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Statistical Thermodynamics and Adsorption

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The proper correlation of thermodynamic quantities derived from experimental gas-solid adsorption systems with those derived from statistical mechanical models is discussed; the usual method of making the correlation is found to be unsatisfactory, and a new method is proposed.

The considerations of this paper apply to systems involving the physical adsorption of gases on solids.

In some treatments of the thermodynamics of gas-solid adsorption[1,2] the change of pertinent bulk (not merely surface) properties of the solid component with amount adsorbed is an important feature of the development. It is not customary, however, in the usual statistical mechanical treatments of gas-solid adsorption explicitly to allow for changes in the bulk properties of the solid component.[3] Given that the macro-thermodynamic considerations of references 1 and 2 are correct, should not the usual statistical mechanical procedure be mended so as to allow for, at least implicitly, changes in the bulk properties of the solid component?

A Special Case

In order to show clearly the issues involved, let us first examine the special case of an ideal localized monolayer.[4] Consider an enclosure containing a solid component and a gas component, with N_A of the gas molecules adsorbed on the surface of the solid. For purposes of discussion attribute to the solid surface a site structure and consider the ideal localized monolayer adsorption of the N_A molecules on N_S sites.

Represent the (Helmholtz) free energy of the solid component *in vacuo* as

$$F^{0}_{sol(id)} = F^{0}_{b(ulk)} + F^{0}_{sur(face)}, \tag{1}$$

and with N_A molecules adsorbed on its surface as

$$F_{sol} = F_b + F_{sur}. \tag{2}$$

We can then write for the total free energy of the enclosure

$$F_{tot(al)} = F_b + F_{gas} + F_{mix}, \tag{3}$$

where F_{gas} is the free energy contribution of the unadsorbed gas molecules and F_{mix} is the contribution of the "mixture" of N_A adsorbed molecules and N_S sites. We can now define an excess free energy F_f by

$$F_f \equiv F_{tot} - F_{gas} - F^{0}_{sol} = F_{mix} - F^{0}_{sur} + F_b - F^{0}_{b}. \tag{4}$$

We find[2,3] that F_f is expressible as

$$F_f = \mu N_A - \phi A, \tag{5}$$

where $\mu \equiv (\partial F_f/\partial N_A)_{T,A}$ is the chemical potential of an adsorbed molecule, A is the surface area of the solid, and $\phi \equiv -(\partial F_f/\partial A)_{T,N_A}$ is commonly called the spreading pressure.

Now the statistical mechanical free energy F of the assembly of N_A molecules adsorbed on N_S sites in just[3]

$$F = -kT \ln Q_{ads}, \tag{6}$$

$$Q_{ads} = \frac{N_S!}{(N_S - N_A)!\,N_A!} e^{N_A \chi/kT} j^S(T)^{N_A c}, \tag{7}$$

where Q_{ads} is the partition function for the adsorbed monolayer, $j^S(T)$ is the partition function for the internal degrees of freedom of an adsorbed molecule (including vibrations relative to its mean position on a site), and $(\pm)N_A\chi$ may be viewed either $(+)$ as a minimum energy required to desorb the N_A molecules and carry them to the gas state at infinite separation or $(-)$ as the potential energy of the N_A asdorbed molecules relative to the gas state at infinite separation.[3,5]

The very crux of the matter is that investigators dealing with the statistical mechanics of gas-solid adsorption customarily assert that

$$F^{(1)} \equiv F_{mix} - F^{0}_{sur} = F_f, \tag{8}$$

$$F_b - F^{0}_{b} = 0, \tag{9}$$

$$\phi A \equiv F^{0}_{sol} - F_{sol} = F^{0}_{sur} - F_{sur}; \tag{10}$$

and consequently also that

$$(\partial F^{(1)}/\partial N_A)_{T,A} = \mu, \tag{11}$$

$$-(\partial F^{(1)}/\partial A)_{T,N_A} = \phi. \tag{12}$$

(The index on F merely shows that this is the first of several assertions about the relationship of F to F_f.)

At this point a brief digression concerning the structure of Eq. (5) will prove instructive. Although Eq. (5) is a thermodynamic identity, it is nevertheless possible to produce equations of the same general form, also identities, but subject to different interpretation. For any equation of the form

$$F_*^{(k)} \equiv F_f + A f_*^{(k)}(T, N_A/A), \tag{13}$$

where $f_*^{(k)}(T, N_A/A)$ is an arbitrary function of the indicated arguments, it follows that

$$F_*^{(k)} = N_A(\partial F_*^{(k)}/\partial N_A)_{T,A} + A(\partial F_*^{(k)}/\partial A)_{T,N_A} \tag{14}$$

holds identically. Since Eq. (14) has the same general form as Eq. (5), we may, if we wish, write it as

$$F_*^{(k)} = \mu^{(k)} N_A - \phi^{(k)} A, \tag{15}$$

with $\mu^{(k)} \equiv (\partial F_*^{(k)}/\partial N_A)_{T,A}$ and $\phi^{(k)} \equiv -(\partial F_*^{(k)}/\partial A)_{T,N_A}$. Equations (13)—(15) point up a possible pitfall in the sort of work that we are discussing: we might find ourselves in possession of a free energy such as $F_*^{(k)}$

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[1] T. L. Hill, *J. Chem. Phys.*, **18**, 246 (1950).

[2] R. J. Tykodi, *ibid.*, **22**, 1647 (1954).

[3] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics" Cambridge University Press, Cambridge, (1939) Chap. X, for example.

[4] *ibid.*, pp. 426 and 427.

[5] T. L. Hill, *J. Chem. Phys.*, **17**, 762 (1949).

and, having determined that the functional relationship (14) holds, we might be tempted to conclude that we are dealing with Eq. (5)—clearly such need not be the case, and in general $\mu^{(k)} \neq \mu$ and $\phi^{(k)} \neq \phi$.

Returning now to the case of the ideal localized monolayer, note that the assertions (8)—(10) are not simple deductions from Eqs. (4), (6), and (7). In order to investigate the matter more closely, let us express F as $F=E-TS$ and $F^{(i)}$ as $F^{(i)}=E^{(i)}-TS^{(i)}$; then it follows from Eq. (6) that

$$F = -N_A\chi + E_{int} - TS_{config} - TS_{int}, \tag{16}$$

where S_{config} is the configurational entropy deducible from the factorial part of Q_{ads} and E_{int} and S_{int} are, respectively, those parts of E and S deducible from the $j^S(T)^{N_A}$ portion of Q_{ads}.

Suppose first that $-N_A\chi$ represents a change in energy for the process

N_A gas molecules at infinite separation + bare solid component → N_A molecules adsorbed on the solid component;

i.e., suppose that

$$-N_A\chi = E_{mix} + E_b - E^0_{sol} - E^0_{gas}, \tag{17}$$

where $E^0{}_{gas}$ is the energy (potential energy plus that due to internal degrees of freedom) of N_A gas molecules at infinite separation. In addition let the zero of (potential) energy be chosen in such a way that the potential energy of N_A gas molecules at infinite separation is zero. Under the assumptions operative in the case of ideal localized monolayer adsorption[3,5] it then follows that $E^0{}_{gas}=E_{int}$.

From Eqs. (16) and (17) we see that

$$F^{(2)} = E_{mix} + E_b - E^0_{sol} - TS_{config} - TS_{int}. \tag{18}$$

Since $S_{mix} \equiv S_{config} + S_{int} + S_{sur}$, we may express Eq. (18) as

$$F^{(2)} = F_{mix} + TS_{sur} - E^0_{sol} + E_b; \tag{19}$$

and, with some further manipulation, we may reduce it to the form

$$F^{(2)} = F_{mix} - F^0_{sur} + F_b - F^0_b + T(S_{sol} - S^0_{sol}). \tag{20}$$

Referring back to Eq. (4) we see that under the present assumptions

$$F^{(2)} = F_f + T(S_{sol} - S^0_{sol}); \tag{21}$$

i.e., the statistical mechanical free energy $F^{(2)}$ fails to take into account possible changes in the entropy content of the solid component with varying amounts adsorbed.

Suppose next, in Eq. (16), that a different interpretation is given to the term $-N_A\chi$. Let $-N_A\chi$ now be considered as representing a form of (potential) energy associated (merely by convention) with the adsorbed molecules alone; *i.e.* suppose that

$$-N_A\chi = E_{mix} - E_{int} - E_{sur}. \tag{22}$$

Substituting from Eq. (22) into Eq. (16), we obtain

$$\begin{aligned} F^{(3)} &= E_{mix} - E_{sur} - TS_{config} - TS_{int} \\ &= F_{mix} - F_{sur}. \end{aligned} \tag{23}$$

Referring back to Eq. (4), we note that Eq. (23) can be written as

$$F^{(3)} = F_f - (F_{sol} - F^0_{sol}) = F_f + \phi A. \tag{24}$$

Thus the statistical mechanical free energy $F^{(3)}$ fails to take into account possible changes in the free energy content of the solid component with varying amounts adsorbed.

(The preceding material relating to $F^{(2)}$ and $F^{(3)}$, shows that *contrary to expectation* $F^{(i)} \neq F_f$ $(i=2,3)$ and that the reason for $F^{(i)} \neq F_f$ is the indicated one in each case.)

Since we usually assume the $\phi=\phi(T,N_A/A)$, we see that Eq. (24) is of the general form of Eq. (13); consequently the relation

$$\begin{aligned} F^{(3)} &= N_A(\partial F^{(3)}/\partial N_A)_{T,A} + A(\partial F^{(3)}/\partial A)_{T,N_A} \\ &= \mu^{(3)}N_A - \phi^{(3)}A, \end{aligned} \tag{25}$$

where $\mu^{(3)} \equiv (\partial F^{(3)}/\partial N_A)_{T,A}$ and $\phi^{(3)} \equiv -(\partial F^{(3)}/\partial A)_{T,N_A}$, holds identically.

A relation similar to (25) would hold in the case of $F^{(2)}$ also, provided we could show that $T(S_{sol}-S^0{}_{sol})=Af_*{}^{(2)}(T,N_A/A)$.

General Considerations

The foregoing considerations pose a serious problem for the comparison of statistical mechanical models with experimental adsorption systems. In the experimental case we deal with quantities such as μ, ϕ, F_f, S_f, *etc.* and with relations between such quantities —hereafter called *proper quantities* and *proper relations*—; whereas in the statistical mechanical case we produce quantities such as $\mu^{(i)}$, $\phi^{(i)}$, $F^{(i)}$, $S^{(i)}$, *etc.* and relations between such quantities—hereafter called *eikonic quantities* and *eikonic relations.* There would be no problem if we found that the assertions of Eqs. (8)—(12) hold true; however, in view of the considerations advanced in references 1 and 2 and in view of experimental results such as those of Yates[6,7] (*e.g.*), the assertions of Eqs. (8)—(12) appear to be untenable.

It appears then that the usual statistical mechanical treatment of the physical adsorption of gases on solids (whether couched in terms of ordinary or grand partition functions) always produces eikonic quantities and relations rather than proper ones, the exact nature of the eikonic quantities depending upon how the various parts of $E^{(i)}$ are interpreted. The notation $F^{(i)}$ in this section is used to denote the free energy derived from *any statistical mechanical model whatsoever* in which —speaking somewhat loosely— the "energy of the adsorbed molecules" is interpreted in the same manner as the term $-N_A\chi$ was interpreted in the discussion of the ideal localized monolayer. The conventional statistical mechanical treatments of gas-solid adsorption, therefore, fail to consider either (a) changes in the entropy content or (b) changes in the free energy content of the solid component with varying amounts adsorbed; and so, unwittingly, in the past, we have been led to compare theoretical eikonic quantities with experimental proper ones —the correct procedure is to make a comparison either on an eikonic-eikonic or on a proper-proper basis *via* suitable equations of transformation.

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[6] D. J. C. Yates, *Proc. Roy. Soc., Ser. A*, **224**, 526 (1954).

[7] D. J. C. Yates, *J. Phys. Chem.*, **60**, 543 (1956).

It appears that the statistical mechanical work to date has produced statistical free energies $F^{(3)}$ and associated eikonic quantities and variables, in that most treatments of gas-solid adsorption take the quantity analogous to $-N_A\chi$ as being the potential energy of interaction of the adsorbed molecules with the solid component, this potential energy of interaction being conventionally treated as a property of the assembly of adsorbed molecules. As we saw previously, such a treatment leads to free energies of the type $F^{(3)}$.

In the remainder of this paper we will therefore limit our attention to $F^{(3)}$ and related eikonic quantities, with no further mention of $F^{(2)}$.

The comparison of statistical mechanical models with experimental gas-solid adsorption systems may proceed along either of two different lines: (a) we may transform the proper quantities and relations derived from the experimental data to appropriate eikonic quantities and relations by means of suitable equations of transformation and so compare them to the eikonic quantities and relations generated from $F^{(3)}$ by standard methods; or (b) we may attempt to win from the statistical mechanical model proper quantities and relations and compare these directly with the proper quantities and relations derived from experiment. Procedure (a) is a relatively easy and mechanical procedure; whereas procedure (b) can be exceedingly difficult to put into practice.

At this point let us drop the uncomfortable formalism (bulk properties, surface properties, *etc.*) thus far developed, and carry on the remainder of the discussion in terms of the molar macroscopic thermodynamic formalism established in reference 2.

For purposes of orientation note that the Gibbs adsorption is written as

$$\mu_f = -\boldsymbol{R}T\int_0^P X d\ln P, \tag{26}$$

where μ_f is the change in the chemical potential of the solid component due to the adsorption process and $X\equiv\Gamma/n_s$ is the adsorption excess (in terms of moles of gas component) per mole of solid. Integral molar excess properties are indicated by a superior bar and differential molar excess properties by a superscript partial differential operator; thus

$$Z_f^{\partial} \equiv (\partial Z_f/\partial\Gamma)_{T,n_s} = \bar{Z}_f + X(\partial\bar{Z}_f/\partial X)_T. \tag{27}$$

The change in a molar property for an adsorption process

$$i(\text{gas}) \rightarrow i(\text{adsorbed})$$

is written as $\Delta\bar{Z}\equiv\bar{Z}_f-\bar{Z}_g$; thus, the integral molar heat of adsorption $Q\equiv\bar{H}_f-\bar{H}_g$, according to this convention, is normally a *negative* quantity. For convenience functions appropriate to processes at constant μ_f —*isomunal* processes— are defined; in reference 2, script capital letters were used to designate these special functions; in this paper they are designated by means of square brackets, which thus correspond to the script capital symbols in reference 2. As an example, note that the ordinary integral molar heat of adsorption is related to the isomunal integral molar heat of adsorption by the equation

$$\Delta[H] \equiv \Delta\bar{H} - (\mu_f/X). \tag{28}$$

Eikonic Relations

In terms of the present notation[8] we would write relation (13) as

$$F_*^{(k)} \equiv F_f + n_s f_*^{(k)}(T,X); \tag{29}$$

correspondingly, the identity (14) would appear as

$$F_*^{(k)} \equiv \Gamma(\partial F_*^{(k)}/\partial\Gamma)_{T,n_s} + n_s(\partial F_*^{(k)}/\partial n_s)_{T,\Gamma} \tag{30}$$

and the form (15) as

$$F_*^{(k)} = \Gamma\mu_g^{(k)} + n_s\mu_f^{(k)}, \tag{31}$$

with $\mu_g^{(k)}\equiv(\partial F_*^{(k)}/\partial\Gamma)_{T,n_s}$ and $\mu_f^{(k)}\equiv(\partial F_*^{(k)}/\partial n_s)_{T,\Gamma}$.

For convenience let us write $\mu_g^{(k)}$ as

$$\mu_g^{(k)} = \mu^{\dagger}(T) + \boldsymbol{R}T\ln P^{(k)} \tag{32}$$

and refer to $P^{(k)}$ as the eikonic pressure; we may call a relation such as $P^{(k)}=P^{(k)}(T,X)$ an eikonic isotherm relation. Of course eikonic quantities and variables are merely mathematical constructs and are related to the proper experimental quantities and variables by suitable equations of transformation.

The proper equilibrium condition for gas-solid adsorption systems is[2]

$$\mu_g = G_f^{\partial} \equiv [G_f]. \tag{33}$$

The corresponding eikonic relations are

$$F^{(3)} = G_f - n_s\mu_f, \tag{34}$$

$$\mu_g^{(3)} = (G_f - n_s\mu_f)^{\partial}. \tag{35}$$

The following transformation relations hold between proper variables and the corresponding eikonic variables:

$$X^{(3)} = X, \tag{36}$$

$$T^{(3)} = T, \tag{37}$$

$$\mu_g^{(3)} = \mu_g - (\partial\mu_f/\partial X)_T, \tag{38}$$

$$\mu_f^{(3)} = X(\partial\mu_f/\partial X)_T. \tag{39}$$

Equations (26), (32), (38), and the perfect gas assumption lead to the relations

$$\ln(P^{(3)}/P) = (\partial\ln P/\partial\ln X)_T, \tag{40}$$

$$q_{st}^{(3)} = q_{st} - (\partial\mu_f/\partial X)_T + T(\partial^2\mu_f/\partial T\partial X), \tag{41}$$

$$Q^{(3)} = Q - (\mu_f/X) + TX^{-1}(\partial\mu_f/\partial T)_X = q_{st}, \tag{42}$$

where q_{st} is the proper isosteric heat of adsorption, Q is the proper integral molar heat of adsorption, and

$$q_{st}^{(3)} = -\boldsymbol{R}T^2(\partial\ln P^{(3)}/\partial T)_X,$$

$$Q^{(3)} = X^{-1}\int_0^X q_{st}^{(3)}\,\mathrm{d}X(\text{constant } T).$$

Let us here introduce molar eikonic integral and differential quantities which are related to the proper quantities of the adsorption system in the following way:

$$\bar{G}_f^{(3)} = [G_f], \tag{43}$$

$$\bar{H}_f^{(3)} = [H_f] + TX^{-1}(\partial\mu_f/\partial T)_X, \tag{44}$$

$$\bar{S}_f^{(3)} = \bar{S}_f + X^{-1}(\partial\mu_f/\partial T)_X, \tag{45}$$

and

$$\{Z_f^{(3)}\}^{\partial} \equiv (\partial Z_f^{(3)}/\partial\Gamma)_{T,n_s} = \bar{Z}_f^{(3)} + X(\partial\bar{Z}_f^{(3)}/\partial X)_T \tag{46}$$

for any extensive property Z. The additional relations

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[8] In passing, note that $E_f\equiv H_f$ and $F_f\equiv G_f$ because of the way in which the adsorption excesses are defined (see Ref. 2).

$$\bar{H}_g{}^{(3)} = \bar{H}_g, \tag{47}$$

$$\bar{S}_g{}^{(3)} = \bar{S}_g + T^{-1}(\partial\mu_f/\partial X)_T, \tag{48}$$

follow from Eq. (38) and the perfect gas assumption. Now a little calculation will show that

$$q_{st}{}^{(3)} = \{H_f{}^{(3)}\}^{\partial} - \bar{H}_g{}^{(3)}, \tag{49}$$

$$q_{st}{}^{(3)}/T = \{S_f{}^{(3)}\}^{\partial} - \bar{S}_g{}^{(3)}, \tag{50}$$

$$Q^{(3)} = \bar{H}_f{}^{(3)} - \bar{H}_g{}^{(3)}, \tag{51}$$

$$Q^{(3)}/T = \bar{S}_f{}^{(3)} - \bar{S}_g{}^{(3)} + (\mu_f{}^{(3)}/TX). \tag{52}$$

A consequence of Eqs. (36)—(39), (43)—(48), and the definitions

$$[H_f{}^{(3)}] \equiv \bar{H}_f{}^{(3)} - (\mu_f{}^{(3)}/X), \tag{53}$$

$$[G_f{}^{(3)}] \equiv [H_f{}^{(3)}] - T\bar{S}_f{}^{(3)}, \tag{54}$$

is that *all the thermodynamic identities of reference 2 remain valid when the proper quantities and variables in each equation are replaced by the corresponding eikonic quantities and variables.*

Isotherm Relations

Let us investigate some of the simpler relations between proper and eikonic isotherm equations, basing our considerations chiefly on Eq. (40). Consider the twin problems (a) Given the form of the proper isotherm deduce from it the eikonic isotherm and (b) Given the form of the eikonic isotherm deduce from it the proper isotherm.

From the proper isotherm relations

$$P = kX^{\nu}\ \text{(Freundlich)}, \tag{55}$$

$$bP = X/(X_m - X) = \theta/(1-\theta)\quad \text{(Langmuir)}, \tag{56}$$

with $\theta \equiv X/X_m$, we obtain by means of Eq. (40) the relations

$$P^{(3)} = Pe^{\nu} = k^{(3)}X^{\nu}, \tag{57}$$

$$bP^{(3)} = bP\exp\{1/(1-\theta)\} = \{\theta/(1-\theta)\}\exp\{1/(1-\theta)\}. \tag{58}$$

Thus Freundlich-type isotherms (of which Henry's law isotherms are a special case) remain formally invariant under the transformation; whereas Langmuir isotherms become changed somewhat in form.

The inverse case for the Langmuir isotherm is a good deal more peculiar. From the relation

$$bP^{(3)} = \theta/1 - \theta \tag{59}$$

and Eq. (40) it follows that

$$bP = \{\theta/(1-\theta)\}(1-\theta)^{1/\theta}\exp(-K/\theta), \tag{60}$$

where K is an arbitrary constant. The rather bizarre relation (60), which implies a finite pressure for $\theta=1$, is simply a consequence of the fact that $F^{(3)} \neq F_f$.

First Order Phase Changes

Statistical mechanical considerations[3)] indicate that first order phase changes should be possible in theoretical gas-solid adsorption systems. In some previous work[2,9)] it was argued that first order phase changes in experimental gas-solid adsorption systems are thermodynamically unlikely. We can reconcile the apparent discrepancy between the preceding two conclusions if we consider that the statistical mechanical deductions pertain to *eikonic* relations rather than to *proper* relations.

In experimental adsorption systems we assume that a first order phase change occurs when $(\partial X/\partial P)_T = \infty$ or, equivalently, when $(\partial P/\partial X)_T = 0$ or $(\partial \ln P/\partial X)_T = 0$. Now these statistical mechanical considerations[3)] merely imply that $(\partial \ln P^{(3)}/\partial X)_T = 0$ and not that $(\partial \ln P/\partial X)_T = 0$ (eikonic interpretation of statistical mechanical procedures).

We see from Eq. (40) that

$$\left(\frac{\partial \ln P^{(3)}}{\partial X}\right)_T = \frac{1}{X}\frac{\partial}{\partial X}\{X^2(\partial \ln P/\partial X)_T\}. \tag{61}$$

The condition $(\partial \ln P^{(3)}/\partial X)_T = 0$ then leads to the relation

$$\ln P = -L_m(T)X^{-1} + M_m(T), \tag{62}$$

where L_m and M_m are constants of integration and the subscript m allows for the possibility that the condition $(\partial \ln P^{(3)}/\partial X)_T = 0$ may be satisfied at several different points on the adsorption isotherm.

In the case of the eikonic interpretation of $F^{(3)}$ the condensation type phenomena predicted by theory will probably produce smooth, rolling bumps in the *proper* adsorption isotherm;[10,11)] in the regions where the theoretically predicted "phase changes" take place the proper isotherm relation will satisfy Eq. (62).

In statistical mechanical discussions of first order phase changes in gas-solid adsorption systems we may retain all those thermodynamic relations developed for such changes[2)] provided we understand that they deal in the statistical mechanical case with *eikonic* quantities and variables; *e.g.* during the "phase change" $\delta\mu_f{}^{(3)} = 0$ (and not $\delta\mu_f = 0$).

Eikonic Programming

The foregoing considerations indicate that in the construction of partition functions for various statistical mechanical models of gas-solid adsorption systems we must have clearly in mind the type of statistical free energy —Eq. (8), (21), or (24)— that we expect to generate. Whereas in the past free energies $F^{(3)}$ were produced by ignoring possible variations in the properties of the solid component with changing amounts adsorbed, we can make such a procedure a well-defined technical operation, an operation to which the name *eikonic programming* will be attached. Under the eikonic programming procedure we would concern ourselves only with the energetic behavior of the gas component, treating the solid component as merely the source of the requisite potential field, and we would *deliberately* ignore the changes in the properties of the solid concomitant with the adsorption process. We would then derive eikonic quantities and variables from the eikonic programming free energy $F^{(3)}$ by the usual methods, and we would either (a) convert such eikonic quantities and variables into proper ones by means of Eqs. (34), (36)—(39), (43)—(48), (53), and (54) (also see below) in order to compare them to the proper quantities and variables of experimental adsorption systems or (b)

[9)] R. J. Tykodi, *J. Phys. Chem.*, **59**, 383 (1955).

[10)] R. A. Beebe and D. M. Young, *ibid.*, **58**, 93 (1954).

[11)] J. H. Singleton and G. D. Halsey, Jr., *ibid.*, **58**, 1011 (1954).

convert the proper quantities and variables of experimental adsorption systems into eikonic ones by means of the appropriate equations of transformation and compare the experimental eikonic quantities to those derived from the statistical mechanical model.

Under an eikonic programming procedure the comparison of theory with experiment is relatively easy. From Eq. (34) and section 2 of reference 2 it follows that

$$F^{(3)} = \Gamma \mu_g; \tag{63}$$

so in order to establish the *proper* isotherm appropriate to the theoretical model we need merely set $F^{(3)}/\Gamma$ equal to the chemical potential in the gas phase. Of course if we wish, we may derive the *eikonic* isotherm from the relation $(\partial F^{(3)}/\partial \Gamma)_{T,n_s} = \mu_g{}^{(3)}$. *Another attractive feature of the eikonic programming procedure is that eikonic integral molar quantities are identical with proper differential molar quantities,*[12] *i.e.* $\bar{Z}_f{}^{(3)} \equiv Z_f^{\partial}$. *Thus in discussing the entropy or the heat capacity of the adsorbed molecules we should compare the appropriate integral molar (eikonic) properties of the theoretical model with the differential molar (proper) properties of experimental adsorption systems.*

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12) See Eqs. (43)—(45) and Ref. 2.