

Oxford Chemistry Primers: Foundations of Surface Science

Solutions for Chapter One: Thermodynamics

1.1. Confirm that Eqns. 1.12 and 1.13 are together equivalent to Eqn. 1.10, and that substitution of Eqn. 1.11 into Eqn. 1.10 is indeed consistent with Eqn. 1.5. Derive the condition that permits replacement of γ' with γ in Eqn. 1.13.

Let us begin with Eqns. 1.12 and 1.13 from Section 1.4

$$dW^s = A \sum_{ij} \sigma_{ij} d\epsilon_{ij}$$

and

$$\sigma_{ij} = \gamma' \delta_{ij} + \frac{\partial \gamma'}{\partial \epsilon_{ij}}$$

and substitute the latter into the former.

We then obtain

$$\begin{aligned} dW^s &= A \sum_{ij} \left[\gamma' \delta_{ij} + \frac{\partial \gamma'}{\partial \epsilon_{ij}} \right] d\epsilon_{ij} \\ &= \gamma' A (d\epsilon_{11} + d\epsilon_{22}) + A \sum_{ij} \frac{\partial \gamma'}{\partial \epsilon_{ij}} d\epsilon_{ij} \end{aligned}$$

by noting that δ_{ij} (the Kronecker delta) can only, by definition, take the values one ($i = j$) or zero ($i \neq j$).

Next, we note that

$$A(d\epsilon_{11} + d\epsilon_{22}) = dA$$

from the definition of surface strain, and that

$$\sum_{ij} \frac{\partial \gamma'}{\partial \epsilon_{ij}} d\epsilon_{ij} = d\gamma'$$

from the standard mathematical properties of partial derivatives.

Substituting both of these into our last expression for the reversible work gives

$$dW^s = \gamma' dA + A d\gamma'$$

which is Eqn. 1.10 as required.

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If we now insert Eqn. 1.11

$$\gamma' = \gamma + \sum_i \mu_i \Gamma_i$$

into this last equation (Eqn. 1.10) we obtain

$$dW^s = \gamma dA + Ad\gamma + \sum_i \mu_i \Gamma_i dA + Ad \left(\sum_i \mu_i \Gamma_i \right)$$

which we must demonstrate is consistent with Eqn. 1.5 from the text.

Turning to Eqn. 1.5 from Section 1.3, we have

$$F^s = \gamma A + \sum_i \mu_i N_i^s$$

and from this we can say that the reversible work (under the relevant conditions of constant temperature and particle quantities) is given by

$$dW^s = dF^s = \gamma dA + Ad\gamma + d \left(\sum_i \mu_i N_i^s \right)$$

where it should be recalled that N_i^s represents the quantity of particles (of each species) associated with the surface, equivalent simply to $\Gamma_i A$. Making this substitution, we find

$$\begin{aligned} dW^s &= \gamma dA + Ad\gamma + d \left(A \sum_i \mu_i \Gamma_i \right) \\ &= \gamma dA + Ad\gamma + \sum_i \mu_i \Gamma_i dA + Ad \left(\sum_i \mu_i \Gamma_i \right) \end{aligned}$$

which is clearly the same result obtained above by substituting Eqn. 1.11 into Eqn. 1.10.

Finally, let us consider Eqn. 1.13 from Section 1.4

$$\sigma_{ij} = \gamma' \delta_{ij} + \frac{\partial \gamma'}{\partial \epsilon_{ij}}$$

and evaluate explicitly the error, E_{ij} , that we would make in replacing γ' throughout with γ .

Clearly, that means

$$\begin{aligned} E_{ij} &= \gamma' \delta_{ij} - \gamma \delta_{ij} + \frac{\partial \gamma'}{\partial \epsilon_{ij}} - \frac{\partial \gamma}{\partial \epsilon_{ij}} \\ &= (\gamma' - \gamma) \delta_{ij} + \frac{\partial (\gamma' - \gamma)}{\partial \epsilon_{ij}} \end{aligned}$$

while from Eqn. 1.11 we have¹

$$\gamma' - \gamma = \sum_n \mu_n \Gamma_n$$

so that

$$\begin{aligned} E_{ij} &= \sum_n \mu_n \Gamma_n \delta_{ij} + \frac{\partial}{\partial \epsilon_{ij}} \left(\sum_n \mu_n \Gamma_n \right) \\ &= \sum_n \left[\Gamma_n \left(\mu_n \delta_{ij} + \frac{\partial \mu_n}{\partial \epsilon_{ij}} \right) + \mu_n \frac{\partial \Gamma_n}{\partial \epsilon_{ij}} \right] \end{aligned}$$

is the expression that we must evaluate, in order to judge whether the $\gamma' \rightarrow \gamma$ replacement is permissible or not.

Now, looking at the final term, we may make progress by writing

$$\begin{aligned} \frac{\partial \Gamma_n}{\partial \epsilon_{ij}} &= \left(\frac{\partial \Gamma_n}{\partial A} \right) \left(\frac{\partial A}{\partial \epsilon_{ij}} \right) \\ &= \left(\frac{\partial (N_n^s/A)}{\partial A} \right) \left(\frac{\partial A}{\partial \epsilon_{ij}} \right) \\ &= - \left(\frac{N_n^s}{A^2} \right) \left(\frac{\partial A}{\partial \epsilon_{ij}} \right) \\ &= - \left(\frac{N_n^s}{A^2} \right) A \delta_{ij} \\ &= - \Gamma_n \delta_{ij} \end{aligned}$$

where we made use, in the penultimate step, of the definition of strain.

¹N.B. We change the dummy variable i , from Eqn. 1.11, into n at this point, to avoid confusion with the i and j indices labelling tensor components of the surface stress and strain.

Inserting this useful result into our last expression for the error, we note a convenient cancellation of terms, and hence obtain

$$E_{ij} = \sum_n \Gamma_n \frac{\partial \mu_n}{\partial \epsilon_{ij}}$$

as our ultimate result.

Under what circumstances, then, might we expect E_{ij} to vanish, for all i and j ?

Perhaps the first point to note is that the partial derivatives of individual chemical potentials with respect to strain components will generally be non-zero, and fixed by the properties of the bulk. That is, the values of these derivatives, be they positive or negative, will be independent of any choice we may make for the position of the dividing plane.

Secondly, note that the values of the surface excesses will vary much depend upon the position chosen for the dividing plane. Indeed, for species that have non-zero concentration in the bulk, their values will change linearly as one moves the dividing plane. It follows, therefore, that not only will the value of each E_{ij} component generally be dependent upon the position of the dividing plane, this value too will vary in a linear manner as the dividing plane is shifted.

So long as the gradient of E_{ij} (with respect to changes in location of the dividing plane) is non-zero, it will therefore be possible always to find some location for the dividing plane at which E_{ij} vanishes for some combination of i and j . There is no reason to suppose, however, either that this position for the dividing plane will be physically reasonable (e.g. being anywhere near the last plane of atoms) or that the same position will do the trick for all components of E_{ij} .

Consider, however, one important constraint upon the chemical potentials when the bulk stress vanishes. This condition is equivalent to insisting that the bulk (in the absence of the surface) would exist at an equilibrium defined by

$$\sum_n X_n \frac{\partial \mu_n}{\partial \epsilon_{ij}} = 0$$

where X_n represents the quantity of particles (of species n) in the bulk. If this expression holds *and* the Γ_n values are in the same relative proportion as the corresponding X_n values, then clearly E_{ij} will vanish for all i and j (and for all positions of the dividing plane). The additional requirement, on top of vanishing bulk stress, is therefore that the stoichiometry of the surface region matches that of the bulk.

1.2. Water rises up a capillary of diameter 0.32 mm, achieving a height of 9.2 cm above the external level. Assuming a contact angle of zero with the capillary walls, calculate the surface tension of water. Take $997.07 \text{ kg}\cdot\text{m}^{-3}$ for the density of water (at $25 \text{ }^\circ\text{C}$) and $9.81 \text{ m}\cdot\text{s}^{-2}$ for the acceleration due to gravity.

Since we are told that the contact angle of water with the capillary walls is zero, we must be dealing with a situation where the liquid surface within the capillary displays a concave curvature (as per Fig. 1.9a in Section 1.5). Furthermore, the radius of curvature must equal the radius of the capillary in this case, permitting us to use this value as r in

$$\frac{2\gamma}{r} = \Delta P$$

which is Eqn. 1.18 (the Young-Laplace equation).

For a cylindrical liquid column of density ρ , cross-sectional area A , and height h , the total weight that must be supported by the curvature-induced pressure differential, ΔP , is ρAhg , with g the acceleration due to gravity. Thus, we must have

$$A\Delta P = \rho Ahg$$

and hence

$$\gamma = \rho rhg/2$$

after substitution of the Young-Laplace equation and some rearrangement.

Inserting $r = 0.00016 \text{ m}$, $h = 0.092 \text{ m}$, $\rho = 997.07 \text{ kg}\cdot\text{m}^{-3}$, and $g = 9.81 \text{ m}\cdot\text{s}^{-2}$, we obtain

$$\gamma = 7.199 \times 10^{-2} \text{ J}\cdot\text{m}^{-2}$$

for the surface tension.

1.3. In dry air (we state without proof) the instantaneous evaporation rate of a spherical water droplet is proportional both to its radius and to its saturated vapour pressure. If a single such droplet, of radius $0.01 \mu\text{m}$, were to be mechanically dispersed into eight mutually identical smaller droplets, by what factor would the instantaneous evaporation rate of the ensemble (at 25°C) exceed that of the original droplet? Take the molar mass of water to be $18.015 \text{ g}\cdot\text{mol}^{-1}$, and any other necessary parameters from Exercise 1.2.

Before beginning, let us first briefly discuss the question's statement regarding the dependence of instantaneous evaporation rate on radius and saturated vapour pressure. Naively, one might have expected the rate to be proportional to the droplet's surface area, and hence to the square of the radius, but this fails to account for the rate at which vapour can diffuse away from the droplet after evaporation. The earliest treatment to account for this effect appears to be that of Langmuir [Phys. Rev. 12, 368 (1918)] who argued, by analogy with heat loss through gaseous media, that proportionality to the non-squared radius must be correct. A particularly clear modern treatment, including the influence of variation in the saturated vapour pressure, may be found in a paper by Ho [Wat. Res. Res. 33, 2665 (1997)]. In this, it is shown that the evaporation rate actually depends upon the *difference* between the saturated vapour pressure of the droplet and the ambient pressure of water infinitely far from the droplet's surface. The latter quantity may, however, be taken as zero in the case of perfectly dry air.

Turning to the solution for our present problem, we note that the volume and/or mass of a spherical droplet is proportional to the cube of its radius, so dispersing the original droplet into eight mutually identical droplets implies that each should have precisely half the radius of the original. If the radius were the only important consideration, we would then anticipate the instantaneous evaporation rate of each small droplet to be precisely half that of the original droplet (given the proportionality noted above) and the total rate for the ensemble of eight such droplets to exceed that of the original by a factor of four.

Now, however, we must account for changes in the saturated vapour pressure, which we recall may be obtained from Eqn. 1.27 in Section 1.5 (the Kelvin equation). That is, we have

$$\ln [P_v(a)/P_v(\infty)] = \frac{2\gamma\bar{V}_l}{RTa}$$

where $P_v(a)$ is the saturated vapour pressure for a droplet of radius a , and $P_v(\infty)$ is the saturated vapour pressure for a flat liquid surface.

Rearranging this equation, we find

$$P_v(a) = P_v(\infty) \exp\left(\frac{2\gamma\bar{V}_l}{RTa}\right)$$

and hence

$$\begin{aligned} P_v(a)/P_v(b) &= \exp\left(\frac{2\gamma\bar{V}_l}{RT}\left(\frac{1}{a} - \frac{1}{b}\right)\right) \\ &= \exp\left(\frac{2\gamma\bar{V}_l}{RT}\left(\frac{b-a}{ab}\right)\right) \end{aligned}$$

where b simply represents some alternative droplet radius.

Substituting $b = 2a$ into this last result, we find

$$P_v(a)/P_v(2a) = \exp\left(\frac{\gamma \bar{V}_l}{RTa}\right)$$

for the ratio of saturated vapour pressures associated with droplets having radii in the ratio 1:2.

Let us then take $R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ as the molar gas constant, and $T = 298.15 \text{ K}$ for 25°C . The molar volume of liquid water at this temperature can be worked out from its molar mass ($18.015 \text{ g.mol}^{-1}$) and density (given in the previous problem as 997.07 kg.m^{-3}) to be $\bar{V}_l = 0.018015/997.07 = 1.807 \times 10^{-5} \text{ m}^3$. In addition, we have $\gamma = 7.199 \times 10^{-2} \text{ J.m}^{-2}$ from our solution to the previous problem, so putting $a = 0.005 \mu\text{m}$, we calculate that

$$P_v(0.005 \times 10^{-6})/P_v(0.010 \times 10^{-6}) = 1.11$$

which implies that the evaporation rate for the ensemble of eight droplets will exceed that of the original droplet by a factor of $4 \times 1.11 = 4.44$ overall.

Note that the size chosen for the original droplet in the problem (i.e. $0.01 \mu\text{m}$) is fairly typical of fine particles within atmospheric aerosols, so this result suggests that deviations in evaporation rate due to curvature-induced variation in saturated vapour pressure ought to be accounted for in such cases. For coarse aerosol particles, the effect is relatively negligible, while for ultrafine particles it may well be dominant.

1.4. Adsorption of N₂ on a porous graphite sample at 77 K yields the tabulated data (see margin) as a function of gas-phase pressure. Suggest which type of isotherm best fits the data, and hence estimate the sample's surface area (assuming that a single molecule occupies an area of 16 Å²). If needed, take the saturated vapour pressure of N₂ at this temperature to be 973.1 mbar.

An obvious first step in deciding which isotherm best fits the data provided is simply to plot the adsorbed mass as a function of gas-phase pressure. Both the Langmuir isotherm and the Kisiuk isotherm ought to show saturation in the adsorbed amount at some pressure, but the graph in Fig. 1 clearly shows that this is not the case here. Indeed, it appears to be broadly consistent with the Brunauer-Emmett-Teller (BET) isotherm, which accounts for the formation of multilayers as the pressure approaches the saturated vapour pressure of the adsorbate species.

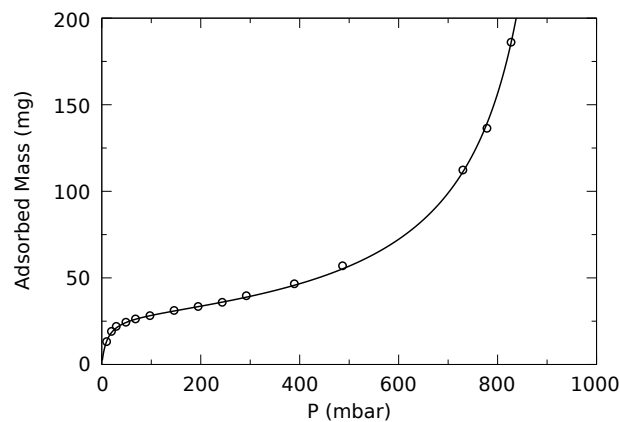


Figure 1: *Plot of adsorbed mass versus pressure.*

In order to confirm true BET behaviour, however, it is sensible to make use of the rearranged form of the isotherm, given as Eqn. 1.49 in Section 1.7. That is, we expect that the data should satisfy

$$\frac{P}{N(P_0 - P)} = \frac{(c - 1)}{cN_s} \left(\frac{P}{P_0} \right) + \frac{1}{cN_s}$$

and hence should produce a straight line when $P/N(P_0 - P)$ is plotted against P/P_0 .

Here, N is the quantity of adsorbed molecules, and N_s the quantity of adsorption sites for these molecules. It will be convenient, therefore, to convert the adsorbed masses provided in the table into adsorbed quantities expressed in moles. This involves, of course, dividing by a factor of 28014 (to account for the mass of N₂ expressed in mg.mol⁻¹).

Pressure, P (mbar)	Adsorbed Mass (mg)	Adsorbed Quantity, N (mol)
9.7	13.2	4.712×10^{-4}
19.5	19.1	6.818×10^{-4}
29.2	22.0	7.853×10^{-4}
48.7	24.4	8.710×10^{-4}
68.1	26.3	9.388×10^{-4}
97.3	28.2	1.007×10^{-3}
146.1	31.2	1.114×10^{-3}
194.7	33.5	1.196×10^{-3}
243.4	35.9	1.282×10^{-3}
292.1	39.7	1.417×10^{-3}
389.2	46.6	1.663×10^{-3}
486.6	57.0	2.035×10^{-3}
729.8	112.3	4.009×10^{-3}
778.5	136.4	4.869×10^{-3}
827.2	186.1	6.643×10^{-3}

Plotting $P/N(P_0 - P)$ against P/P_0 (using $P_0 = 973.1$ mbar) we do indeed obtain a tolerably straight line (see Fig. 2) with slope 1002.6 mol^{-1} and intercept 1.1309 mol^{-1} . As per our straight line equation, we expect the intercept to be given by $1/cN_s$ and the slope to be given by $(c - 1)/cN_s$. Combining these expressions with the values obtained from the graph, we find $c = 887.551$ and $N_s = 9.963 \times 10^{-4} \text{ mol} = 6.000 \times 10^{20}$ adsorption sites.

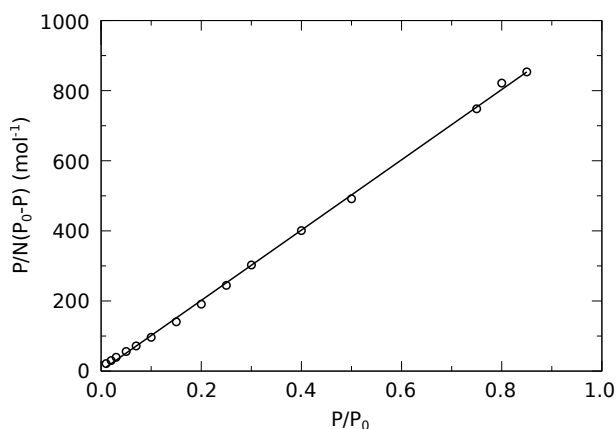


Figure 2: Plot of $P/N(P_0 - P)$ versus P/P_0 to verify BET behaviour.

Since the size of each adsorption site is determined by its ability to accommodate a single N_2 molecule in the first layer, we can simply multiply the number of adsorption sites by the nominal footprint of each molecule (i.e. 16 \AA^2) to obtain an estimate for the total surface area, giving $(6.000 \times 10^{20}) \times (16 \times 10^{-20}) = 96.0 \text{ m}^2$.

Although this estimate might, at first, seem surprisingly large (about the size of the “six-yard box” of a soccer pitch) for what is presumably a fairly small sample (small enough to fit within the experimental chamber), porous graphite can often exhibit effective surface areas of several hundred square metres per gram, so the value derived here is actually fairly modest.

1.5. Use the Clausius-Clapeyron equation to prove that for Langmuirian adsorption the parameter b must be proportional to $\exp(q_a/RT)$ with no other temperature dependence. Armed with this knowledge, how might one extract a value for the constant of proportionality by comparing isotherms collected at different temperatures?

We begin by recalling that the Clausius-Clapeyron equation (Eqn. 1.50 in Section 1.8)

$$\ln(P_2/P_1) = -\frac{q_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

links two temperature/pressure combinations, (T_1, P_1) and (T_2, P_2) that correspond to one specific relative coverage, which we shall simply call θ . Let us, therefore, seek to find relationship between P_1 and P_2 from the Langmuir isotherm, with a view to substituting the results into the above equation.

Starting with the Langmuir isotherm in the version for intact adsorption (Eqn. 1.39 in Section 1.7) we find

$$\theta = \frac{b_1 P_1}{1 + b_1 P_1} = \frac{b_2 P_2}{1 + b_2 P_2}$$

where we explicitly allow that the parameter b may depend upon temperature. That is, b_1 and b_2 apply at temperatures T_1 and T_2 respectively.

From this, we may readily see that

$$b_1 P_1 = b_2 P_2$$

and indeed the Langmuir isotherm for dissociative adsorption (Eqn. 1.42 in Section 1.7)

$$\theta = \frac{\sqrt{b_1 P_1}}{1 + \sqrt{b_1 P_1}} = \frac{\sqrt{b_2 P_2}}{1 + \sqrt{b_2 P_2}}$$

clearly implies the same result. Note that when using the Langmuir isotherm, none of the analysis above depends crucially upon the particular choice made for θ , and indeed this quantity will be absent from the remainder of our discussion. All that matters is that we keep this quantity fixed.

The importance of our finding is that for Langmuirian adsorption we may simply replace P_2/P_1 in the Clausius-Clapeyron equation with b_1/b_2 , giving us

$$\ln(b_1/b_2) = -\frac{q_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

from which we obtain

$$\begin{aligned} \frac{b_1}{b_2} &= \exp \left[\frac{q_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \\ &= \frac{\exp(q_a/RT_1)}{\exp(q_a/RT_2)} \end{aligned}$$

Now, it should be evident that we have always been free to write

$$b = f(T) \exp(q_a/RT)$$

without any loss of generality, since the prefactor $f(T)$ could take literally any functional form, including one that would cancel the exponential factor and replace it with some other temperature dependence entirely. Our latest result, however, provides us with the strict constraint

$$f(T_1) = f(T_2)$$

for any arbitrarily chosen pair of temperatures, T_1 and T_2 , and clearly this condition can only be satisfied when $f(T)$ is, in fact, independent of temperature altogether. The only temperature dependence in the value of b is, therefore, captured by the exponential factor, and the pre-factor may be treated as a constant of proportionality, f , whose value we must now attempt to extract by comparing isotherms obtained at different temperatures.

Having thus established that the pre-factor, f , must indeed be constant with respect to changes in temperature, we may now note that

$$b = f \exp(q_a/RT)$$

implies that

$$\ln b = \frac{q_a}{RT} + \ln f$$

and hence that a plot of $\ln b$ versus $1/T$ (for Langmuir isotherms recorded at a range of temperatures) ought to have gradient q_a/R and intercept $\ln f$, thus permitting the constant of proportionality to be determined.