steinle[6] who also finds that it is 100 atmospheres. Both Basset and Steinle provide photographic evidence for their conclusions. But, according to the temperature-pressure relation of Brewer et al., the vapor pressure reaches 100

atmospheres above 6000°K. This would place the melting point of graphite at an impossible figure well above those of the refractory metal carbides, whereas, for example, graphite can be fused in a crucible of tantalum carbide which has a reputed melting point of 4150°K. Other experimental figures for the melting point of graphite are variously given as 3800,[7] 3900,[8] 3760,[9] and 3845°K.[10] It thus does not appear that Basset's figure is an underestimate, nor can it be presumed that all of the various investigators cited here have erred in their temperature measurements by such an enormous and approximately constant amount.

(iii) If the vapor pressure of graphite reaches 1 atmosphere at 4630°K, it is surprising that temperatures reported for the positive crater of the carbon arc, which are generally regarded to be limited by the vapor pressure, are never sensibly above 4000°K, even under elevated pressures.

(iv) Apart from absolute temperature measurements, Mott[11] has determined the relative volatilities of a number of substances by a variety of methods. His placing of carbon offers support to the measurements of Basset and of Thiel and Ritter, but is decidedly out of harmony with those of Brewer et al.

The consensus of opinion is thus that graphite possesses a very much higher vapor pressure and consequently lower heat of sublimation than Brewer et al. affirm. It is relevant to note in conclusion that these authors in their experiments with replaceable graphite tubes found that rapid volatilization occurred which limited the life of the tubes. This observation is scarcely compatible with their own temperature-pressure relation, which in all cases necessitates pressures well below 0.1 mm at the temperatures of their experiments.

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Elution Equations for Adsorption and Ion Exchange in Flow Systems

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ELUTION, the process of separating from a granular adsorbent bed one or more components previously adsorbed upon it, is an essential step in any regenerative cycle of ion exchange, chromatography, or gas adsorption.

The typical "elution bell" i.e., the concentration-time curve which displays a maximum, has been fitted approximately by the stepwise-discontinuous method of equilibrium stages.[1-3] For the special case where the bed is initially fully saturated, Thomas[4] has provided exact kinetic
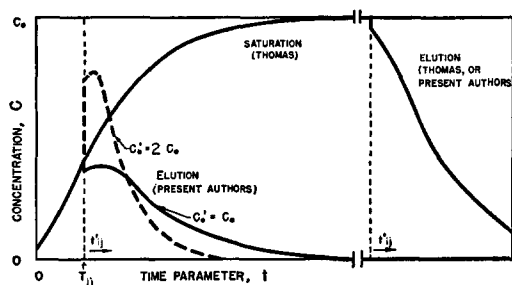

FIG. 1. Concentration curves for a saturating component in an eluting fluid stream passing a given cross section of granular bed; calculated from Eq. (4).

equations which include the result of Boyd, Myers, and Adamson.[5] By an extension of Thomas's method, we have now derived general kinetic equations for the elution bell for any fractional extent of previous saturation.

Our study has shown, incidentally, that Thomas's equations for saturation of an initially empty bed[6] contain the equations proposed by several other investigators. For the concentrations of saturating component in the fluid (c) and on the bed (p), Thomas obtained

$$\frac{c}{c_0} = \frac{\varphi(t, rs) + I_0(2(rst)^{\frac{1}{2}})}{\varphi(t, rs) + I_0(2(rst)^{\frac{1}{2}}) + \varphi(s, rt)}, \quad (1)$$

$$\frac{p}{p_\infty} = \frac{\varphi(t, rs)}{\varphi(t, rs) + I_0(2(rst)^{\frac{1}{2}}) + \varphi(s, rt)}, \quad (2)$$

where we utilize his notation except for r, s, t, and p_∞ which have the values given in Table I. Only when $r = 1$ can c/c_0 and p/p_∞ be evaluated exactly from the heat-transfer charts of Furnas.[7] The functions $F(c, p)$ in Table I contain in each case the rate constants for a second-order forward-second-order reverse reaction (typified by exchanging ions of equal valence). For kinetically simpler cases, the constant factors (k_1a) or (k_2c_0) must be replaced in the tabulated terms by whatever rate constants are appropriate.

Consider now that a fluid containing a single saturating component at concentration c_0 has passed through the bed during a time interval, τ_{sat}, which corresponds to a particular value of y and thus of $t_{ij}(=T_{ij})$. At this instant, an eluting fluid (the same fluid, but without saturating component) begins to pass through the bed at an unchanged rate of flow. (For ion exchange, the fluid is assumed to contain an eluting component identical with the species on the bed prior to saturation; its concentration will temporarily be taken equal to that of the saturating component, c_0, in the preceding fluid.)

The equations for elution will depend, first, upon the bed concentration at each point at passage of the (assumedly sharp) new fluid front. Thus at $y' = (r' - l/R)/m = 0$, where r' is time reckoned from the start of regeneration, we have

$$\frac{p}{p_\infty} = \frac{\varphi(T, rs)}{\varphi(T, rs) + I_0(2(rsT)^{\frac{1}{2}}) + \varphi(s, rT)}. \quad (3)$$

In addition, since the component of interest is no longer entering the bed, $c = 0$ at $x = 0$. Thomas's conservation and

TABLE I. Rate, distance and time parameters for Thomas equations.

Reaction order Forward Reverse (i) (j)	Rate, $F(c, p)$	$p\infty$	r_{ij}	s_{ij}	t_{ij}	Previous investigators
Surface reaction controlled						
2 2	$k_1c(a-p)$ $-k_2p(c_0-c)$	a	k_2/k_1	mk_1ax	mk_1c_0y	a
2 1	$k_1c(a-p)$ $-(k_2c_0)p$	$\dfrac{k_1a}{k_1+k_2}$	$\dfrac{k_2}{(k_1+k_2)}$	mk_1ax	$m(k_1+k_2)c_0y$	b
2 0	$k_1c(a-p)$	a	0	mk_1ax	mk_1c_0y	c-f
1 1	$(k_1a)c$ $-(k_2c_0)p$	$\dfrac{k_1a}{k_2}$	1	$m(k_1a)x$	$m(k_2c_0)y$	b, e
1 0	$(k_1a)c$	—	1	$m(k_1a)x$	0	g
Diffusion controlled						
1 1	$k_D\left(\dfrac{k_1a}{k_2c_0}c - p\right)$	$\dfrac{k_1a}{k_2}$	1	$mk_D\dfrac{k_1}{k_2c_0}ax$	mk_Dy	h-j

a See reference 6.
b See reference 4.
c G. S. Bohart and E. Q. Adams, J. Am. Chem. Soc. 42, 523 (1920).
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g Drew, Spooner, and Douglas: D. M. Klotz, Chem. Rev. 39, 241 (1946), reference 10.
h See reference 5.
i O. A. Hougen and W. R. Marshall, Chem. Eng. Progress 43, 197 (1947).
j R. H. Beaton and C. C. Furnas, Ind. Eng. Chem. 33, 1500 (1941).

rate conditions are then applied, with replacement of y by y', and lead to the equations:

$$\frac{c}{c_0} = \frac{\begin{array}{c}e^{-T}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})] \\ -[\varphi(t', rs)+I_0(2(rst)^{\frac{1}{2}})]\end{array}}{\begin{array}{c}e^{-T}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})] \\ +\varphi(s, rT+rt')]+[\varphi(rt', s)-\varphi(t', rs)]\end{array}}, \quad (4)$$

$$\frac{p}{p_\infty} = \frac{e^{-T}[\varphi(T+t', rs)]-[\varphi(t', rs)]}{\begin{array}{c}e^{-T}[\varphi(T+t', rs)]+I_0(2(rsT+rst')^{\frac{1}{2}}) \\ +\varphi(s, rT+rt')+[\varphi(rt', s)-\varphi(t', rs)]\end{array}}, \quad (5)$$

where r and s remain as before, and t'_{ij} corresponds to the values of t_{ij} in Table I with y replaced by y'. Figure 1 presents typical elution curves as calculated from these equations, with r_{ij} and s_{ij} constant. At large T the equations become identical with those of Thomas,[4] as is indicated in the figure; for instance:

$$\frac{c}{c_0} = \frac{\varphi(rs, t')}{\varphi(rs, t')+I_0(2(rst')^{\frac{1}{2}})+\varphi(rt', s)}. \quad (6)$$

As the new fluid front travels down the bed, the discontinuity in c/c_0 decreases and rapidly becomes negligible; in actual practice, it may be obscured by diffusional effects even at small distances. For ion exchange, the above equations may be extended to regenerant concentrations other than c_0 (i.e., c_0') by replacing c_0 by c_0' (except in the calculation of T which is a "memory" term); in this case a discontinuity is always encountered at the front. Figure 1 shows also how regeneration time is reduced by doubling the concentration level of regenerant.

The curve for p is continuous, but otherwise of the same general shape as for c; its maximum represents a true equilibrium condition, at the time that net reaction at that particular cross section finally shifts from saturation to elution.

Where $r=1$, Eqs. (4) and (5) take on an especially simplified form:

$$\frac{c}{c_0} = e^{-(T+t'+rs)}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})]$$
$$-e^{-(t'+rs)}[\varphi(t', rs)+I_0(2(rst)^{\frac{1}{2}})], \quad (7)$$

$$\frac{p}{p_\infty} = e^{-(T+t'+rs)}[\varphi(T+t', rs)]-e^{-(t'+rs)}[\varphi(t', rs)]. \quad (8)$$

The two terms in each of the above equations represent pairs of values in the Furnas charts that are displaced along the t' scale by a value of T.

Saturation and elution equations have also been derived for cases involving more than one "memory" term. We are preparing tables of φ to facilitate exact evaluation of the above equations, and also are charting solutions of Eq. (1) for values of r other than unity. Complete derivations will be reported and applications discussed in a forthcoming paper.

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Absorption Spectrum of Hexavalent Plutonium

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THE chemical similarity between uranium and plutonium now appears to be firmly established.[1,2] Recently, Kasha[3] has used this analogy to explain certain features of the absorption spectrum of PuO_2^{++} in $0.1N$ perchloric acid. Now the absorption spectrum of UO_2^{++} is well known;[4] it contains eleven regularly spaced bands in the region 3400–5000A. These bands are believed to arise from symmetrical vibrations in the U–O bonds of
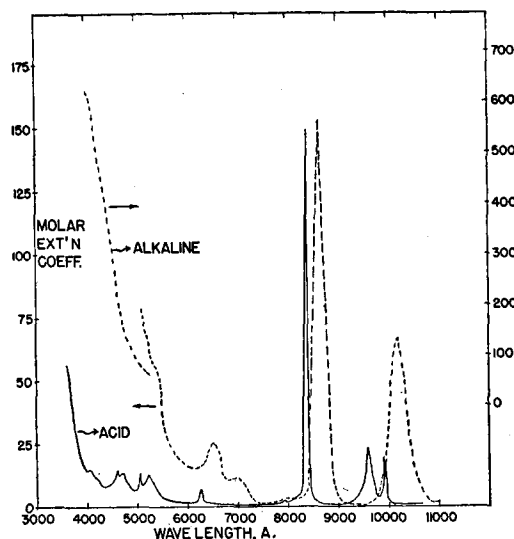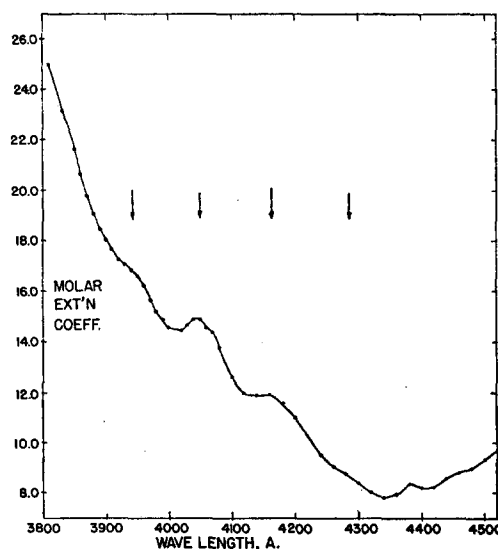

FIG. 1. Absorption spectrum of Pu(VI).

FIG. 2. Absorption spectrum of Pu(VI) in HNO₃ solution.