

## Statistical Mechanics of Adsorption. IX. Adsorption Thermodynamics and Solution Thermodynamics

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The article by Thorne Lay and Hiroo Kanamori is an excellent review of the energy released by the 1994 Chilean earthquake. The authors estimate that the total strain energy release was approximately five times as much energy as that of a 100-megaton nuclear bomb. I believe the authors underestimated the total strain energy release by a factor of about 3, or 10 times. The seismic energy release would increase the earthquake energy number by orders of magnitude. Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

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Written by Edgar McCarroll, 14 July 2012 19:59

## Statistical Mechanics of Adsorption. IX. Adsorption Thermodynamics and Solution Thermodynamics†

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This paper is a generalization of Part V of this series. We show here that the usual solution thermodynamics can be recast into an equivalent but alternative form which is more natural and useful in adsorption work. Relations between the two systems of thermodynamics are pointed out. The extension to the case of sorption from a mixture of gases is included.

### I. INTRODUCTION

IF we consider a list of sorption systems such as argon-graphite, hydrogen-tungsten, hydrogen-charcoal, hydrogen-palladium, benzene-rubber, water-sodium chloride, and water-sulfuric acid, it is clear that, from the point of view of pure thermodynamics, no really significant division of these systems into separate classes can be made, and therefore that the same thermodynamic treatment should apply to the entire list. This is a well-known point of view, and has been especially emphasized by Coolidge.<sup>1</sup> Thus, ordinary solution thermodynamics can quite correctly be applied, for example, to the phase argon-graphite (this phase being in equilibrium with argon vapor).

We are interested, however, not only in obtaining correct thermodynamic data but also in *understanding* the data. For this latter purpose, solution thermodynamics leaves something to be desired when applied to a system such as argon-graphite because the argon-graphite phase is treated *symmetrically* in the two components.<sup>2</sup> This is a perfectly natural arrangement for a solution of sugar in water or rubber in benzene, but is very unnatural for argon-graphite, where the two components obviously play completely different roles in the condensed phase (and in the vapor phase). We should therefore anticipate that an alternative but equivalent thermodynamic system which is properly *asymmetric* in the two components might be more directly useful in interpreting data relating to a large number of sorption systems. The above conclusion is confirmed by the fact that, as far as the author is aware, all statistical mechanical theories of physical and chemical adsorption which have been proposed up to the present time treat the condensed phase as a *one component* system of adsorbed molecules in a potential field presented by the adsorbent. The asymmetric thermodynamic system referred to above thus turns out to be the same system which is implicit in statistical mechanical theories.<sup>3</sup>

In paper V of this series<sup>4</sup> we have used this asymmetric point of view almost exclusively in a detailed discussion of the thermodynamics of adsorption of a single gas on an inert adsorbent (approximated in physical adsorption). In the present paper we now wish to give proper emphasis to the generality of the method (as applied, say, to any of the systems in the list above) (Section II), to the relations between solution thermodynamics and the alternative system (Section II), and to sorption from a mixture of gases<sup>4a</sup> (Section III).

### II. ONE-COMPONENT SORBATE<sup>5</sup>

Consider a two-component ("A" and "1") condensed phase in equilibrium with gaseous "1," "A" being non-volatile.<sup>6</sup> The condensed phase has energy  $E$ , entropy  $S$ , etc., and contains  $N_A$  and  $N_1$  molecules of the two types. We include only those cases in which  $E$  is completely determined by  $S$ ,  $V$ ,  $N_A$  and  $N_1$ . This requires no further comment if  $A$  is a liquid (e.g.,  $A$  = sulfuric acid, 1 = water) or a solid (e.g.,  $A$  = palladium, 1 = hydrogen) such that surface effects are negligible compared to bulk effects. However, if  $A$  is, for example, a finely divided solid with appreciable surface effects (the case of primary interest) it is to be understood that in all of the thermodynamic processes contemplated a change

*Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), Chapter X.

<sup>4</sup> T. L. Hill, *J. Chem. Phys.* **17**, 520 (1949); see also *J. Chem. Phys.* **17**, 507 (1949).

<sup>4a</sup> It is rather obvious that sorption from a liquid solution bears a considerable thermodynamic resemblance to sorption from a gas. We shall not discuss sorption from a solution here but we hope to at some other time.

<sup>5</sup> We use "sorption" as a general term to include adsorption and absorption. As in paper V, "sorbatе" refers to sorbed molecules and does *not* include gas molecules in equilibrium with sorbed molecules.

<sup>6</sup> There is no difficulty in extending the present paper to cases in which all components are volatile *provided* all significant surface properties (e.g., the "surface area" of a volatile finely divided solid) of the "sorber" (*one* component must be chosen as sorber) are independent of amount of sorber volatilization. In practice, except as an approximation, this probably means that the all-volatile case must be restricted to systems with *no* significant surface properties; that is, to solutions. But in this case adsorption thermodynamics (see reference 10) does not at present seem to have anything to recommend it.

Equations such as Eqs. (48) and (59) are unchanged in the all-volatile case. The determinants in equations such as Eqs. (46) and (58) have one more row and column.

† Presented at an American Chemical Society Meeting, Atlantic City, September 20, 1949.

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<sup>1</sup> A. S. Coolidge, *J. Am. Chem. Soc.* **48**, 1795 (1926).

<sup>2</sup> See, for example, Eq. (1).

<sup>3</sup> See, for example, R. H. Fowler and E. A. Guggenheim,

in  $N_A$ ,  $dN_A$ , refers to an addition of pure  $A$  in the same state of subdivision, etc., as the pure  $A$  used in preparing the original sample. Thus, in cases where the term "surface area" has meaning, the area is proportional to  $N_A$  and is not an additional independent variable.<sup>7</sup> The use of  $N_A$  in place of  $\mathcal{A}$  as an independent variable is the fundamental step allowing the generality of paper V to be extended to cases in which the adsorbent is perturbed by the adsorbate,<sup>8</sup> and to systems (such as hydrogen-palladium) without an "area."

We now review very briefly an application of solution thermodynamics.<sup>9</sup> We have

$$dE = TdS - PdV + \mu_1 dN_1 + \mu_A dN_A, \quad (1)$$

$$dF = -SdT + VdP + \mu_1 dN_1 + \mu_A dN_A, \quad (2)$$

$$d\mu_1 = -\bar{S}_1 dT + \bar{v}_1 dP + (\partial\mu_1/\partial T)_{T,P} dT, \quad (3)$$

where

$$\Gamma = N_1/N_A, \quad \bar{S}_1 = (\partial S/\partial N_1)_{N_A, P, T}, \text{ etc.}$$

$P$  is the hydrostatic pressure, exerted by a hypothetical inert piston or (in part) by a hypothetical inert additional gas (see also Appendix I). At equilibrium with gas,  $d\mu_1 = d\mu_G$ ,<sup>9a</sup> and

$$-\bar{S}_1 dT + \bar{v}_1 dP + (\partial\mu_1/\partial T)_{T,P} dT = -S_G dT + v_G dp \quad (4)$$

$$= [-S_G + (H_G - H_G^*)/T] dT + kT d \ln f, \quad (5)$$

where  $p$  is the equilibrium vapor pressure,  $f$  the vapor fugacity,  $S_G = S_G/N_G$ , etc.  $H_G^*$  is the value of  $H_G$  as  $p \rightarrow 0$  (same temperature). Hence

$$(\partial p/\partial T)_\Gamma = (S_G - \bar{S}_1)/(v_G - \bar{v}_1) \quad (P = p) \quad (6)$$

$$(\partial p/\partial T)_{\Gamma, P} = (S_G - \bar{S}_1)/v_G \quad (7)$$

$$(\partial \ln f/\partial T)_{\Gamma, P} = [(S_G - \bar{S}_1)/kT] + [(H_G^* - H_G)/kT^2] = (H_G^* - \bar{H}_1)/kT^2. \quad (8)$$

The "isosteric heat" of adsorption terminology is defined here as  $q_{st} = H_G - \bar{H}_1 = T(S_G - \bar{S}_1)$ .

Equations (6), (7) and (8) all give in the usual approximation (perfect gas,  $\bar{v}_1 = 0$ )

$$(\partial \ln p/\partial T)_\Gamma = (S_G - \bar{S}_1)/kT = (H_G - \bar{H}_1)/kT^2 = q_{st}/kT^2. \quad (9)$$

<sup>7</sup> The area  $\mathcal{A}$  is not necessarily constant if  $N_A$  is constant (e.g., swelling):  $\mathcal{A} = N_A f(T, P, N_1/N_A)$ .

<sup>8</sup> See Appendix I.

<sup>9</sup> See, for example, F. H. MacDougall, *Thermodynamics and Chemistry* (John Wiley and Sons, Inc., New York, 1939), Chapter X.

<sup>9a</sup> In the adsorption, say, of  $H_2$  on tungsten, if  $H_2$  is chosen as the single independent component of both the gas and adsorbed phase, then the equations given in this paper apply. If it is convenient from a statistical mechanical point of view to choose  $H_2$  as the independent component for the gas and  $H$  as the independent component for the adsorbed phase, then  $\mu_1 = \frac{1}{2}\mu_G$ , as is well known, and a factor of  $\frac{1}{2}$  or 2 will appear in various thermodynamic equations. This of course does not alter the essential thermodynamic content of these equations.

We now turn to adsorption thermodynamics.<sup>10</sup> We consider a sample of pure  $A$  with the same state of subdivision, etc., as used in preparing the "solution" of Eq. (1), and with the same  $N_A$ ,  $P$  and  $T$ :

$$dE_{0A} = TdS_{0A} - PdV_{0A} + \mu_{0A} dN_A. \quad (10)$$

We define

$$\begin{aligned} E_s &\equiv E - E_{0A} & V_s &\equiv V - V_{0A} \\ S_s &\equiv S - S_{0A} & \Phi &\equiv \mu_{0A} - \mu_A. \end{aligned} \quad (11)$$

On subtracting Eq. (10) from Eq. (1), we find

$$dE_s = TdS_s - PdV_s - \Phi dN_A + \mu_1 dN_1. \quad (12)$$

By use of this simple device we now have a pseudo one component (component "1") system in place of the two component solution.  $\Phi$  plays the role of a second "pressure." In the special case of adsorption on an inert adsorbent (paper V),  $E_s$ , for example, according to Eqs. (11), is just the energy of a system of adsorbed molecules in the potential field of the surface (the energy of the adsorbent subtracts out *except* for the interaction energy between adsorbent and adsorbed molecules which is left in  $E_s$ ); also,  $\Phi N_A = \varphi \mathcal{A}$ .<sup>8</sup>

We define the Gibbs free energy  $F_s \equiv N_1 \mu_1$ . On integrating Eq. (12),

$$F_s = E_s - TS_s + PV_s + \Phi N_A, \quad (13)$$

$$= A_s + PV_s + \Phi N_A, \quad (14)$$

$$A_s \equiv E_s - TS_s.$$

We define  $H_s \equiv F_s + TS_s$ . Hence

$$H_s = E_s + PV_s + \Phi N_A. \quad (15)$$

These definitions of  $F_s$  and  $H_s$  insure that

$$H_G - H_s = T(S_G - S_s) \quad (16)$$

at equilibrium between gas and sorbate, where  $H_s = H_s/N_1$ , etc.

From Eqs. (12) and (13),

$$dF_s = -S_s dT + V_s dP + N_A d\Phi + \mu_1 dN_1. \quad (17)$$

Equations (2) and (17) give

$$\mu_1 = (\partial F/\partial N_1)_{T, P, N_A} = \bar{F}_1 = \bar{H}_1 - T\bar{S}_1 \quad (18)$$

$$= (\partial F_s/\partial N_1)_{T, P, \Phi} = F_s/N_1 = F_s = H_s - TS_s. \quad (19)$$

At equilibrium between gas and sorbate,

$$\begin{aligned} d\mu_1 &= -S_s dT + v_s dP + (1/\Gamma) d\Phi \\ &= d\mu_G = -S_G dT + v_G dp \\ &= [-S_G + (H_G - H_G^*)/T] dT + kT d \ln f. \end{aligned} \quad (20)$$

Hence

$$(\partial p/\partial T)_\Phi = (S_G - S_s)/(v_G - v_s) \quad (P = p) \quad (21)$$

$$(\partial p/\partial T)_{\Phi, P} = (S_G - S_s)/v_G \quad (22)$$

<sup>10</sup> For want of a better term, we shall refer hereafter to the alternative asymmetric system of thermodynamics as "adsorption thermodynamics," as contrasted to "solution thermodynamics." Although both systems apply to both adsorption and solution, the names emphasize the principal field of usefulness.

$$(\partial \ln f / \partial T)_{\Phi, P} = [(S_G - S_s) / kT] + [(H_G^* - H_G) / kT^2] \\ = (H_G^* - H_s) / kT^2. \quad (23)$$

In the usual approximation (perfect gas,  $v_s = 0$ )

$$(\partial \ln f / \partial T)_{\Phi} = (S_G - S_s) / kT \\ = (H_G - H_s) / kT^2 \equiv q_{\Phi} / kT^2. \quad (24)$$

Equation (23), for example, is analogous to

$$(\partial \ln f / \partial T)_P = (H_G^* - H_L) / kT^2 \quad (25)$$

for the equilibrium between a pure liquid (or solid) and its vapor.

We may also derive from Eq. (20)

$$d\Phi = \Gamma(v_G - v_s)dp \quad (P = p, T \text{ const.}) \quad (26)$$

$$= \Gamma v_G dp = \Gamma kT d \ln f \quad (P, T \text{ const.}) \quad (27)$$

$$(\partial \Phi / \partial T)_P = \Gamma(S_s - S_G) \quad (P = p). \quad (28)$$

By definition  $\Phi = 0$  when  $p = 0$ , so we have the usual approximate integral form (due to Bangham) of the "Gibbs equation"

$$\Phi = kT \int_0^p \Gamma d \ln f \quad (T \text{ const.}). \quad (29)$$

It is clear that this equation is not exclusively a "surface" equation. Indeed, this is precisely the well-known relation giving the activity of one component ( $A$ ) of a solution when the activity of the other (1) is known<sup>11, 12</sup> (see also Appendix III).

It is important to keep in mind that the calculation of  $\Phi$  or any other thermodynamic function from experimental data alone can never give us any information about the existence or magnitude of sorbent perturbation. If it is present, it will automatically be included in the thermodynamic functions. Non-thermodynamic experiments or theoretical calculations are necessary to investigate this question.

TABLE I. Entropy of adsorption.

Source	Quantity derived
A. 1. Statistical mechanics	$S_s$
2. Heat capacity*	$S_s(T_2) - S_s(T_1)$
3. $q_{\Phi}$ , etc.	$S_s$
B. 1. $q_{st}$	$(\partial S_s / \partial N_1)_{T, N_A}$
2. Calorimetric*	$(\partial S_s / \partial N_1)_{T, N_A}$

\* See Section III and paper V.

<sup>11</sup> See, for example, G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), Eq. XXII-20. It may also be noted that Eq. XXII-24 resembles Eq. (3) of G. Jura and W. D. Harkins, J. Am. Chem. Soc. **66**, 1356 (1944).

<sup>12</sup> When adsorption thermodynamics is applied to a perfect solution with only one volatile component (or a semi-permeable membrane), the sorption isotherm is just Raoult's law and

$$\Phi = kT \ln[(N_1 + N_A) / N_A].$$

## Discussion

In physical adsorption we presumably have, to a satisfactory order of *approximation*, essentially the case of adsorption on an inert (unperturbed) adsorbent. In any case, all theories advanced in this field up to the present time have made this assumption. Even with this simplification the problem is much more complicated than the theory of an isotropic liquid. Thus the statistical mechanical model of an adsorbate in the external field presented by an inert adsorbent will presumably be a common one for some time to come. Even in chemisorption (and in solutions such as hydrogen-palladium) or in cases intermediate between chemisorption and physical adsorption this model has been and will no doubt continue to be used extensively as a valuable first approximation.

Adsorption thermodynamics finds its most natural application in the above special case. Thus, if nitrogen is adsorbed on graphite we are primarily interested in measuring and interpreting the entropy, energy, etc. of the *assembly of nitrogen molecules alone* in terms of intermolecular interactions, configurations of the assembly, rotations and vibrations of the molecules, etc. These functions are just the  $S_s$ ,  $E_s$ , etc. defined and are the functions which are obtained from statistical mechanical partition functions for this model using the standard relations between statistical mechanics and thermodynamics (e.g.,  $A_s = -kT \ln Q$ ). *This entropy  $S_s$  of the adsorbed molecules alone (inert adsorbent)*<sup>13</sup> is obtained from experimental data by direct use of Eq. (24) and not Eq. (9).

For a system such as water-sulfuric acid, adsorption thermodynamics is perfectly correct but no longer has particular usefulness, as far as the writer is aware at the present time. In the gradual transition from physical adsorption systems to solution systems it is not yet clear at what point adsorption thermodynamics loses its relative advantages.

An interesting intermediate case is exemplified by benzene-rubber (or water-protein, etc.). At low benzene vapor pressures this system is no doubt fairly well characterized as sorption on an inert sorbent. At higher benzene pressures we have a solution of rubber in benzene.<sup>14</sup> In studies where the low pressure sorption aspect is of primary interest it may prove advantageous

<sup>13</sup> Equation (24) gives in any case  $S_s = S - S_{0A}$ . If adsorbent perturbations are appreciable  $S_s$  is of course still a well-defined quantity but with a less direct physical significance.

<sup>14</sup> A related system is the type water-sodium chloride. At low pressures water is adsorbed on salt. At a certain intermediate pressure we will have salt in equilibrium with a saturated solution of salt in water as the condensed "phase." The adsorption isotherm is perpendicular here. Above this pressure all the salt will have dissolved—water vapor is in equilibrium with an unsaturated salt solution. This region is a "solution isotherm." See, for example, R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc. **70**, 1870 (1948). Equation (29) applies, of course, to the entire range in  $p$ . Contributions to the integral from pressures greater than the vapor pressure of the saturated solution will be relatively large. Surface properties of the salt affect the isotherm only below this vapor pressure.

to use adsorption thermodynamics at low pressures and, for the sake of continuity, carry its use over into the high pressure solution region.

A significant general property of  $S_s$  and  $H_s$  is the following. The quantity  $H_G - H_s = T(S_G - S_s)$  of Eq. (24) is the equilibrium heat of sorption which is analogous to the usual  $\Delta H$  of fusion, vaporization, etc. of a pure substance (Eq. (25)).  $\Delta H$  refers to a reversible process at constant pressure while  $H_G - H_s$ , by analogy, refers to constant  $P$  and  $\Phi$  (see Section III). In both cases *all* intensive properties stay constant during the vaporization (desorption) process.

The isosteric heat  $q_{st}$  of Eq. (9) gives<sup>15</sup>

$$\bar{S}_1 = (\partial S / \partial N_1)_{P, T, N_A} = (\partial S_s / \partial N_1)_{P, T, N_A} \cong (\partial S_s / \partial N_1)_{T, N_A} \quad (33)$$

since  $S_{0A}$  is independent of  $N_1$ , and the dependence on  $P$  is usually negligible. Thus  $q_{st}$  gives a differential  $S_s$  while  $q_*$  gives the "integral"  $S_s (= N_1 S_s)$ . This suggests an alternative method of calculating  $S_s$  from experimental data.<sup>16</sup> We write

$$q_{st} = T(S_G - \bar{S}_1),$$

multiply by  $dN_1$  and integrate from  $N_1 = 0$  to  $N_1$ . Using

$$\begin{aligned} \mu_G &= H_G - TS_G \\ d\mu_G &= kT d \ln p \quad (T \text{ const.}) \end{aligned}$$

and a partial integration, we find

$$T(S_G - S_s) = - \int_0^{N_1} q_{st} dN_1 - (\Phi/T) (N_A, T \text{ const.}) \quad (34)$$

Eq. (34) also follows from Eq. (V-91).

Being a differential entropy,  $\bar{S}_1 = (\partial S_s / \partial N_1)_{T, N_A}$  contains less thermodynamic information than  $S_s$ . This is of course related to the fact that more work is involved in using Eq. (24) than Eq. (9), as  $\Phi$  must first be calculated by integration from Eq. (29) (which requires low pressure experimental data). Indeed, there is no way of avoiding an integration if  $S_s$  is to be found. Eqs. (34) and (37) involve *two* integrations each, the extra integration in each case having been introduced for computational convenience. In the language of solution thermodynamics, the entropy  $S$  of the solution is not known unless *both*  $\bar{S}_1$  and  $\bar{S}_A$  are known:

$$S = N_1 \bar{S}_1 + N_A \bar{S}_A. \quad (35)$$

However, from isotherm data alone we can obtain no information about  $S_{0A}$  so the best we can expect to do in this case is to find  $S - S_{0A} = S_s$ . Thus, we get  $\bar{S}_1$  from Eq. (9) (if  $S_G(p)$  is known) and  $\bar{S}_A - S_{0A}$  from integration of

$$d\bar{S}_A = - (N_1/N_A) d\bar{S}_1 \quad (T \text{ const.}) \quad (36)$$

Integration of this equation is inconvenient, but using  $Td\bar{S}_A = d\bar{H}_A - d\mu_A$  we have

$$T(\bar{S}_A - S_{0A}) = \Phi - \int_{\bar{H}_1^0}^{\bar{H}_1} (N_1/N_A) d\bar{H}_1 \quad (T \text{ const.}), \quad (37)$$

where  $\bar{H}_1^0$  is the value of  $\bar{H}_1$  at  $p=0$ . Substitution of Eq. (37) into Eq. (35) gives  $S - S_{0A}$  in terms of calculable quantities.

Finally, in this section, we wish to emphasize that entropies calculated in adsorption work fall into two classes. In Table I we list various sources of entropy data and the type of quantity which is derived in each case. It is obviously incorrect, for example, to compare directly an experimental entropy calculated from  $q_{st}$  with the statistical mechanical entropy (this has been done several times in the literature). To make a comparison either  $S_s$  must be differentiated<sup>17</sup> or  $(\partial S_s / \partial N_1)_{T, N_A}$  integrated (Eq. (34)), or Eq. (24) or (68) may be used.

### III. MULTI-COMPONENT SORBATE

Some of the most important practical applications of adsorption involve adsorption from a mixture of gases. In order to gain a fundamental understanding of this field it will eventually be necessary to compare statistical mechanical theories with thermodynamic quantities derived from experimental data. In physical adsorption we may anticipate that the theory of liquid solutions will have to be extended in the same way that the theory of liquids will have to be extended to treat a one component sorbate. Very little fundamental work has been done on mixtures so far.<sup>18-20</sup> Measurements at neighboring temperatures are especially lacking.

In the physical adsorption of, say, a mixture of two gases on a solid, the condensed phase is a three-component phase but for the same reasons as before it is illuminating to treat this phase as a pseudo two-component phase, using adsorption thermodynamics.

It is the purpose of this section, then, to generalize the previous work (above; and paper V) to mixtures, pointing out the type of thermodynamic data which might be useful in interpretation and which can be derived from experiment. We first treat isotherm data,<sup>21</sup> and then calorimetric data.

<sup>17</sup> For example, this was done in effect by Davis and DeWitt, J. Am. Chem. Soc. **70**, 1135 (1948). Incidentally, the expression they give for  $q_{st}$  (BET theory) can be shown to be identical with a simpler equation for  $q_{st}$  in paper VII of this series (J. Chem. Phys. **17**, 772 (1949)).

<sup>18</sup> T. L. Hill, J. Chem. Phys. **14**, 268 (1946).

<sup>19</sup> J. R. Arnold, J. Am. Chem. Soc. **71**, 104 (1949).

<sup>20</sup> L. White and C. H. Schneider, J. Am. Chem. Soc. **71**, 2593 (1949).

<sup>20a</sup> S. Brunauer, *Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1943), Chapter 14.

<sup>21</sup> We might emphasize at the outset that with gas mixtures there are a large number of possible useful equations of the Clausius-Clapeyron type. We shall give only a few which appear to the writer to be most important; others can be written down using the same general methods.

<sup>15</sup> We might note here that  $H = E + PV \cong E$  but  $H_s \neq E_s$  in general ( $\Phi N_A$  is not negligible). Also  $H_s \neq H - H_{0A}$  and  $F_s \neq F - F_{0A}$ .

<sup>16</sup> Four other ways were pointed out in paper V: Eqs. (66), (85), (88), and (112).

### Solution Thermodynamics

The condensed phase has components 1, 2,  $\dots$ ,  $i$ ,  $\dots$ ,  $m$  and  $a$ ,  $b$ ,  $\dots$ ,  $\alpha$ ,  $\dots$ ,  $z$  of which only 1, 2,  $\dots$ ,  $i$ ,  $\dots$ ,  $m$  are volatile.<sup>6</sup> We restrict ourselves to cases such that  $E$ , say, is completely determined by  $S$ ,  $V$ ,  $N_1$ ,  $N_2$ ,  $\dots$ ,  $N_m$ ,  $N_A$  where  $N_A = \sum N_a$ . That is, the pure sorbent has constant composition, state of subdivision, etc., in all processes to be considered; hence there is only *one* independent variable of the type  $N_a$ ; we choose  $N_A$ . If an "area" exists, it is proportional to  $N_A$ . The case of most interest is of course a one component sorbent, as in Section II.

We have

$$dE = TdS - PdV + \sum \mu_i dN_i + \mu_A dN_A, \quad (42)$$

$$dF = -SdT + VdP + \sum \mu_i dN_i + \mu_A dN_A, \quad (43)$$

where  $\mu_A$  is defined as  $(\partial E / \partial N_A)_{S, V, N_i}$ .

At equilibrium,  $d\mu_i = d\mu_{iG}$  for  $i = 1, \dots, m$ . Now  $\mu_i$  is a function of  $T$ ,  $P$ ,  $\Gamma_1, \dots, \Gamma_m$  where  $\Gamma_i = N_i/N_A$  and  $\mu_{iG}$  is a function of  $T$ ,  $p$ ,  $x_1, \dots, x_{m-1}$ , where  $x_i$  is a gas composition variable. With  $P \neq p$  there are then  $2m+2$  variables, with  $m$  equilibrium relations, giving  $m+2$  degrees of freedom.<sup>22</sup> In writing, for example,  $\partial p / \partial T$ , then, we must specify  $m+1$  variables to be held constant. If  $P = p$ ,  $m$  variables must be held constant.

We may write ( $d\mu_i = d\mu_{iG}$ )

$$\begin{aligned} -\bar{S}_i dT + \bar{v}_i dP + \sum_{k=1}^m (\partial \mu_i / \partial \Gamma_k) d\Gamma_k \\ = -\bar{S}_{iG} dT + \bar{v}_{iG} dp + \sum_{k=1}^{m-1} (\partial \mu_{iG} / \partial x_k) dx_k \\ (i = 1, \dots, m). \end{aligned} \quad (45)$$

For brevity we shall let  $n$  denote the composition of the condensed phase ( $\Gamma_1, \dots, \Gamma_m$ ) and  $n_G$  the composition of the gas ( $x_1, \dots, x_{m-1}$ ). Holding  $n$  and  $P$  constant, and dividing by  $dT$ , Eqs. (45) may be regarded as  $m$  linear non-homogeneous equations in the  $m$  unknowns  $\partial p / \partial T$  and  $\partial x_k / \partial T$ . Then

$$\left( \frac{\partial p}{\partial T} \right)_{n, P} = \frac{\begin{vmatrix} \bar{S}_{1G} - \bar{S}_1 & \frac{\partial \mu_{1G}}{\partial x_1} & \dots & \frac{\partial \mu_{1G}}{\partial x_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{S}_{mG} - \bar{S}_m & \frac{\partial \mu_{mG}}{\partial x_1} & \dots & \frac{\partial \mu_{mG}}{\partial x_{m-1}} \end{vmatrix}}{\begin{vmatrix} \bar{v}_{1G} & \frac{\partial \mu_{1G}}{\partial x_1} & \dots & \frac{\partial \mu_{1G}}{\partial x_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{v}_{mG} & \frac{\partial \mu_{mG}}{\partial x_1} & \dots & \frac{\partial \mu_{mG}}{\partial x_{m-1}} \end{vmatrix}} \quad (46)$$

Using fugacities  $f_i$  we have alternatively

$$\begin{aligned} -\bar{S}_i dT + \bar{v}_i dP + \sum_{k=1}^m (\partial \mu_i / \partial \Gamma_k) d\Gamma_k \\ = [-\bar{S}_{iG} + (\bar{H}_{iG} - H_{iG}^*) / T] dT + kT d \ln f_i \\ (i = 1, \dots, m). \end{aligned} \quad (47)$$

With  $n$  and  $P$  constant, these equations have a particularly simple solution:

$$\begin{aligned} (\partial \ln f_i / \partial T)_{n, P} = [(\bar{S}_{iG} - \bar{S}_i) / kT] + [(\bar{H}_{iG}^* - \bar{H}_{iG}) / kT^2] \\ = (H_{iG}^* - \bar{H}_i) / kT^2 \quad (i = 1, \dots, m). \end{aligned} \quad (48)$$

For a perfect gas and taking  $\bar{v}_i = 0$ ,

$$\begin{aligned} (\partial \ln p_i / \partial T)_n = (S_{iG} - \bar{S}_i) / kT = (H_{iG} - \bar{H}_i) / kT^2 \\ = q_{s, i(i)} / kT^2 \quad (i = 1, \dots, m), \end{aligned} \quad (49)$$

where  $p_i$  is a partial pressure, and  $S_{iG}$  and  $H_{iG}$  are the entropy and heat content per molecule of (perfect) pure  $i$  gas at  $p_i$  and  $T$ . In Eq. (46), in this special case, we have  $\bar{v}_{iG} = kT/p$ ,  $\bar{S}_{iG} = S_{iG}$  and, taking the  $x_i$  as mole fractions with  $x_m = 1 - x_1 - x_2 - \dots - x_{m-1}$ ,

$$\begin{aligned} \partial \mu_{iG} / \partial x_i = kT / x_i, \quad \partial \mu_{iG} / \partial x_j = 0, \\ (i, j = 1, 2, \dots, m-1) \\ \partial \mu_{mG} / \partial x_i = -kT / x_m. \end{aligned}$$

Equations (46), (48), and (49) are "isosteric" equations. An equation analogous to Eq. (46) but with *gas* composition constant (as in the experiments of Arnold<sup>19</sup>) is

$$\left( \frac{\partial p}{\partial T} \right)_{n_G, \Gamma_1, P} = \frac{\begin{vmatrix} \bar{S}_{1G} - \bar{S}_1 & -\frac{\partial \mu_1}{\partial \Gamma_2} & \dots & -\frac{\partial \mu_1}{\partial \Gamma_m} \\ \vdots & \vdots & & \vdots \\ \bar{S}_{mG} - \bar{S}_m & -\frac{\partial \mu_m}{\partial \Gamma_2} & \dots & -\frac{\partial \mu_m}{\partial \Gamma_m} \end{vmatrix}}{\begin{vmatrix} \bar{v}_{1G} & -\frac{\partial \mu_1}{\partial \Gamma_2} & \dots & -\frac{\partial \mu_1}{\partial \Gamma_m} \\ \vdots & \vdots & & \vdots \\ \bar{v}_{mG} & -\frac{\partial \mu_m}{\partial \Gamma_2} & \dots & -\frac{\partial \mu_m}{\partial \Gamma_m} \end{vmatrix}} \quad (50)$$

If  $P = p$ , the subscript  $P$  is omitted in Eqs. (46) and (50), and  $\bar{v}_{iG}$  is replaced by  $\bar{v}_i - \bar{v}_i$ .

### Adsorption Thermodynamics

Equations (10) and (42), with  $\mu_{0A}$  defined as  $(\partial E_{0A} / \partial N_A)_{S_{0A}, V_{0A}}$  and  $N_A = \sum N_a$ , give

$$dE_s = TdS_s - PdV_s - \Phi dN_A + \sum \mu_i dN_i \quad (51)$$

$$dF_s = -S_s dT + V_s dP + N_A d\Phi + \sum \mu_i dN_i \quad (52)$$

$$F_s = \sum N_i \mu_i. \quad (53)$$

<sup>22</sup> See reference 9, pp. 140-141. No "new" phase rule is necessary.

We define

$$\bar{G}_i^* = (\partial G_s / \partial N_i)_{T, P, \Phi, N_j} \quad (54)$$

(this asterisk when combined with the "bar" in this way has nothing to do with the  $p \rightarrow 0$  notation). This is an obvious generalization of the usual definition of a partial molal quantity. Thus, from Eq. (52), at equilibrium

$$\begin{aligned} \mu_i &= \bar{F}_i^* = \bar{H}_i^* - T\bar{S}_i^* \\ &= \bar{H}_i - T\bar{S}_i = \mu_{iG} = \bar{H}_{iG} - T\bar{S}_{iG}, \end{aligned} \quad (55)$$

where, as usual,

$$\bar{G}_i = (\partial G / \partial N_i)_{P, T, N_j, N_A}.$$

It is clear that  $G_s = G_s(\Phi, P, T, N_i)$  is a homogeneous function of degree one in the  $N_i$  at constant  $\Phi, P, T$ . Hence,

$$G_s = \sum \bar{G}_i^* N_i; \quad (56)$$

Eq. (53) is an example. For a one component sorbate,  $\bar{G}_1^* = G_s / N_1 = G_s$ .

Now  $\mu_i$  is a function of  $T, P, \Phi, y_1, \dots, y_{m-1}$  where  $y_i$  is a composition variable for the sorbate.<sup>5</sup> For example, for the  $y_i$ , one might use  $N_2/N_1, N_3/N_1, \dots, N_m/N_1$ . We let  $n_s$  represent the composition of the sorbate.<sup>5</sup> From Eq. (52) we obtain, for the equilibrium between gas and sorbate,

$$\begin{aligned} d\mu_i &= -\bar{S}_i^* dT + \bar{v}_i^* dP + \bar{N}_{Ai}^* d\Phi + \sum_{k=1}^{m-1} (\partial \mu_i / \partial y_k) dy_k \\ &= d\mu_{iG} = -\bar{S}_{iG} dT + \bar{v}_{iG} dp + \sum_{k=1}^{m-1} (\partial \mu_{iG} / \partial x_k) dx_k \\ &= [-\bar{S}_{iG} + (\bar{H}_{iG} - H_{iG}^*)/T] dT + kT d \ln f_i \end{aligned} \quad (i=1, \dots, m). \quad (57)$$

We can now easily derive equations analogous to Eqs. (46), (48), and (50), respectively:

$$\left( \frac{\partial p}{\partial T} \right)_{n_s, \Phi, P} = \frac{\begin{vmatrix} \bar{S}_{iG} - \bar{S}_i^* & \frac{\partial \mu_{1G}}{\partial x_1} & \dots & \frac{\partial \mu_{1G}}{\partial x_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{S}_{mG} - \bar{S}_m^* & \frac{\partial \mu_{mG}}{\partial x_1} & \dots & \frac{\partial \mu_{mG}}{\partial x_{m-1}} \end{vmatrix}}{\begin{vmatrix} \bar{v}_{1G} & \frac{\partial \mu_{1G}}{\partial x_1} & \dots & \frac{\partial \mu_{1G}}{\partial x_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{v}_{mG} & \frac{\partial \mu_{mG}}{\partial x_1} & \dots & \frac{\partial \mu_{mG}}{\partial x_{m-1}} \end{vmatrix}}. \quad (58)$$

$$\begin{aligned} (\partial \ln f_i / \partial T)_{n_s, \Phi, P} &= [(\bar{S}_{iG} - \bar{S}_i^*) / kT] \\ &+ [(\bar{H}_{iG}^* - \bar{H}_{iG}) / kT^2] = (H_{iG}^* - \bar{H}_i^*) / kT^2 \end{aligned} \quad (i=1, \dots, m). \quad (59)$$

$$\left( \frac{\partial p}{\partial T} \right)_{n_G, \Phi, P} = \frac{\begin{vmatrix} \bar{S}_{1G} - \bar{S}_1^* & \frac{\partial \mu_1}{\partial y_1} & \dots & \frac{\partial \mu_1}{\partial y_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{S}_{mG} - \bar{S}_m^* & \frac{\partial \mu_m}{\partial y_1} & \dots & \frac{\partial \mu_m}{\partial y_{m-1}} \end{vmatrix}}{\begin{vmatrix} \bar{v}_{1G} & \frac{\partial \mu_1}{\partial y_1} & \dots & \frac{\partial \mu_1}{\partial y_{m-1}} \\ \vdots & \vdots & & \vdots \\ \bar{v}_{mG} & \frac{\partial \mu_m}{\partial y_1} & \dots & \frac{\partial \mu_m}{\partial y_{m-1}} \end{vmatrix}}. \quad (60)$$

In the usual approximation we omit  $P$ , replace  $f_i$  by  $p_i$ ,  $\bar{S}_{iG}$  by  $S_{iG}$ , and put  $H_{iG}^* = \bar{H}_{iG}$  in Eq. (59). If  $P = p$ , the subscript  $P$  is omitted in Eqs. (58) and (60) and  $\bar{v}_{iG}$  is replaced by  $v_{iG} - \bar{v}_i^*$ .

If we replace  $d\Phi$  in Eq. (57) by  $Td(\Phi/T) + (\Phi/T)dT$  we have

$$\left( \frac{\partial \ln f_i}{\partial T} \right)_{n_s, \Phi, T, P} = \frac{T(\bar{S}_{iG} - \bar{S}_i^*) + \bar{N}_{Ai}^* \Phi + H_{iG}^* - \bar{H}_{iG}}{kT^2} \quad (i=1, \dots, m). \quad (61)$$

For a perfect gas and  $\bar{v}_i^* = 0$  this becomes

$$(\partial \ln p_i / \partial T)_{n_s, \Phi, T} = (E_{iG} + kT - \bar{E}_i^*) / kT^2 \quad (i=1, \dots, m). \quad (62)$$

We now derive the "Gibbs equation." From Eqs. (52) and (53),

$$\sum N_i d\mu_i = \sum N_i d\mu_{iG} = -S_s dT + V_s dP + N_A d\Phi \quad (63)$$

$$d\Phi = \sum \Gamma_i kT d \ln f_i \quad (P, T \text{ const.}). \quad (64)$$

For a perfect gas and  $V_s = 0$ ,

$$d\Phi = \sum \Gamma_i kT d \ln p_i \quad (T \text{ const.}). \quad (65)$$

$\Phi$  is obtained in practice by integration of Eq. (65) from  $p_1 = \dots = p_m = 0$  ( $\Phi = 0$ ) to  $p_1, \dots, p_m$ .  $\Phi$  is a function of the state of the system only so various alternative paths may be used in carrying out the integration. For example, if the composition of the gas is held constant,<sup>19</sup> Eq. (65) becomes, in integral form,

$$\Phi = kT \int_0^p (\sum \Gamma_i) d \ln p \quad (T, n_G \text{ const.}). \quad (66)$$

Another obvious path is to increase  $p_1$  from  $p_1=0$  to  $p_1=p_1'$  keeping  $p_2=0$  ( $m=2$ ), then increase  $p_2$  from  $p_2=0$  to  $p_2=p_2'$  keeping<sup>20</sup>  $p_1=p_1'$ , thus reaching the final state  $p_1', p_2', T$ .

Equation (65), as applied to adsorption, has been discussed previously, for example, by Kemball, Rideal, and Guggenheim<sup>23</sup> and Innes and Rowley.<sup>24</sup>

Finally, we shall obtain explicit relations between  $\bar{S}_i$  and  $\bar{S}_i^*$ , etc. We have  $\mu_i=\mu_i(P, \Phi, T, n_i)$ , in which we may regard  $\Phi=\Phi(P, T, n)$ . This gives

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\Phi,n_s} + \left(\frac{\partial \mu_i}{\partial \Phi}\right)_{P,T,n_s} \left(\frac{\partial \Phi}{\partial T}\right)_{P,n} \quad (67)$$

or

$$\bar{S}_i = \bar{S}_i^* - \bar{N}_{Ai}^* (\partial \Phi / \partial T)_{P,n} \quad (i=1, \dots, m). \quad (68)$$

For a one component sorbate,  $\bar{S}_1^* = S_s$  and  $\bar{N}_{A1}^* = 1/\Gamma$ . Interchanging  $P$  and  $T$  in Eq. (67) gives

$$\bar{v}_i = \bar{v}_i^* + \bar{N}_{Ai}^* (\partial \Phi / \partial P)_{T,n} \quad (i=1, \dots, m). \quad (69)$$

Also,

$$\bar{H}_i = \bar{H}_i^* - T \bar{N}_{Ai}^* (\partial \Phi / \partial T)_{P,n} \quad (i=1, \dots, m) \quad (70)$$

follows from Eqs. (68) and (55).

Various equations, which may be of some use, involving  $\partial \Phi / \partial T$ ,  $\partial \Phi / \partial p$ , etc. can be written down from Eq. (57) if desired.

### Two Component Perfect Gas; $\bar{v}_i = \bar{v}_i^* = 0$

This is the most important case, so we give a few additional results here (these can be generalized) which should be helpful in interpreting experimental data.

First, we write, from Eq. (47),

$$-\bar{S}_1 dT + (\partial \mu_1 / \partial \Gamma_1) d\Gamma_1 + (\partial \mu_1 / \partial \Gamma_2) d\Gamma_2 = -S_{1G} dT + kT d \ln p_1. \quad (71)$$

This corresponds to  $p_1=p_1(\Gamma_1, \Gamma_2, T)$ . Now suppose we want instead  $p_1=p_1(\Gamma_1, u, T)$ , where  $u=p_2$ ,  $p_1/p_2$  or  $p$  ( $=p_1+p_2$ ). Then we use

$$d\Gamma_2 = (\partial \Gamma_2 / \partial \ln p_1) d \ln p_1 + (\partial \Gamma_2 / \partial u) du + (\partial \Gamma_2 / \partial T) dT \quad (72)$$

in place of  $d\Gamma_2$  in Eq. (71). Hence

$$\left(\frac{\partial \ln p_1}{\partial T}\right)_{\Gamma_1,u} = \frac{S_{1G} - \bar{S}_1 + (\partial \mu_1 / \partial \Gamma_2)_{T,\Gamma_1} (\partial \Gamma_2 / \partial T)_{p_1,p_2}}{kT - (\partial \mu_1 / \partial \Gamma_2)_{T,\Gamma_1} (\partial \Gamma_2 / \partial \ln p_1)_{u,T}}. \quad (73)$$

$u=p_1/p_2$  in Arnold's work,<sup>19</sup>  $u=p_2$  in the paper of White and Schneider,<sup>20</sup> and  $u=p$  in the work of Markham and Benton.<sup>25</sup>

White and Schneider<sup>20</sup> also plot  $\Gamma_1$  against  $p_2$  at

<sup>23</sup> Kemball, Rideal, and Guggenheim, *Trans. Faraday Soc.* **44**, 948 (1948). A somewhat simplified version of their statistical model has been used to check many of the equations of Section III.

<sup>24</sup> W. B. Innes and H. H. Rowley, *J. Phys. Chem.* **49**, 411 (1945).

<sup>25</sup> E. C. Markham and A. F. Benton, *J. Am. Chem. Soc.* **53**, 497 (1931).

constant  $p_1$ . We derive, as above, for this case

$$\left(\frac{\partial \ln p_2}{\partial T}\right)_{\Gamma_1,u} = \frac{S_{2G} - \bar{S}_2 + (\partial \mu_2 / \partial \Gamma_2)_{\Gamma_1,T} (\partial \Gamma_2 / \partial T)_{p_1,p_2}}{kT - (\partial \mu_2 / \partial \Gamma_2)_{\Gamma_1,T} (\partial \Gamma_2 / \partial \ln p_2)_{u,T}}, \quad (74)$$

where  $u=p_1$  (White and Schneider),  $p_1/p_2$  or  $p$ .

From Eq. (57),

$$-\bar{S}_1^* dT + \bar{N}_{A1}^* d\Phi + (\partial \mu_1 / \partial y) dy = -S_{1G} dT + kT d \ln p_1. \quad (75)$$

Putting  $y=y(\ln p_1, u, T)$  (alternatively,  $y$  can be replaced by  $\Phi$ ), we find

$$\left(\frac{\partial \ln p_1}{\partial T}\right)_{\Phi,u} = \frac{S_{1G} - \bar{S}_1^* + (\partial \mu_1 / \partial y)_{T,\Phi} (\partial y / \partial T)_{p_1,p_2}}{kT - (\partial \mu_1 / \partial y)_{T,\Phi} (\partial y / \partial \ln p_1)_{u,T}}, \quad (76)$$

where  $u=p_2$ ,  $p_1/p_2$  or  $p$ .

Arnold found it helpful to plot  $\Gamma_1 + \Gamma_2 (= \Gamma_{12})$  against  $p$  at constant  $p_1/p_2$ . Here, in place of Eq. (71), we use

$$\begin{aligned} -\bar{S}_1 dT + (\partial \mu_1 / \partial \Gamma_{12}) d\Gamma_{12} + (\partial \mu_1 / \partial y) dy \\ = -S_{1G} dT + kT d \ln p + kT d \ln x \\ -\bar{S}_2 dT + (\partial \mu_2 / \partial \Gamma_{12}) d\Gamma_{12} + (\partial \mu_2 / \partial y) dy \\ = -S_{2G} dT + kT d \ln p + kT d \ln(1-x), \end{aligned} \quad (77)$$

where  $x$  is the mole fraction of component 1 in the gas. Then

$$\left(\frac{\partial \ln p}{\partial T}\right)_{\Gamma_{12},x} = \frac{(\partial \mu_2 / \partial y)_{\Gamma_{12},T} (S_{1G} - \bar{S}_1) - (\partial \mu_1 / \partial y)_{\Gamma_{12},T} (S_{2G} - \bar{S}_2)}{kT [(\partial \mu_2 / \partial y)_{\Gamma_{12},T} - (\partial \mu_1 / \partial y)_{\Gamma_{12},T}]}. \quad (78)$$

In a complete thermodynamic treatment we want  $S_s$ . If the individual  $\bar{S}_i^*$  are found from say, Eq. (59), then

$$S_s = \sum N_i \bar{S}_i^*. \quad (79)$$

Also, using a generalization of Eq. (34), we can find  $S_s(N_1, N_2, \dots) - S_s(0, N_2, \dots)$ . By using  $m$  successive integrations of this type we get finally  $S_s(N_1, N_2, \dots)$  itself.

### Summary: Clausius-Clapeyron Equations for Mixtures

Workers who obtain isotherm data for mixtures will be interested in making calculations of the Clausius-Clapeyron type and in knowing just what thermodynamic quantities they are obtaining from such calculations. Equations (46)–(78) answer the latter question for the most obvious types of calculation. The final equations fall into four classes:

(1) Equations (49) and (59) give the simplest and most useful results: individual  $\Delta S_i^*$ 's.

(2) The quantities obtained from Eqs. (46) and (48) involve all the  $\Delta S_i^*$ 's, and, in addition, certain properties of the equilibrium vapor, which, however, are easily evaluated if the vapor is a perfect gas mixture.

(3) Equations (73), (74), and (76) give individual



$\Delta S_i$ 's, but certain derivatives (e.g.,  $(\partial \Gamma_2 / \partial T)_{p_1, p_2}$ ) have to be evaluated from isotherm data and others (e.g.,  $(\partial \mu_1 / \partial \Gamma_2)_{T, \Gamma_1}$ ) have to be evaluated from theory or from isotherm data (using—provided  $\mu_{1G}(p_1, T)$  is known—the fact that, for example,  $\mu_1 = \mu_{1G}$  at equilibrium\*). In any case, in comparing an explicit statistical theory with experiment, the right-hand members of all the equations in (1)–(4), regardless of complexity, can of course be calculated from the theoretical model and compared with left-hand members calculated from experimental data.

(4) Equations (50), (60), and (78) contain quantities of the type mentioned in (2), and, in addition, derivatives involving  $\mu_i$ , as in (3).

### Calorimetric Quantities

In this section it will be seen that the calorimetric equations of paper V actually apply without formal change to sorption on any type of sorbent, regardless of sorbent perturbation, etc. The equations are also extended to gas mixtures.

*Integral heat of sorption.* Suppose we have a system consisting of a closed container immersed in a large isolated constant temperature bath. The bath has an initial energy  $E_b$ . The container is divided into two parts connected by a stop-cock. Initially one part contains  $N_1^0, N_2^0, \dots$  molecules of a perfect gas mixture and the other part contains  $N_A = \sum N_\alpha$  molecules of an evacuated sorbent. The stop-cock is opened and equilibrium is eventually established. Initially the total energy of the complete system is  $E_b + E_{0A}(P=0) + \sum N_i^0 E_{iG}$ . Let  $E_b'$  be the internal energy of the bath in the final equilibrium state and suppose  $N_i$  molecules of type  $i$  have been sorbed. Then the total final energy of the system is  $E_b' + E + \sum (N_i^0 - N_i) E_{iG}$ . But

$$E_b + E_{0A}(P=0) + \sum N_i^0 E_{iG} = E_b' + E + \sum (N_i^0 - N_i) E_{iG} \quad (80)$$

so

$$Q = E_b' - E_b = \sum N_i E_{iG} - E_s = \sum N_i (E_{iG} - \bar{E}_i^*) \quad (T, N_A \text{ const.}), \quad (81)$$

where  $Q$  is the integral heat of sorption and the difference between  $E_{0A}(P=0)$  and  $E_{0A}(p)$  has been ignored.

*Differential and isothermal heat of sorption.* We have a container as above. The perfect gas mixture is in equilibrium with sorbate. Let  $V_c$  be the volume of the container:  $V_c = V_G + V$ . A frictionless piston forms one wall of the container. The piston is moved ( $T$  constant) so that  $V_c$  changes by  $dV_c$  and a new equilibrium state is reached. Let  $E_t$  be the total initial internal energy of the complete system:

$$E_t = E_b + E + \sum (N_i^0 - N_i) E_{iG} \quad (82)$$

$$dE_t = -pdV_c = dE_b + dE - \sum E_{iG} dN_i. \quad (83)$$

\* Thus, in Eq. (73) (perfect gas),

$$\mu_1 = \mu_{1G} = \mu_{1G}^0(T) + kT \ln p_1$$

$$\left( \frac{\partial \mu_1}{\partial \Gamma_2} \right)_{T, \Gamma_1} = kT \left( \frac{\partial \ln p_1}{\partial \Gamma_2} \right)_{T, \Gamma_1}.$$

Now  $E$  is a function of  $P, T, N_i, N_A$ .  $N_A$  and  $T$  are constant in Eq. (83) and the effect of  $dP = dp$  is neglected, so we write

$$dE = \sum (\partial E / \partial N_i)_{N_j, N_A, T} dN_i \cong \bar{E}_i dN_i \quad (84)$$

and

$$dE_b = \sum q_{d(i)} dN_i - pdV_c \quad (T, N_A \text{ const.}) \quad (85)$$

$$q_{d(i)} = E_{iG} - \bar{E}_i. \quad (86)$$

We digress to note that<sup>15</sup> (Eq. (49))

$$q_{st(i)} = H_{iG} - \bar{H}_i \cong E_{iG} + kT - \bar{E}_i = q_{d(i)} + kT. \quad (87)$$

$dE_b$  in Eq. (85) is the isothermal heat of sorption for a volume change  $dV_c$ . If the piston is omitted and the expansion  $dV_c$  takes place irreversibly through a stop-cock, say, then the external work term  $pdV_c$  is omitted from Eq. (85) and the resulting  $dE_b$  is the differential heat of sorption for a volume change  $dV_c$ . In either case we wish to evaluate  $dN_i$  in terms of  $dV_c$ . We have

$$p_i(V_c - V) = (N_i^0 - N_i)kT \quad (i=1, \dots, m) \quad (88)$$

$$p_i dV_c + V_G dp_i = -kT dN_i \quad (i=1, \dots, m), \quad (89)$$

where we neglect  $dV$ . Also, using the equilibrium adsorption isotherm data in the form  $N_i = N_i(p_1, p_2, \dots, T)$ , we have

$$dN_i = \sum_k (\partial N_i / \partial p_k) dp_k \quad (i=1, \dots, m). \quad (90)$$

Equations (89) and (90) constitute  $2m$  linear non-homogeneous equations in the  $2m$  unknowns  $dN_i, dp_i$ . Thus we can easily solve for each

$$dN_i = dV_c f(p_k, T, V_G, \partial N_i / \partial p_k).$$

For a one-component sorbate Eq. (85) reduces to

$$(\partial E_b / \partial N_1)_{N_A, T} = q_{th} = q_{st} + [V_G / (\partial N_1 / \partial p) T]. \quad (91)$$

We may note that in the special case  $dp=0$ ,  $q_{th} = q_{st} = H_G - \bar{H}_1$  as expected for a reversible constant pressure process. Of course in general  $dp \neq 0$ .

Professor J. G. Aston has pointed out to the writer that a calorimeter<sup>26</sup> which gives directly  $\Delta H$  of vaporization of a pure liquid should, when used in adsorption work, give  $q_{th}$  of Eq. (91) and not  $q_d$ . With such a calorimeter the uncertainty in calorimetric measurements mentioned in paper V would appear to be removed.

*"Equilibrium" heat and entropy of sorption.* In the reversible process we now describe all intensive properties remain constant, giving what we may call the "equilibrium" entropy of sorption (since it is analogous to the entropy of vaporization, etc., carried out reversibly—maintaining the same equilibrium point between liquid and vapor).

The following equations are exact (perfect gas not assumed, etc.). We have a container as in the "iso-

<sup>26</sup> See, for example, Aston *et al.*, J. Am. Chem. Soc. 66, 1171 (1944); 68, 52 (1946); Giaque and Johnston, J. Am. Chem. Soc. 51, 2300 (1929).

thermal" arrangement, but with the following modification: there is an additional hypothetical piston which separates  $N_A^0 - N_A$  molecules of pure sorbent from  $N_A$  molecules of sorbent in contact with sorbate. That is, this piston prevents the sorbate from spreading over the entire sorbent—it is impermeable to sorbate but, when the piston moves, stationary sorbent can pass through it (see Appendix III). When the gas piston is moved by an amount  $dV_e$ , the sorbent piston is moved an "amount"  $dN_A$  such that all intensive properties are kept constant—doing external work  $\Phi dN_A$ . We have

$$E_t = E_b + E(N_A, N_i, p, T) + E_{0A}(N_A^0 - N_A, p, T) + \sum (N_i^0 - N_i) \bar{E}_{iG}. \quad (92)$$

Now

$$E_{0A}(N_A^0 - N_A, p, T) = E_{0A}(N_A^0, p, T) - E_{0A}(N_A, p, T) \quad (93)$$

and

$$E_s = \sum N_i \bar{E}_i^*,$$

so

$$E_t = E_b + \sum N_i \bar{E}_i^* + E_{0A}(N_A^0, p, T) + \sum (N_i^0 - N_i) \bar{E}_{iG} \quad (94)$$

$$dE_t = -pdV_e - \Phi dN_A = dE_b + \sum (\bar{E}_i^* - \bar{E}_{iG}) dN_i. \quad (95)$$

Also

$$V_e = V_G + V(N_A, N_i, p, T) + V_{0A}(N_A^0 - N_A, p, T) = \sum (N_i^0 - N_i) \bar{v}_{iG} + \sum N_i \bar{v}_i^* + V_{0A}(N_A^0, p, T) \quad (96)$$

$$dV_e = \sum (\bar{v}_i^* - \bar{v}_{iG}) dN_i \quad (97)$$

and

$$dN_A = \sum \bar{N}_{Ai}^* dN_i. \quad (98)$$

Putting Eqs. (97) and (98) into Eq. (95) gives

$$dE_b = \sum [(\bar{E}_{iG} + p\bar{v}_{iG}) - (\bar{E}_i^* + p\bar{v}_i^* + \Phi \bar{N}_{Ai}^*)] dN_i = \sum (\bar{H}_{iG} - \bar{H}_i^*) dN_i = \sum T(\bar{S}_{iG} - \bar{S}_i^*) dN_i. \quad (99)$$

As this is a reversible process, the entropy change in the material inside the container must be  $-dE_b/T$ . This entropy change in the above process may easily be calculated independently and is found to check Eq. (99). The  $dN_i$  in Eq. (99) are not all independent. In fact,  $N_i/N_A = \Gamma_i = \text{const.}$ , so  $dN_i = \Gamma_i dN_A$ .

*Heat capacity and entropy.* We have a perfect gas mixture in equilibrium with sorbate in a container of constant volume. The temperature of the entire system (container plus bath) is changed by  $dT$  owing to an absorption of heat in amount  $q$  from an external source. Then Eq. (82) holds and

$$dE_t = q = dE_b + dE + \sum N_{iG} dE_{iG} - \sum E_{iG} dN_i \quad (100)$$

where, neglecting pressure effects,

$$dE = \sum [(\partial E / \partial N_i)_{N_j, T, N_A} dN_i] + (\partial E / \partial T)_{N_i, N_A} dT. \quad (101)$$

Writing  $E = E_s + E_{0A}$ , Eq. (101) becomes

$$dE = \sum \bar{E}_i dN_i + C_n dT + C_{0A} dT,$$

where the definitions of  $C_n$  and  $C_{0A}$  are obvious. As we

are ignoring pressure effects,  $C_{0A}$  is also the heat capacity of the evacuated pure sorbent. Returning to Eq. (100),

$$C_n = (q/dT) = C_b - \sum C_{iGV} - C_{0A} + \sum q_{d(i)} (dN_i/dT) \quad (N_A, V_e \text{ const.}), \quad (102)$$

where  $C_b$  is the heat capacity of the bath and  $C_{iGV}$  is the heat capacity at constant volume of the  $i$ -th component of the gas. The  $dN_i/dT$  may be found from (see Eqs. (88) and (90))

$$V_G dp_i = k N_{iG} dT - k T dN_i \quad (i = 1, \dots, m) \quad (103)$$

$$dN_i = \sum_k [(\partial N_i / \partial p_k)_{p_j, T} dp_k] + (\partial N_i / \partial T)_{p_k} dT \quad (i = 1, \dots, m). \quad (104)$$

The  $dN_i/dT$  will depend on the  $(\partial N_i / \partial T)_{p_k}$ , among other things. These derivatives may be more easily evaluated from isotherm data using

$$\left( \frac{\partial N_i}{\partial T} \right)_{p_k} = - \left( \frac{\partial N_i}{\partial p_i} \right)_{p_j, T} \left( \frac{\partial p_i}{\partial T} \right)_{p_j, \Gamma_i}. \quad (105)$$

We now relate  $S_s$  to  $C_n$ . We have

$$dE_s = T dS_s + \sum \mu_i dN_i = \sum (\partial E_s / \partial N_i) dN_i + C_n dT \quad (N_A \text{ const.}) \quad (106)$$

$$(\partial S_s / \partial T)_n = C_n / T \quad (107)$$

$$dS_s = \sum [(\partial S_s / \partial N_i) dN_i] + (\partial S_s / \partial T) dT = \sum \bar{S}_i dN_i + (C_n / T) dT \quad (N_A \text{ const.}), \quad (108)$$

where the  $dN_i$  are given by Eqs. (103) and (104). Integration of this equation between  $T_1$  and  $T_2$  gives  $S_s(N_i(T_2), T_2) - S_s(N_i(T_1), T_1)$  (see paper V). In order to use Eq. (102),  $C_{0A}$  must be measured. Hence  $S_{0A}(T_2) - S_{0A}(T_1)$  and  $S(T_2) - S(T_1)$  are also available (indeed, if we do not use  $E = E_s + E_{0A}$  in Eq. (101),  $dS$  is obtained directly in place of  $dS_s$  in Eq. (108)).

I am indebted to Drs. J. G. Aston, P. H. Emmett, G. Halsey, G. Jura and G. B. Kistiakowsky for very stimulating discussions and comments.

## APPENDIX I

We discuss here some relations with surface thermodynamics. Gibbs' treatment<sup>27</sup> of surfaces is of course classical. Guggenheim<sup>28</sup> has given an equivalent but alternative treatment of surface thermodynamics which is more satisfactory from a physical point of view, and which can more readily be compared with the present paper than Gibbs' work. Guggenheim considers the thermodynamic functions for a surface region  $\sigma$  between two phases,  $\sigma$  extending into each phase far enough to reach the homogeneous region of the phase, but otherwise being arbitrary in extent. We now characterize

<sup>27</sup> E. A. Guggenheim, *Modern Thermodynamics* (Methuen and Company, London, 1933), Chapter XII.

<sup>28</sup> E. A. Guggenheim, *Trans. Faraday Soc.* **36**, 397 (1940).

our special case. In the first place, we take one of the homogeneous phases as a gas,<sup>4a</sup> neglect molecular interactions between the gas and the condensed phase, and take  $\sigma$  as the *entire* condensed phase. Similarly, we take an equivalent (see discussion preceding Eq. (10)) sample of pure sorbent and call it  $\sigma_0$ . We then subtract thermodynamic properties of  $\sigma_0$  from those of  $\sigma$  to obtain  $S_s$ ,  $E_s$ , etc. In our notation, Guggenheim writes in general for  $\sigma$ ,

$$dE = TdS - PdV + \gamma'd\alpha + \sum \mu_i' dN_i + \sum \mu_\alpha' dN_\alpha, \quad (109)$$

where  $\gamma'$ ,  $\mu_i'$  and  $\mu_\alpha'$  are defined as derivatives by Eq. (109), and  $\alpha$  is a further *independent* variable. In our special case each  $N_\alpha$  is determined by  $\alpha$  (but our discussion is more general in that we are not restricted to "surface" problems— $\alpha$  is replaced by  $N_A$ ), so

$$dE = TdS - PdV + \gamma d\alpha + \sum \mu_i dN_i, \quad (110)$$

where  $\gamma$  and  $\mu_i$  are defined as derivatives by Eq. (110). Also,

$$dE_{0A} = TdS_{0A} - PdV_{0A} + \gamma_0 d\alpha \quad (111)$$

$$dE_s = TdS_s - PdV_s - \varphi d\alpha + \sum \mu_i dN_i \quad (112)$$

$$\varphi = \gamma_0 - \gamma. \quad (113)$$

If we are concerned with strictly surface effects it is obviously not necessary to take  $\sigma$  and  $\sigma_0$  as including the entire sorbent, but it has the considerable advantage of extending the generality to solutions, etc.

The concept of "area" is useful, when it can be defined, so long as the only perturbations of the sorbent by the sorbate are non-structural: that is, the volume and equilibrium molecular structure of the sorbent stay essentially constant (as in most physical and chemisorptions) but vibration frequencies of surface atoms, rotational and electronic energy levels, etc. may change. With structural perturbations, Eq. (112) must be replaced by Eq. (51).

Guggenheim points out that in general with curved interfaces there is ambiguity in  $P$  in the external work term  $-PdV$ . However, in our special case there is no ambiguity because the only  $PV$  external work the condensed phase can do is against the vapor pressure or an additional hydrostatic pressure exerted, say, by an inert gas. From another point of view, since adsorption systems are thermodynamically indistinguishable from solution systems, the pressure  $P$  exerted on an adsorbent-adsorbate has precisely the same significance as the pressure  $P$  exerted on a solution.

Finally, it must be pointed out that for some systems the *volume* of the condensed phase cannot be defined precisely because of the importance of surface configurations down to the molecular level. Using the approximate guide that the transfer of a certain number of molecules from the gas phase to the condensed phase increases the volume of the condensed phase by an amount equal to the concomitant decrease in free volume available to the (remaining) gas molecules, it is

clear that this effect is in general not important. The rigorous way of avoiding this difficulty, however, is to use the Gibbs or Guggenheim<sup>28</sup> treatment of the surface region between bulk gas and bulk condensed phase; or to treat gas plus condensed phase, combined, as the "thermodynamic system."

## APPENDIX II

We discuss briefly here a "fugacity" of the sorbate: a generalization of  $\Phi$  in the same sense that gas fugacity is a generalization of gas pressure.<sup>29</sup> The concept does not seem to be particularly useful for present purposes but may be important in other connections. For simplicity we shall consider a one-component sorbate only, the extension to any number of components being straightforward.

For a sufficiently small pressure  $p^*$ , we assume that Henry's law holds:<sup>30</sup>

$$\Gamma^* = a(P, T)p^*, \quad (114)$$

where  $P$  is the hydrostatic pressure on the "solution" and the asterisk refers to the limiting case  $p \rightarrow 0$ . Then, from Eq. (27),

$$\Phi^* = akT p^* = \Gamma^* kT. \quad (115)$$

Now

$$\begin{aligned} \mu_G^* &= \mu_G^0(T) + kT \ln p^* \\ &= \mu_1^* = \mu_G^0(T) + kT \ln(\Phi^*/akT). \end{aligned} \quad (116)$$

Hence,

$$\mu_1^* = \mu_1^0(P, T) + kT \ln \Phi^* \quad (117)$$

with

$$\mu_1^0(P, T) = \mu_G^0(T) - kT \ln a(P, T)kT. \quad (118)$$

Noting the analogy between Eq. (116) and Eq. (117), we define a fugacity  $f_s$  by the equations

$$\begin{aligned} \mu_1 &= \mu_1^0(P, T) + kT \ln f_s \\ f_s &\rightarrow \Phi \quad \text{as} \quad \Phi \rightarrow 0 \quad (p \rightarrow 0). \end{aligned} \quad (119)$$

We have immediately the properties of  $f_s$

$$\left( \frac{\partial \ln f_s}{\partial \mu_1} \right)_{P, T} = \frac{1}{kT}, \quad \left( \frac{\partial \ln f_s}{\partial \Phi} \right)_{P, T} = \frac{1}{\Gamma kT}. \quad (120)$$

Also, one finds with no difficulty

$$\left( \frac{\partial \ln f_s}{\partial T} \right)_{P, \Phi} = \frac{H_s^* - H_s}{kT^2}, \quad \left( \frac{\partial \ln f_s}{\partial P} \right)_{T, \Phi} = \frac{v_s - v_s^*}{kT}. \quad (121)$$

<sup>29</sup> W. B. Innes and H. H. Rowley, J. Phys. Chem. **46**, 548 (1942). These authors have already discussed the unimolecular case (strictly two-dimensional systems).

<sup>30</sup> If, owing to dissociation (or association) of the gas molecules on the surface,  $\Gamma^* = a(P, T)p^{*1/n}$ , where  $\Gamma^*$  is the surface concentration taking the dissociated species as the fundamental component on the surface (e.g.  $n=2$  for  $H_2 \rightarrow 2H$  on adsorption), then from Eq. (27))

$$d\Phi = (1/n)\Gamma kT d \ln f_s \quad (P, T \text{ const.})$$

we get  $\Phi^* = akT p^{*1/n} = \Gamma^* kT$ . Using  $n\mu_1^* = \mu_G^*$ , Eq. (117) is obtained again with

$$\mu_1^0(P, T) = [\mu_G^0(T)/n] - kT \ln akT.$$

It is of interest to consider  $\mu_1$  as a function of  $T, P$  and  $\ln f_s$  so that

$$d\mu_1 = \left(\frac{\partial\mu_1}{\partial T}\right)_{P, f_s} dT + \left(\frac{\partial\mu_1}{\partial P}\right)_{T, f_s} dP + \left(\frac{\partial\mu_1}{\partial \ln f_s}\right)_{T, P} d \ln f_s \quad (122)$$

$$= [-S_s + (H_s - H_s^*)/T] dT + v_s^* dP + kT d \ln f_s \quad (123)$$

$$= d\mu_G = [-S_G + (H_G - H_G^*)/T] dT + kT d \ln f. \quad (124)$$

Hence, in analogy with Eq. (23),

$$\left(\frac{\partial \ln f}{\partial T}\right)_{f_s, P} = \frac{H_G^* - H_s^*}{kT^2}. \quad (125)$$

At *any* vapor pressure  $p$  this equation merely gives the information that Eq. (23) already gives at *low* pressures. The reason for this is clear from the following:

$$\begin{aligned} \mu_1^0(P, T) + kT \ln f_s &= \mu_G^0(T) + kT \ln f \\ K(P, T) = f_s/f &= \exp\{[\mu_G^0(T) - \mu_s^0(P, T)]/kT\} \end{aligned} \quad (126)$$

$$= a(P, T) kT, \quad (127)$$

where  $K$  is an "equilibrium constant," independent of  $p$ , which can be evaluated from Eq. (114). Thus, at any pressure  $p$ ,  $f_s$  is essentially determined by the behavior of the adsorption isotherm at low pressures.

In solution thermodynamics, in place of  $f_s$  the fugacity  $f_1=f$  would of course be used.

### APPENDIX III

We discuss here the relation between  $\Phi$  and the osmotic pressure. Referring to Eqs. (92)–(99) and the related discussion, we note that pure sorbent  $A$  at  $P$  and  $T$  is separated from a solution of sorbate in sorbent at  $P$  and  $T$  by a kind of semi-permeable piston. The chemical potential of pure sorbent is  $\mu_{0A}$  and of sorbent in the solution is  $\mu_A$ . We define (as usual) the osmotic pressure  $\Pi$  as the excess hydrostatic pressure on the solution needed in order to increase  $\mu_A$  up to the value  $\mu_{0A}$ . We find

$$\mu_{0A} - \mu_A = \Phi = \int_P^{P+\Pi} \bar{v}_A dP \quad (T, n \text{ const.}). \quad (128)$$

If  $\bar{v}_A$  is essentially constant between  $P$  and  $P+\Pi$ ,  $\Phi = \Pi \bar{v}_A$ . For an inert adsorbent with a well-defined surface area  $\mathcal{A}$ ,  $\bar{v}_A = v_{0A}$  to a very high approximation and

$$\begin{aligned} \Phi N_A &= \varphi \mathcal{A} = \Pi V_{0A}, \\ \Phi dN_A &= \varphi d\mathcal{A} = \Pi dV_{0A}. \end{aligned} \quad (129)$$

There are two unusual features about the present osmotic system: (1) the solvent (sorbent) is non-volatile, and (2) it is the escaping or diffusing tendency of the solute (sorbate) which is *in effect* operative when the hypothetical sorbent piston moves. This is especially clear when the spreading pressure  $\varphi = \gamma_0 - \gamma$  has meaning.