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ADSORPTION THEORY INTERPRETATION OF Ca^{45} AND P^{32} EXCHANGE WITH HYDROXYAPATITE

by

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ADSORPTION THEORY INTERPRETATION OF Ca^{45} and P^{32} EXCHANGE WITH HYDROXYAPATITE

W. V. Loebenstein

ABSTRACT

A theory has been developed for characterizing adsorption from solution based on Langmuir kinetics. An unusual application of the theory has been made to the simultaneous interaction of Ca^{45}--calcium ions and of P^{32}--phosphate ions in solution with synthetic hydroxyapatite crystals. The saturated solution is comprised primarily of non-radioactive calcium and phosphate ions in order to assure no net change in the overall ionic concentration. In applying the adsorption theory to each radioactive species in turn, as solute-adsorbate, it is convenient to consider everything else in solution as solvent. In analyzing the model, a distinction is made between two processes:

(1) an irreversible process where the tagged ion is so strongly adsorbed that it is no longer accessible. This process is assumed to be confined to a certain weight fraction of the substrate.

(2) A reversible process where the tagged ion occupies one of the surface crystal sites

> yet is free to dissolve (desorb), and this process is confined to the remaining weight fraction of the substrate.

Modern high-speed digital computer techniques have been employed to solve the problem in terms of physically-significant characteristic parameters. This has been accomplished for a number of experiments over a range of pH values for systems varying in slurry densities and tagged-ion concentrations. Based on the assumed model, no change in calcium to phosphate ratio of the surface composition was evident, regardless of variations in the solutions of pH, total ionic concentration, and ionic ratio.

1. INTRODUCTION

Studies of the solubility and crystallization of hydroxyapatite are of fundamental importance to an understanding of the chemical dynamics of tooth structure. Batch adsorption kinetics have been useful in earlier studies[1,2,3] in characterizing the adsorptive properties of a surface with respect to one or more components in solution. Through such studies it has been possible, for example, to measure the population of sites capable of adsorbing a solute without having to fill them all in the process.

This measurement of the site population would constitute one of the characteristic parameters of the system and should be independent of variable quantities such as the mass of the adsorbent, the amount of solution, the initial concentration of solute, the time of measurement, or the amount of solute initially adsorbed.

The possibility of distinguishing simultaneously the respective concentrations in solution of radioactive calcium and phosphorous from their untagged counterparts affords an unusual opportunity to observe the deposition of these radioactive ions from solution under conditions of equilibrium between crystals of synthetic hydroxyapatite and saturated solutions of their non-radioactive ions.

The so-called "adsorption" sites are in reality the positions in the crystal lattice which are available to each specific ion, since the crystal does not distinguish between tagged and untagged isotopes of the same element.

The concentrations of radioactive ions in solution were always several orders of magnitude smaller than their non-radioactive counterpart. This is a necessary condition for a valid application of the proposed adsorption model to isotopic exchange. The model used in the present treatment permitted an irreversibly adsorbed radioactive ion to migrate to the interior of the substrate by diffusion, exchange, or other mechanism, just as long as it retained its adsorbed status. On the other hand, a reversibly adsorbed radioactive ion was constrained to the actual interface layers always accessible for desorption back into the solution.

2. MATERIALS AND PROCEDURE*

The hydroxyapatite was prepared by a slow addition of stoichiometric aliquots of $Ca(OH)_2$ in suspension with H_3PO_4 in a CO_2-free environment, the resultant precipitate being stabilized by prolonged boiling. Its composition was confirmed by infrared absorption and by chemical analysis. Its BET area was 26.4 m^2g^{-1} determined by N_2 adsorption at 77°K.

Details of the preparation of the saturated solutions in equilibrium with the hydroxyapatite (HA) suspension together

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* Dr. Yoram Avnimelech (present address: Israel Institute of Technology, Haifa, Israel) carried out the experiments described herein. He has kindly made available his experimental data for the purpose of the present investigation.

with the stock solution of the tagged ions have been provided by Avnimelech.[4] The isotopic exchange experiments were carried out in a manner identical with batch adsorption. The suspension consisting of several hundred milliliters was kept agitated in a constant temperature bath held at 25 ± 0.02°C during the course of the experiment. Zero time was taken as the instant of innoculation with the radioactive tracer ions. Five milliliter samples of the suspension were withdrawn for activity analyses of the solution at frequent time intervals beginning at one minute, or less, and continuing for durations ranging up to nearly four hours.

In demonstrating the existence of reversibility, Avnimelech introduced an unusual innovation which is seldom encountered[5] in adsorption work because of the complexities it entails in the fitting of theory with experiment. This consisted of making sudden additions, from time to time, of tracer-free saturated solution to the reaction vessel. This brought about an abrupt dilution of the radioactive ions without disturbing the concentrations (or pH) of the non-radioactive components of the solution. As many as three such dilutions were made in most of the experiments. The several experiments differed from one another in weight of solid, volume of solution, concentration of radioactive tracer ions, concentration of non-radioactive saturated solutions (which is related to pH at equilibrium), times and frequency of sampling, and time and amount of dilution.

3. BACKGROUND THEORY

A three-parameter equation based on Langmuir kinetics was derived and tested in earlier work[2,3] and found to apply rather well to reversible adsorption from solution. That equation was expressed as follows:

$$\frac{(M-N)-\hat{q}}{(M+N)-\hat{q}} = \frac{(M-N)-q_{IN}}{(M+N)-q_{IN}} \quad e^{-2\left(\frac{W}{V}\right) N k_1 t} \tag{1}$$

where

$$M = \frac{V}{2W}\left[\frac{k_2}{k_1} + c_o\left(1 + \frac{Wq_o}{Vc_o}\right)\right] \tag{2}$$

and

$$N = (M^2 - q_o\, c_o\, V/W)^{1/2} \tag{3}$$

and where

$\hat{q}$ = the amount of solute adsorbed per unit mass of the adsorbent at any time t;

q_o = the maximum value q would have if all of the adsorption sites were filled;

c = the instantaneous solute concentration whose value would be c_o if no ions were adsorbed;

W = the mass of the adsorbent;

V = the volume of the solution;

k_1 = the specific adsorption rate constant;

k_2 = the specific desorption rate constant;

q_{IN} = the amount of solute adsorbed per unit mass of the adsorbent at onset of the sorption process.

Equation (1) can be rewritten in a more useful form in which $\hat{q}$ is explicitly expressed:

$$\hat{q} = M + \frac{\frac{(M-N)-q_{IN}}{(M+N)-q_{IN}} e^{-2Nk_1 t\, W/V} + 1}{\frac{(M-N)-q_{IN}}{(M+N)-q_{IN}} e^{-2Nk_1 t\, W/V} - 1} \cdot N \qquad (4)$$

A distinction is made between $\hat{q}$ and q in that the former quantity is the theoretical or computed value, while the latter is used to designate the experimental amount adsorbed per unit mass at any instant and is related to the concentration in solution according to the conservation equation which is always valid; namely:

$$q = (c_o - c)\ V/W \qquad (5)$$

Equation (4) was derived from the differential equation which expressed the rate of adsorption dq/dt as the difference between the forward and reverse processes:

$$dq/dt = k_1(q_o - q)\ c - k_2 q \qquad (6)$$

The concentration factor c was eliminated between Eqs. (5) and (6) prior to integration.

If k_2 in Eq. (6) were set equal to zero, an irreversible adsorption would result and the integrated form Eq. (4) subject to Eqs. (2) and (3) would simplify considerably.

In the practical case of adsorption from solution, most systems exhibit to some extent both reversible and irreversible attributes. Since this dual behavior was also observed in the present investigation, it follows that a two-process representation would be the very simplest combination that could account for all the results observed.

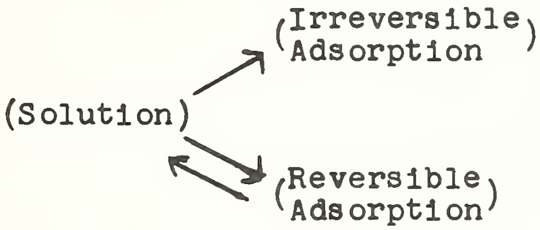
At this point it is necessary to distinguish between different possible models or mechanisms. The choice of the particular model for treatment in this paper was not based on any preference of a fundamental nature. Other mechanisms (one of which is discussed in the text) are equally plausible from a theoretical point of view. They can also and, indeed, should be tested against experiment before any choice is made as to which mechanism is preferred. The principal purpose of this paper is to illustrate how an assumed model can be tested. The two most probable mechanisms for the adsorption kinetics of the dissolved species are:

(a) Sequential Adsorption

$$(\text{Solution}) \rightleftarrows \begin{pmatrix}\text{Reversible}\\ \text{adsorption}\end{pmatrix} \rightarrow \begin{pmatrix}\text{Irreversible}\\ \text{adsorption}\end{pmatrix}$$

and

(b) Competitive Adsorption



In the present paper, the latter mechanism was arbitrarily chosen for detailed study.

A crude model applicable to the present investigation is illustrated in Fig. 1.

The first few surface layers of the solid are depicted in some regular array at the bottom of the figure. Only the calcium ions (small circles) and the phosphate ions are represented. The shaded circles identify the tagged ions. It is evident that a tagged ion which is depicted as inaccessible would correspond to an irreversibly adsorbed state. However, an ion which occupies a site on the outermost layer in contact with the solution might still be irreversibly adsorbed. Both adsorption sites, reversible and irreversible, may be thought of as competing for each ion in solution.

This situation is indicated mathematically by Eqs. (7) and (8):

$$dq_1/dt = k_{11}(q_{01}-q_1)c \tag{7}$$

$$dq_2/dt = k_{12}(q_{02}-q_2)c - k_{22}q_2 \tag{8}$$

where the irreversibility of Eq. (7) is assured by the absence of a desorption term. Equations (7) and (8) are logical extensions of Eq. (6) in which the additional subscripts 1 and 2 identify the process as either irreversible or reversible. The parameters q_{01} and q_{02}, for example, now represent the concentrations of irreversible and reversible adsorption sites, respectively. The interdependence of the two processes is determined by the common factor, c, the concentration of the particular tagged ion under investigation.

Before attempting to integrate this system of equations, it is necessary to express c in terms of q_1 and q_2, the amounts irreversibly and reversibly adsorbed per unit mass, respectively. The overall conservation Equation (5) is always valid and may be rewritten as:

$$c = c_o - qW/V \qquad (9)$$

It was convenient to consider that the entire mass of adsorbent W was partitioned into two parts W_1 and W_2, such that all of the irreversible adsorption q_1 was confined to W_1, while the reversible adsorption q_2 could take place only on W_2. A partition parameter θ was introduced to designate that fraction of the adsorbent available for reversible adsorption. Thus,

$$W_1 = (1 - \theta)W \qquad (10)$$

$$W_2 = \theta W \qquad (11)$$

Now, since the total amount adsorbed is Wq, overall, it is clear that:

$$Wq = W_1q_1 + W_2q_2 \qquad (12)$$

from which it follows that

$$q = (1 - \theta)\, q_1 + \theta\, q_2 \qquad (13)$$

This value of q may be substituted in Eq. (9) to get

$$c = c_o - [(1 - \theta)\, q_1 + \theta\, q_2]\, W/V \qquad (14)$$

for the conservation equation applicable to Eqs. (7) and (8).

If appropriate values could be found for the six parameters q_{01}, q_{02}, k_{11}, k_{12}, k_{22}, and θ, it would be possible to integrate Equations (7) and (8) numerically[6,7] and thus obtain values for $\hat{q}_1$ and $\hat{q}_2$, the amounts computed to be adsorbed per unit mass of each of the two respective partitioned portions of the adsorbent. The experimental quantities q_1 and q_2, however, cannot be measured individually. The overall amount adsorbed per unit mass of total adsorbent q can be compared with its computed counterpart $\hat{q}$ using Eqs. (5) and (13). This affords a means of determining goodness of fit according to the principle of "least squares".

Accordingly, a first estimate was made of each of the six parameters, q_{01}, q_{02}, k_{11}, k_{12}, k_{22} and θ. Based on these values, Equations (7) and (8) were integrated numerically and estimates of $\hat{q}_1$ and $\hat{q}_2$ were obtained. Using these, together with Eq. (13), a first estimate of $\hat{q}$ was determined corresponding to each time at which a sampling was made.

The experimental value of q from Eq. (5) was also evaluated at each measured point. Next, the "deviation", $q-\hat{q}$, was squared and summed over all points in an experiment. This resultant "sum of squares" is a measure of the extent of agreement with "theory" and should be as small as possible for the best fit. This is a generalized statement of the so-called "Principle of Least Squares". A rather involved mathematical procedure (which is beyond the scope of this paper) was used based on the Gauss-Newton[8] method of Non-Linear Least Squares with Levenberg[9] damping for obtaining an up-dated second estimate of the six parameters. The entire calculations were repeated and gave rise to a lower value for the sum of squares. If the initial choice of each parameter was within certain broad bounds and the amount of change from iteration to iteration was sufficiently restricted, a sum of squares would ultimately be found which could not be reduced by further change of any of the parameters. These limiting values were then taken for the best fit of the theory based on the assumed model.

It is significant that the method described for evaluation of the parameters for the exchange of calcium and of phosphorous arising from measurements made simultaneously from the same solution were, nevertheless, treated independently as though they were separate and distinct experiments.

4. RESULTS

Pairs of isotopic exchange experiments are reported in which the pH values were 5.64, 5.77, 5.82, 6.41, 6.72, and 6.92* (see Table 4). These values had been selected to be within the range in which hydroxyapatite is the most insoluble of the possible crystalline species in the calcium phosphate series, such as dicalcium phosphate and octacalcium phosphate, which could form from solution.

Experiment IE-13, which was carried out at the lowest pH, is summarized in Tables 1a and 1b for the isotopic exchange of Ca^{45} and P^{32}, respectively. The first five columns comprise the experimental measurements (variables). The last five columns list the quantities computed by using the present theory together with the best estimate that could be made of the six parameters involved. Column (10) contains the numerical values computed for the overall adsorption which may be compared with the corresponding experimental values given in column (1).

The computed values for $\widehat{q_1}$ and $\widehat{q_2}$ shown in columns (8) and (9) are especially interesting in light of the competitive aspect of the theoretical model. During the initial stages of the experiment (before the first dilution) where the overall uptake of tagged ions increased continuously, the amount computed to be reversibly adsorbed, $\widehat{q_2}$, increased very

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* Two additional pairs of Avnimelech's experiments were not treated either because of insufficient points or inability to obtain convergence.

rapidly at first from its initial value of zero at zero time, then decreased. The reason for this reversal was the increasing inroads made by $\hat{q}_1$, the amount computed to be adsorbed irreversibly. As more of the tagged ions were irreversibly removed from solution, ions which had adsorbed reversibly during the earlier stages of the experiment could no longer be accommodated on the solid. Consequently, in order to be consistent with the assumed model, they desorbed to compensate. The overall adsorption, q, during this first phase showed a continual increase with time. In subsequent phases of the experiment after dilutions were made, the computed desorption as shown by the decrease of $\hat{q}_2$ was more than enough to override any possible increase attributable to $\hat{q}_1$ and the overall effect upon $\hat{q}$ was a net desorption. These observations are graphically illustrated in Figures 2 and 3.

Experiment IE-8 (Tables 2a and 2b) differs from the other experiments in that only one dilution was performed and that was close to the end of the experiment. Accordingly, a somewhat different procedure was used in fitting the parameters. A "best" fit was obtained based on the initial phase of the exchange experiment which involved 25 points. The remaining eight points were then compared with their extrapolated values. This experiment is graphically illustrated in Figures 4 and 5. Fig. 4 shows the overall adsorption along with the agreement between experiment and theory while Fig. 5 compares the computed values of irreversible adsorption with reversible adsorption. The agreement between average values of q with $\hat{q}$ corresponded to a coefficient of variation of about two to three percent in most of the experiments.

Values obtained for the characteristic parameters are listed in Table 3 in the order of increasing pH values.

5. DISCUSSION

It is conceivable that many generalities could be made concerning the physical significance of these parameters either singly or in combination in attempting to correlate the results with known experience. Some inconsistencies can also be detected which will be discussed later. One relationship, R, which has been evaluated is shown in the last column of Table 4 where $R = (\theta \times q_{02})_{Ca}/(\theta \times q_{02})_P$. The product of θ and q_{02} for the same adsorbate is proportional to the maximum capacity for reversible adsorption per unit mass of overall adsorbent. The ratio of this product for calcium to that for phosphorous should be proportional* to the relative population of calcium to phosphate sites at the outermost surface layers of the solid.

While a considerable spread in the values of R is evident, no trend in the ratios was observed. The correlation

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*The proportionality constant does not cancel out because a different proportionality exists between cpm and absolute concentration for Ca^{45} as compared with P^{32}.

coefficients were not significantly different from zero when attempts were made to correlate R with pH; with the ratio of total [Ca] to total [PO_4] in solution; or with total ionic strength. These results may be verified from the data in Table 4.

The specific surface (BET) of the synthetic HA used here was 26 m^2/g. This is small compared with that of anorganic dentin which has been found to be as high[10] as 140 m^2/g. It would be interesting to know whether the product of θ and q_{02} for a given ion such as [Ca] or [PO_4] adsorbed from solution would be proportional to surface area for different preparations of hydroxyapatite.

The maximum amount $\hat{q}_2$ reversibly adsorbed per g of θ fraction of the sample in any given experiment gave no indication of how much of its capacity, q_{02}, was used. For example, almost the same capacities (22 to 23 cpm/mg) were found for q_{02} corresponding to the calcium adsorption in Expts. IE-13 and IE-8 (see Table 3). While Table 1a shows that 17 1/2 cpm/mg of this capacity was attained in IE-13, no more than about 5 1/2 cpm/mg was reached in IE-8, as is seen from Table 2a. If, indeed, the 5-g samples of hydroxyapatite of IE-13 and IE-8 did possess the same capacities, q_{02}, for calcium adsorption as the calculations show, these results would lend credence to the theory that the determination of this capacity does not correlate with the solution concentrations used in the experiments. The total concentration of calcium in the saturated solutions was 7.5×10^{-4} and 4.2×10^{-4} moles/ℓ, respectively, (see Table 4); also, the corresponding initial concentrations of the tagged calcium ions (Tables 1a and 2a) were proportional to 56.2 and 25.5 cpm/$\mu\ell$, respectively.

A comparison of the relative sizes of q_{02} and q_{01} for each experiment (Table 3) shows that the capacity for reversible adsorption, q_{02}, is usually about ten times larger than for the irreversible process.

The forward rate constant for the reversible process, k_{12}, was considerably greater than for the irreversible process, k_{11}, in all cases (except for IE-10). This is consistent with experience. Irreversible adsorption (as described earlier) can involve a series of separate processes which might be expected to slow it down. A preferred orientation of adsorbate seems likely for irreversible adsorption which would also be somewhat time consuming.

Tables 1 and 2 and Figures 3 and 5 show in each case that the increase in $\hat{q}_1$ and the corresponding decline in $\hat{q}_2$ with time are completed in a surprisingly short period of time - usually within the first half hour or so of the experiment. While the compensation effect would preclude this observation in the overall change in q with time, it would seem that the phenomenon would have to extend over a prolonged period of time - perhaps even beyond the duration of the experiment.

It is, of course, an over-simplification to expect that only two processes are sufficient to account for all of the effects involved in adsorption or isotopic exchange. It is reasonable, for example, to expect (neglecting the influence of isotopic decay) that given sufficient time the distribution of radioactive ions should be uniform throughout the entire mass of crystals and that the ratio of tagged ions to untagged ions should be the same in the crystals as in the saturated solutions surrounding them. This long-range aspect of equilibrium is not alluded to in the present results, nor is it approximated in the model. An experiment whose duration is measured in hours within a single working day cannot be expected to extrapolate to months or, possibly, even years.

Some inconsistencies have been noted in the observed parameters. Their precision cannot justify the number of "significant" figures used in Table 3. While the degree of agreement between q and $\hat{q}$ corresponded to about 2 to 3 percent in most cases (as previously stated), no method has been found to estimate the precision of the individual parameters. Fortunately, the two parameters used in the test for stoichiometry (θ and q_{02}) are among those found to be least sensitive to change from iteration to iteration. Nevertheless, it was to be anticipated that θ for Ca^{45} would be the same as for P^{32} in the same isotopic exchange experiment regardless of whether its value might have changed from experiment to experiment. The reason for this is that θ was defined as that fraction of the weight of the adsorbent with which the reversible process was concerned. While the parametric fit was determined for Ca^{45} independently of P^{32}, we know from crystallographic considerations and electroneutrality principles that constant ratios of sites must exist in the adsorbed layers as well as in the crystal substrate. Accordingly, an analysis of variance was performed on all the θ values in order to separate the "between Ca and P" contribution and the "among six experiments" contribution from the total variability. The "discrepance" variability with five degrees of freedom was used as error. The null hypothesis that no statistically significant difference was discernible between θ for Ca and θ for P was confirmed. Indeed, the "among experiments" comparison also supported the null hypothesis. The standard deviation for error determined from the discrepance is 0.059. The mean value of θ for all 12 determinations is 0.372 which, together, correspond to a coefficient of variation for θ of 16%. Furthermore, the variability among the six R-values of Table 4 which have been used in the stoichiometric comparison is indicated by a standard deviation of 0.273 and a mean value of 1.66 which again corresponds to a 16% coefficient of variation. Despite the higher-than-hoped-for experimental error, no variation in stoichiometry at the surface over the range of solution characteristics (ionic concentration, ionic ratio or pH) is consistent with these findings.

6. CONCLUSIONS

Probably the most important outcome of the present investigation is the fact that a means has been developed: (1) for fitting to the experimental points an assumed model for relating isotopic exchange with adsorption theory; and (2) that the reasonableness of the assumed model can be tested by examining and comparing the physical significance of the derived parameters.

The results of the present investigation were consistent with the assumption that the overall exchange (adsorption) process might be represented by two independent processes, one irreversible - the other reversible, both competing for the same ions in solution.

This type of study would then throw light upon the solubility-recrystallization equilibrium of hydroxyapatite, since the chemical behavior of radioactive Ca and P are indistinguishable from their non-radioactive isotopes.

A constant stoichiometric relationship between sites available to Ca and those available to P on the surface of the crystallizing solid appeared to be borne out by the theory, in that neither changes in pH nor changes in ionic concentrations nor their ratios in solution had any observable effect upon this relationship.

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Table 1a - IE-13 Ca^{45}

q (cpm·mg^{-1})	W (mg)	V (ml)	c_o (cpm·μl^{-1})	t (min)	$\hat{q}_{1IN}$ (cpm·mg^{-1})	$\hat{q}_{2IN}$ (cpm·mg^{-1})	$\hat{q}_1$ (cpm·mg^{-1})	$\hat{q}_2$ (cpm·mg^{-1})	$\hat{q}$ (cpm·mg^{-1})
5.502	4711.	575	56.21	1.0	0.000	0.000	0.727	17.58	5.484
5.692	"	"	"	2.0	"	"	1.035	17.34	5.636
5.732	"	"	"	3.0	"	"	1.250	17.05	5.710
5.762	"	"	"	5.0	"	"	1.530	16.66	5.799
5.810	"	"	"	7.0	"	"	1.694	16.41	5.848
5.846	"	"	"	9.0	"	"	1.795	16.26	5.878
5.856	"	"	"	12.0	"	"	1.883	16.12	5.903
5.878	"	"	"	16.0	"	"	1.938	16.04	5.918
5.930	"	"	"	20.0	"	"	1.962	16.00	5.925
5.919	"	"	"	25.0	"	"	1.974	15.98	5.928
5.906	"	"	"	35.0	"	"	1.980	15.97	5.929
5.940	"	"	"	45.0	"	"	1.981	15.97	5.930
5.924	"	"	"	60.0	"	"	1.981	15.97	5.930
5.936	"	"	"	86.0	"	"	1.981	15.97	5.930
5.923	"	"	"	100.0	"	"	1.981	15.97	5.930
5.904	"	"	"	122.0	"	"	1.931	15.97	5.930
5.966	"	"	"	123.0	"	"	1.981	15.97	5.930
	*	*	*	*	*	*	*	*	
5.762	4015.	690	39.91	1.0	1.981	15.97	1.981	15.31	5.745
5.748	"	"	"	2.0	"	"	1.981	15.27	5.731
5.669	"	"	"	3.0	"	"	1.981	15.26	5.731
5.750	"	"	"	4.0	"	"	1.981	15.26	5.731
5.763	"	"	"	5.0	"	"	1.981	15.26	5.731
5.784	"	"	"	6.0	"	"	1.981	15.26	5.731
5.752	"	"	"	10.0	"	"	1.981	15.26	5.731
5.742	"	"	"	16.0	"	"	1.981	15.26	5.731
5.738	"	"	"	17.0	"	"	1.981	15.26	5.731
	*	*	*	*	*	*	*	*	
5.526	3753.	945	27.26	1.0	"	15.26	"	14.47	5.508
5.477	"	"	"	2.0	"	"	"	14.39	5.482
5.405	"	"	"	3.0	"	"	"	14.38	5.480
5.435	"	"	"	4.0	"	"	"	14.37	5.479
5.498	"	"	"	5.0	"	"	"	14.37	5.479

Table 1a (continued)

q (cpm·mg^{-1})	W (mg)	V (ml)	c_o (cpm·µl^{-1})	t (min)	$\hat{q}_{1IN}$ (cpm·mg^{-1})	$\hat{q}_{2IN}$ (cpm·mg^{-1})	$\hat{q}_1$ (cpm·mg^{-1})	$\hat{q}_2$ (cpm·mg^{-1})	$\hat{q}$ (cpm·mg^{-1})
5.471	3753.	945.	27.26	6.0	1.981	15.26	1.981	14.37	5.479
5.507	"	"	"	10.0	"	"	"	"	"
5.447	"	"	"	16.0	"	"	"	"	"
5.497	"	"	"	17.0	"	"	"	"	"
	*	*	*	*	*	*	*	*	
5.202	3574.	1300.	18.86	1.0	"	14.37	"	13.55	5.247
5.210	"	"	"	2.0	"	"	"	13.42	5.209
5.223	"	"	"	3.0	"	"	"	13.39	5.203
5.217	"	"	"	4.0	"	"	"	13.39	5.202
5.211	"	"	"	6.0	"	"	"	13.39	5.202
5.217	"	"	"	10.0	"	"	"	13.39	5.202
5.180	"	"	"	20.0	"	"	"	13.39	5.202
5.210	"	"	"	30.0	"	"	"	13.39	5.202
5.210	"	"	"	43.0	"	"	"	13.39	5.202
5.219	"	"	"	80.0	"	"	"	13.39	5.202
5.234	"	"	"	140.0	"	"	"	13.39	5.202
5.206	"	"	"	141.0	"	"	"	13.39	5.202

Table 1b - IE-13 P^{32}

q $(cpm \cdot mg^{-1})$	W (mg)	V (ml)	c_o $(cpm \cdot ml^{-1})$	t (min)	$\hat{q}_{1IN}$ $(cpm \cdot mg^{-1})$	$\hat{q}_{2IN}$ $(cpm \cdot mg^{-1})$	$\hat{q}_1$ $(cpm \cdot mg^{-1})$	$\hat{q}_2$ $(cpm \cdot mg^{-1})$	$\hat{q}$ $(cpm \cdot mg^{-1})$
3.417	4711.	575.	41.78	1.0	0.0000	0.0000	0.0312	9.752	3.423
3.459	"	"	"	2.0	"	"	0.0519	9.993	3.521
3.520	"	"	"	3.0	"	"	0.0712	10.003	3.536
3.537	"	"	"	5.7	"	"	0.1067	9.990	3.555
3.563	"	"	"	7.0	"	"	0.1386	9.977	3.571
3.588	"	"	"	9.0	"	"	0.1674	9.966	3.586
3.612	"	"	"	12.0	"	"	0.2055	9.950	3.606
3.631	"	"	"	16.0	"	"	0.2482	9.932	3.627
3.645	"	"	"	20.0	"	"	0.2833	9.917	3.645
3.676	"	"	"	25.0	"	"	0.3189	9.902	3.663
3.689	"	"	"	35.0	"	"	0.3698	9.880	3.688
3.707	"	"	"	45.0	"	"	0.4023	9.865	3.704
3.731	"	"	"	60.0	"	"	0.4309	9.852	3.718
3.735	"	"	"	86.0	"	"	0.4522	9.842	3.729
3.759	"	"	"	100.0	"	"	0.4570	9.840	3.731
3.790	"	"	"	122.0	"	"	0.4606	9.838	3.733
3.751	"	"	"	123.0	"	"	0.4607	9.838	3.733
	*	*	*	*	*	*	*	*	
3.626	4015.	690.	29.67	1.0	0.4607	9.838	0.4608	9.529	3.625
3.616	"	"	"	2.0	"	"	0.4609	9.487	3.610
3.602	"	"	"	3.0	"	"	0.4609	9.482	3.608
3.606	"	"	"	4.0	"	"	0.4610	9.481	3.608
3.606	"	"	"	5.0	"	"	0.4611	9.481	3.608
3.640	"	"	"	6.0	"	"	0.4611	9.481	3.608
3.599	"	"	"	10.0	"	"	0.4614	9.481	3.608
3.585	"	"	"	16.0	"	"	0.4617	9.480	3.609
3.589	"	"	"	17.0	"	"	0.4617	9.480	3.609
	*	*	*	*	*	*	*	*	
3.473	3753.	945.	20.26	1.0	0.4617	9.481	0.4617	9.109	3.479
3.464	"	"	"	2.0	"	"	0.4618	9.035	3.453
3.443	"	"	"	3.0	"	"	0.4613	9.021	3.448
3.456	"	"	"	4.0	"	"	0.4613	9.013	3.447
3.427	"	"	"	5.0	"	"	0.4619	9.017	3.447

Table 1b (continued)

q ($cpm \cdot mg^{-1}$)	W (mg)	V ($m\ell$)	c_o ($cpm \cdot \mu\ell^{-1}$)	t (min)	$\widehat{q}_{1IN}$ ($cpm \cdot mg^{-1}$)	$\widehat{q}_{2IN}$ ($cpm \cdot mg^{-1}$)	$\widehat{q}_1$ ($cpm \cdot mg^{-1}$)	$\widehat{q}_2$ ($cpm \cdot mg^{-1}$)	$\widehat{q}$ ($cpm \cdot mg^{-1}$)
3.430	3753.	945.	20.26	6.0	0.4617	9.481	0.4619	9.017	3.447
3.445	"	"	"	10.0	"	"	0.4620	9.017	3.447
3.415	"	"	"	16.0	"	"	0.4621	9.017	3.447
3.418	"	"	"	17.0	"	"	0.4621	9.017	3.447
	*	*	*	*	*	*	*	*	
3.331	3574.	1300.	14.21	1.0	0.4622	9.017	0.4622	8.634	3.314
3.282	"	"	"	2.0	"	"	0.4622	8.532	3.278
3.319	"	"	"	3.0	"	"	0.4622	8.505	3.269
3.319	"	"	"	4.0	"	"	0.4622	8.499	3.266
3.291	"	"	"	6.0	"	"	0.4622	8.497	3.266
3.267	"	"	"	10.0	"	"	0.4623	8.496	3.266
3.260	"	"	"	20.0	"	"	0.4624	8.496	3.266
3.267	"	"	"	30.0	"	"	0.4625	8.496	3.266
3.242	"	"	"	43.0	"	"	0.4626	8.496	3.266
3.245	"	"	"	80.0	"	"	0.4628	8.496	3.266
3.232	"	"	"	140.0	"	"	0.4630	8.496	3.266
3.217	"	"	"	141.0	"	"	0.4630	8.496	3.266

Table 2a - IE-8 Ca^{45}

q $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$	W (mg)	V (ml)	c_o $(\mathrm{cpm}\cdot\mu\mathrm{l}^{-1})$	t (min)	$\hat{q}_{1IN}$ $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$	$\hat{q}_{2IN}$ $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$	$\hat{q}_1$ $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$	$\hat{q}_2$ $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$	$\hat{q}$ $(\mathrm{cpm}\cdot\mathrm{mg}^{-1})$
2.186	4864.	775.	25.48	0.5	0.000	0.000	0.198	5.401	2.170
2.300	"	"	"	1.1	"	"	0.402	5.617	2.379
2.509	"	"	"	2.3	"	"	0.737	5.349	2.485
2.652	"	"	"	4.1	"	"	1.119	5.031	2.602
2.765	"	"	"	6.2	"	"	1.455	4.747	2.703
2.810	"	"	"	9.0	"	"	1.752	4.492	2.791
2.821	"	"	"	12.0	"	"	1.969	4.304	2.854
2.895	"	"	"	16.0	"	"	2.161	4.137	2.910
2.898	"	"	"	20.0	"	"	2.283	4.029	2.945
2.916	"	"	"	25.0	"	"	2.380	3.944	2.973
2.956	"	"	"	30.3	"	"	2.440	3.891	2.990
2.989	"	"	"	36.5	"	"	2.482	3.854	3.002
2.985	"	"	"	42.3	"	"	2.505	3.834	3.008
2.980	"	"	"	49.0	"	"	2.519	3.821	3.013
2.997	"	"	"	56.0	"	"	2.527	3.814	3.015
3.025	"	"	"	65.8	"	"	2.532	3.809	3.016
2.977	"	"	"	72.8	"	"	2.534	3.808	3.017
3.010	"	"	"	81.0	"	"	2.535	3.807	3.017
3.050	"	"	"	90.3	"	"	2.536	3.807	3.017
3.009	"	"	"	100.0	"	"	2.536	3.806	3.017
3.009	"	"	"	111.0	"	"	2.536	3.806	3.017
3.045	"	"	"	144.0	"	"	2.536	3.806	3.017
3.061	"	"	"	169.0	"	"	2.536	3.806	3.017
3.075	"	"	"	196.0	"	"	2.536	3.806	3.017
3.089	"	"	"	225.0	"	"	2.536	3.806	3.017
	*	*	*	*	*	*	*	*	
2.803	4155.	1062.	15.33	1.0	2.536	3.806	2.536	3.099	2.749
2.787	"	"	"	4.0	"	"	2.536	3.097	2.749
2.769	"	"	"	9.0	"	"	2.536	3.097	2.749
2.729	"	"	"	16.0	"	"	2.536	3.097	2.749
2.750	"	"	"	25.0	"	"	2.536	3.097	2.749
2.731	"	"	"	36.0	"	"	2.536	3.097	2.749
2.750	"	"	"	49.0	"	"	2.536	3.097	2.749
2.757	"	"	"	57.0	"	"	2.536	3.097	2.749

Table 2b - IE-8 P^{32}

q (cpm. mg⁻¹)	W (mg)	V (ml)	c_o (cpm. μl⁻¹)	t (min)	$\hat{q}_{1IN}$ (cpm. mg⁻¹)	$\hat{q}_{2IN}$ (cpm. mg⁻¹)	$\hat{q}_1$ (cpm. mg⁻¹)	$\hat{q}_2$ (cpm. mg⁻¹)	$\hat{q}$ (cpm. mg⁻¹)
0.685	4864.	775.	12.61	0.5	0.0000	0.000	0.0353	2.091	0.678
0.738	"	"	"	1.1	"	"	0.0760	2.347	0.736
0.832	"	"	"	2.3	"	"	0.1475	2.305	0.822
0.887	"	"	"	4.1	"	"	0.2380	2.235	0.863
0.923	"	"	"	6.2	"	"	0.3275	2.165	0.902
0.952	"	"	"	9.0	"	"	0.4161	2.096	0.941
1.001	"	"	"	12.0	"	"	0.4882	2.039	0.973
1.003	"	"	"	16.0	"	"	0.5587	1.983	1.004
1.007	"	"	"	20.0	"	"	0.6088	1.944	1.006
1.030	"	"	"	25.0	"	"	0.6523	1.909	1.045
1.036	"	"	"	30.3	"	"	0.6826	1.885	1.059
1.055	"	"	"	36.5	"	"	0.7060	1.866	1.069
1.042	"	"	"	42.3	"	"	0.7200	1.855	1.075
1.059	"	"	"	49.0	"	"	0.7303	1.847	1.079
1.057	"	"	"	56.0	"	"	0.7367	1.842	1.082
1.086	"	"	"	65.8	"	"	0.7416	1.838	1.085
1.068	"	"	"	72.8	"	"	0.7435	1.836	1.085
1.076	"	"	"	81.0	"	"	0.7448	1.835	1.086
1.099	"	"	"	90.3	"	"	0.7456	1.835	1.086
1.085	"	"	"	100.0	"	"	0.7460	1.834	1.086
1.099	"	"	"	111.0	"	"	0.7462	1.834	1.087
1.100	"	"	"	144.0	"	"	0.7464	1.834	1.087
1.111	"	"	"	169.0	"	"	0.7464	1.834	1.087
1.117	"	"	"	196.0	"	"	0.7464	1.834	1.087
1.121	"	"	"	225.0	"	"	0.7464	1.834	1.087
	*	*	*	*	*	*	*	*	
0.983	4155.	1062.	7.86	1.0	0.7464	1.334	0.7464	1.370	0.941
0.953	"	"	"	4.0	"	"	0.7464	1.364	0.940
0.953	"	"	"	9.0	"	"	0.7464	1.364	0.940
0.923	"	"	"	16.0	"	"	0.7464	1.364	0.940
0.931	"	"	"	25.0	"	"	0.7464	1.364	0.940
0.929	"	"	"	36.0	"	"	0.7464	1.364	0.940
0.912	"	"	"	49.0	"	"	0.7464	1.364	0.940
0.922	"	"	"	57.0	"	"	0.7464	1.364	0.940

Table 3

Expt. Designation	q_{01} (cpm·mg^{-1})	k_{11} (μℓ·cpm^{-1}·min^{-1})	θ	q_{02} (cpm·mg^{-1})	k_{12} (μℓ·cpm^{-1}·min^{-1})	k_{22} (min^{-1})
IE-13						
Ca	1.981	0.02666	0.2823	22.38	0.1269	0.3888
P	0.4630	0.003729	0.3489	11.30	0.1457	0.2425
IE- 8						
Ca	2.536	0.01395	0.3790	22.34	0.09408	3.079
P	0.7464	0.01245	0.3128	13.10	0.05805	2.981
IE-14						
Ca	3.375	0.01441	0.4567	16.91	0.1174	0.2356
P	1.219	0.007728	0.3945	13.85	0.1424	0.3483
IE-15						
Ca	2.733	0.01236	0.3334	40.67	0.1101	1.857
P	1.257	0.006377	0.2914	23.43	0.0670	1.572
IE-11						
Ca	11.22	0.04326	0.4328	22.32	0.1313	0.8068
P	1.169	0.03311	0.2439	19.69	0.3533	0.5658
IE-10						
Ca	1.162	0.6322	0.5504	9.061	0.1129	0.1426
P	0.5964	1.101	0.4417	7.958	0.03754	0.2520

Table 4

				Solution Ratio	Surface Ratio (see Text)
Expt. Designation	pH	[Ca] ($M \cdot \ell^{-1}$)	[PO_4] ($M \cdot \ell^{-1}$)	[Ca] /[PO_4]	R
IE-13	5.640	7.469×10^{-4}	14.39×10^{-4}	0.519	1.60
IE- 8	5.766	4.190 "	7.980 "	0.525	1.53
IE-14	5.817	3.493 "	6.214 "	0.563	1.41
IE-15	6.409	1.487 "	2.144 "	0.694	1.99
IE-11	6.713	0.795 "	0.954 "	0.833	2.01
IE-10	6.919	0.734 "	0.667 "	1.100	1.42

CAPTIONS FOR FIGURES

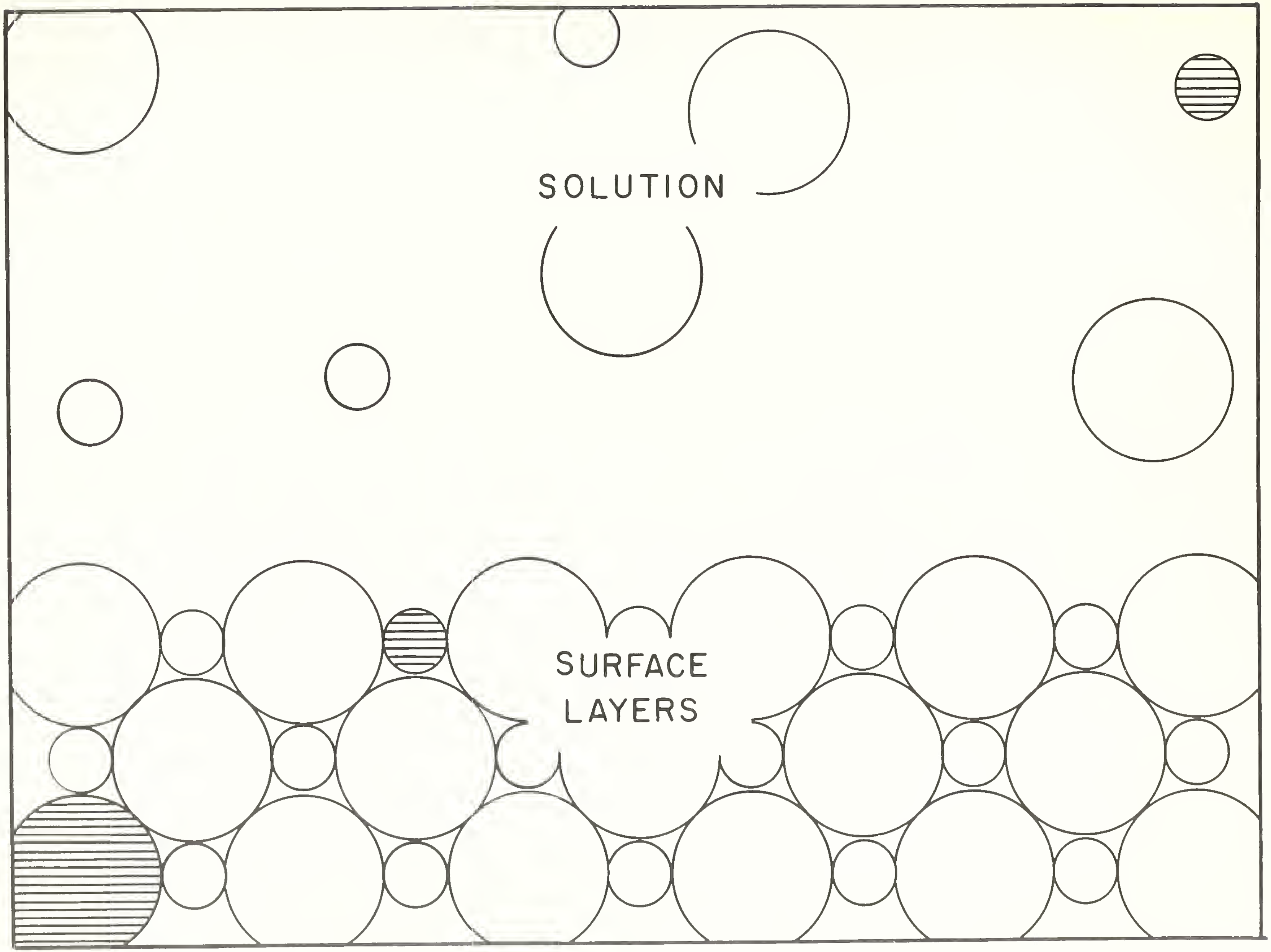
Fig. 1. Simplified Representation of the Solution-Solid Interface showing **Non-radioactive Ions** (open circles) and Tagged Ions (shaded circles) of Calcium and Phosphate.

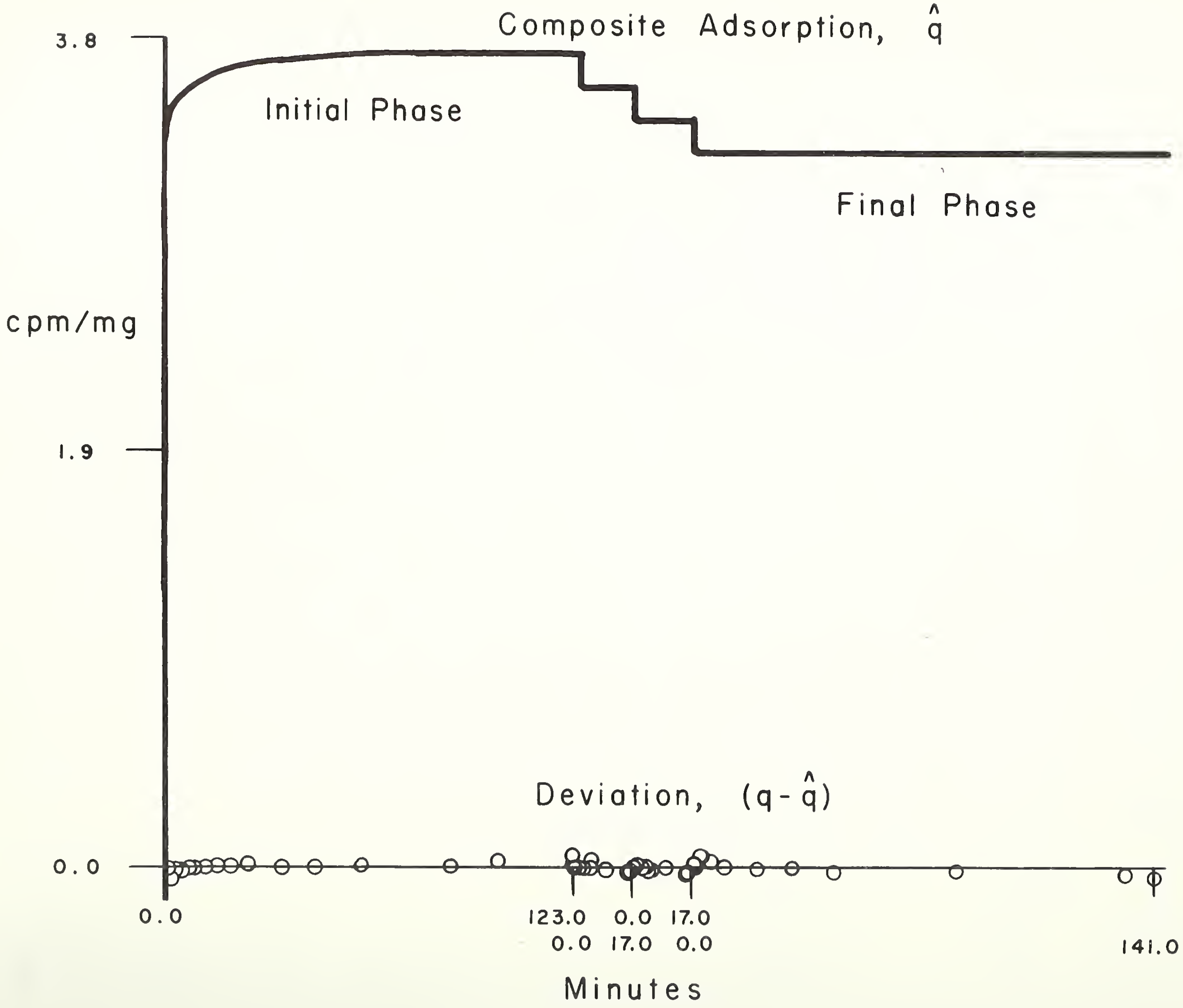
Fig. 2. Computed Overall Adsorption Plotted against Time for P^{32}-Phosphate in Expt. IE-13 showing Three Dilution Desorption Steps. The Agreement between Values Computed and Measured at each Sampling Time is shown at the Bottom.

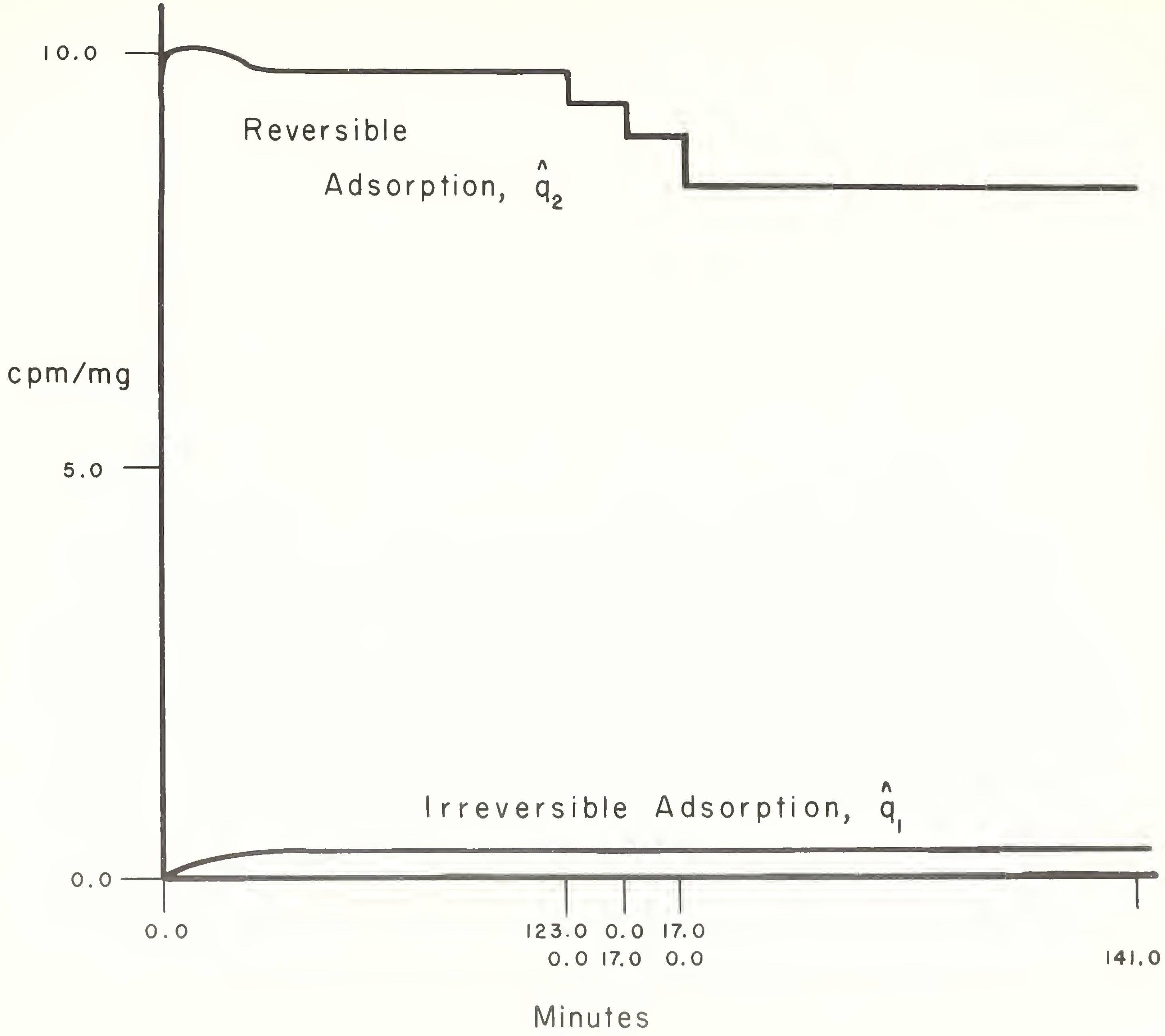
Fig. 3. Computed Reversible and Irreversible Adsorption Processes vs. Time for the Same Experiment whose Composite Adsorption is Depicted in Fig. 2.

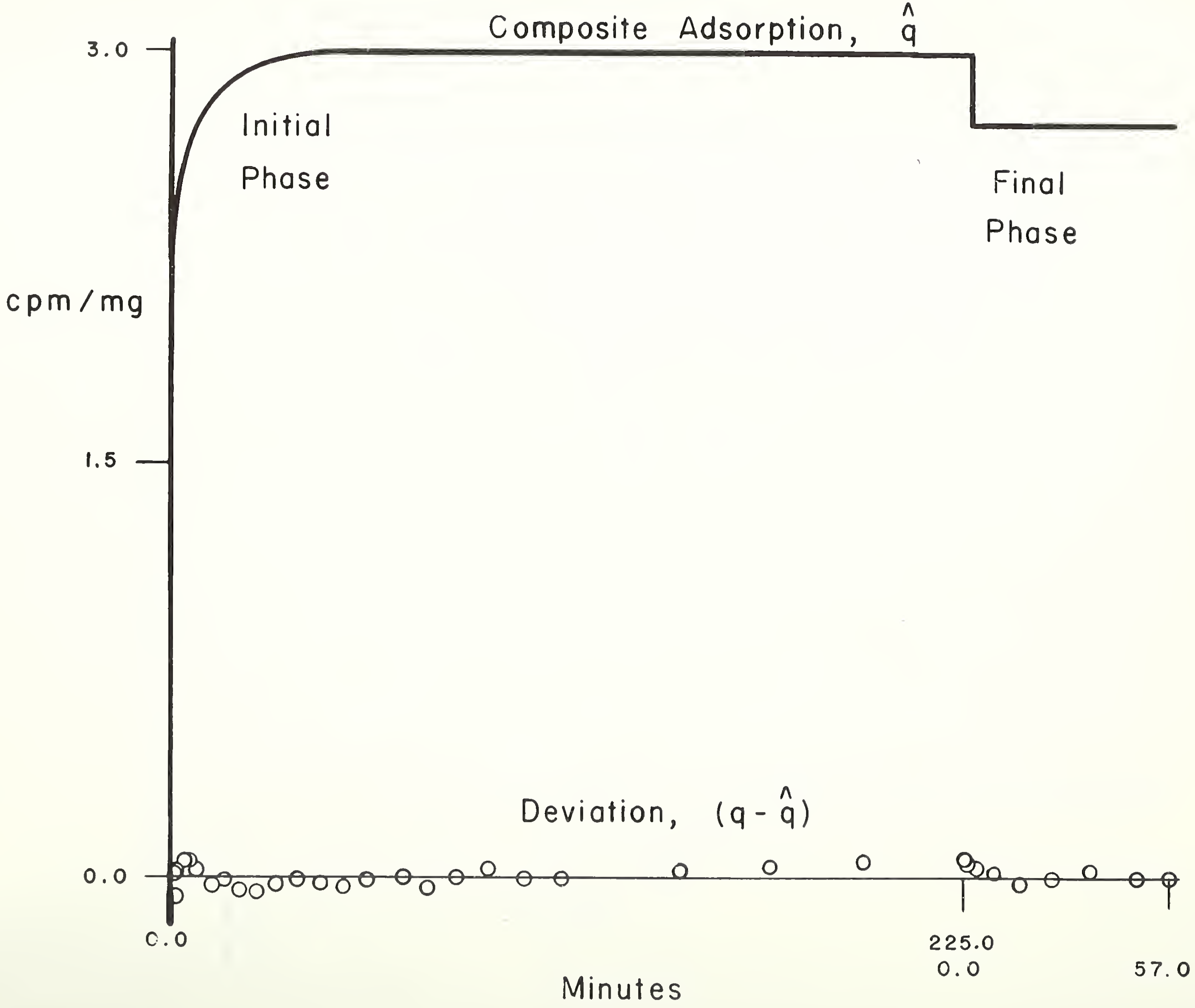
Fig. 4. Computed Overall Adsorption Plotted against Time for Ca^{45}-Calcium in Expt. IE-8 showing one Dilution Desorption Step. The Agreement between Values Computed and Measured at each Sampling Time is Shown at the Bottom.

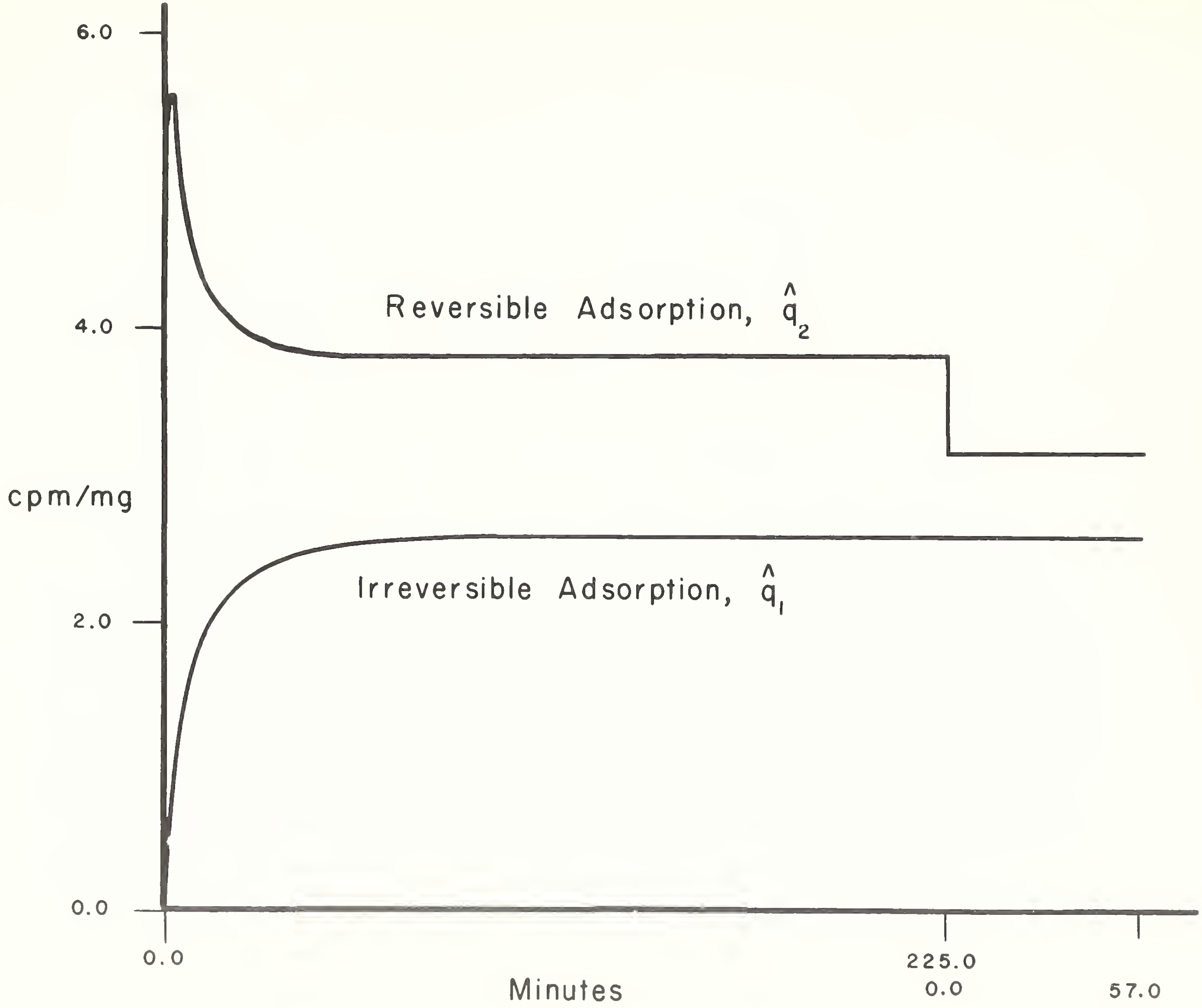
Fig. 5. Computed Reversible and Irreversible Adsorption Processes vs. Time for the Same Experiment whose Composite Adsorption is Depicted in Fig. 4.


SOLUTION
SURFACE
LAYERS


Composite Adsorption, $\hat{q}$
Initial Phase
Final Phase
3.8
cpm/mg
1.9
0.0
Deviation, $(q-\hat{q})$
0.0
123.0
0.0
0.0
17.0
17.0
0.0
141.0
Minutes


10.0
5.0
0.0
cpm/mg
Reversible
Adsorption, $\hat{q}_2$
Irreversible Adsorption, $\hat{q}_1$
0.0
123.0 0.0 17.0
0.0 17.0 0.0
141.0
Minutes


Composite Adsorption, $\hat{q}$
3.0
1.5
0.0
cpm/mg
Initial
Phase
Final
Phase
Deviation, $(q - \hat{q})$
0.0
225.0
0.0
57.0
Minutes


6.0
4.0
2.0
0.0
cpm/mg
Reversible Adsorption, $\hat{q}_2$
Irreversible Adsorption, $\hat{q}_1$
0.0
225.0
0.0
57.0
Minutes

DEPARTMENT OF COMMERCE ★ NATIONAL BUREAU OF STANDARDS ★