

# **Oxford Chemistry Primers: Foundations of Surface Science**

**Solutions for Chapter Four: Kinetics and Dynamics**

**4.1. An initially clean surface is exposed to carbon monoxide at a partial pressure of  $10^{-10}$  mbar ( $10^{-8}$  Pa) and a temperature of 100 K. The initial sticking probability is measured to be 0.5, and the surface density of adsorption sites is  $10^{15}$   $\text{cm}^{-2}$ . Assuming that adsorption is non-dissociative and Langmuirian, and that desorption is negligible, how long would it take to reach half of saturation coverage? Compare with pressures of  $10^{-7}$ ,  $10^{-2}$ , and  $10^3$  mbar.**

We are told to assume non-dissociative Langmuirian adsorption, so from Eqn. 1.35 (in Section 1.7) we may write

$$r_a = k_a P(1 - \theta)$$

for the adsorption rate, with  $k_a$  being a rate constant,  $P$  the gas-phase pressure, and  $\theta$  the relative coverage.

From Eqn. 4.2 (in Section 4.2) we also have

$$r_a = Fs$$

with  $F$  being the molecular flux reaching the surface, and  $s$  the sticking probability.

Let us proceed by considering the clean surface, for which  $s = s_0$  (i.e. the initial sticking probability) and  $\theta = 0$ . Comparing our two expressions for  $r_a$  under these circumstances, we conclude that

$$k_a = \frac{Fs_0}{P}$$

which we may insert into our first expression to obtain

$$r_a = Fs_0(1 - \theta)$$

as a convenient equation for the non-dissociative Langmuirian adsorption rate when both the flux and the initial sticking probability are known.

Since we define  $r_a$  to be the number of adsorbates sticking per site per unit time, we must simply have

$$r_a = \frac{d\theta}{dt}$$

and hence may write

$$\frac{d\theta}{(1 - \theta)} = Fs_0 dt$$

2

Integrating this last expression, we find

$$-\ln(1 - \theta) = F s_0 t + C$$

with  $C$  being some constant. Setting  $\theta = 0$  at  $t = 0$ , however, we readily conclude that we must have  $C = 0$ . Accordingly, we obtain

$$\theta = 1 - \exp(-F s_0 t)$$

which clearly approaches unity asymptotically as time increases without limit.

We have been asked to consider the time taken to reach half of saturation coverage, so let us call this time  $\tau$  and write

$$\frac{1}{2} = 1 - \exp(-F s_0 \tau)$$

before rearranging to get

$$\tau = -\frac{\ln(1/2)}{F s_0}$$

as our general solution.

For our particular case, we need now to calculate the flux,  $F$ , given by Eqn. 4.3 (in Section 4.2) as

$$F = \frac{P A_0 N_A}{\sqrt{2\pi M R T}}$$

with  $A_0$  being the surface area per adsorption site,  $N_A$  the Avogadro constant,  $M$  the molar mass of the adsorbing species,  $R$  the molar gas constant, and  $T$  the gas-phase temperature. Being careful to express each quantity in SI base units, we obtain

$$F = \frac{10^{-8} \times (1/10^{19}) \times (6.022 \times 10^{23})}{\sqrt{2\pi \times (2.801 \times 10^{-2}) \times 8.314 \times 100}} = 4.978 \times 10^{-5} \text{ s}^{-1}$$

where we have used  $2.801 \times 10^{-2}$  kg for the molar mass of carbon monoxide (i.e. 28.01 g.mol<sup>-1</sup>).

Inserting this value into our general expression for the time taken to reach half of the saturation coverage, along with  $s_0 = 0.5$  as given in the question, we find

$$\tau = -\frac{\ln(1/2)}{(4.978 \times 10^{-5}) \times 0.5} = 27848 \text{ s}$$

which amounts to roughly seven and three-quarter hours.

Since the time in question is inversely proportional to the flux, which in turn is directly proportional to the gas-phase pressure, we can work out the additional cases quite easily. At a pressure of  $10^{-7}$  mbar (a typical pressure used for deliberate dosing of samples) the time to reach half of saturation coverage will be about 28 s. At a pressure of  $10^{-2}$  mbar (rough vacuum) this will be reduced to 278  $\mu\text{s}$ , and at a pressure of  $10^3$  mbar (standard pressure) such a coverage would be reached in less than 3 ns.

Clearly, the concept of a truly clean surface only really applies under ultra-high vacuum conditions, and becomes increasingly meaningless as one approaches ambient conditions.

**4.2. Differentiate Eqn. 4.6 with respect to temperature. Set the result to zero, and hence obtain Eqn. 4.8 for the temperature at which the first-order desorption rate is maximised. Why is this procedure much less useful in the zero-order and second-order cases?**

Let us start with Eqn. 4.6 (Section 4.3) for first-order desorption

$$r_d = \nu\theta \exp(-E_d/RT)$$

and differentiate with respect to temperature, obtaining

$$\frac{dr_d}{dT} = \nu \left( \frac{d\theta}{dT} + \frac{\theta E_d}{RT^2} \right) \exp(-E_d/RT)$$

assuming that  $\nu$  is independent of both temperature and coverage.

Now, let us consider that particular temperature,  $T_m$ , at which the derivative disappears (i.e. the rate reaches a maximum). We then have

$$0 = \nu \left( \left( \frac{d\theta}{dT} \right)_{T=T_m} + \frac{\theta_m E_d}{RT_m^2} \right) \exp(-E_d/RT_m)$$

which simplifies to

$$\frac{E_d}{RT_m^2} = -\frac{1}{\theta_m} \left( \frac{d\theta}{dT} \right)_{T=T_m}$$

quite straightforwardly, with  $\theta_m$  being the instantaneous coverage at the moment when  $T = T_m$ .

Less straightforwardly, we may also recall that the surface temperature,  $T$ , is directly linked to the time,  $t$ , by the heating rate,  $\beta$  (i.e.  $dT = \beta dt$ ). Thus we may write

$$\frac{d\theta}{dT} = \frac{1}{\beta} \frac{d\theta}{dt}$$

and so (recognising that  $r_d = -d\theta/dt$ ) we have

$$\begin{aligned} \frac{E_d}{RT_m^2} &= -\frac{1}{\beta\theta_m} \left( \frac{d\theta}{dt} \right)_{T=T_m} = \frac{1}{\beta\theta_m} \nu\theta_m \exp(-E_d/RT_m) \\ &= \frac{\nu}{\beta} \exp(-E_d/RT_m) \end{aligned}$$

which confirms Eqn. 4.8 (Section 4.3) as required.

If we were to start instead with Eqn. 4.5 (Section 4.3) for zero-order desorption

$$r_d = \nu \exp(-E_d/RT)$$

the result of differentiation with respect to temperature would be

$$\frac{dr_d}{dT} = \nu \frac{E_d}{RT^2} \exp(-E_d/RT)$$

which would seem to imply an ever-increasing desorption rate as the temperature is increased. Clearly this cannot be true indefinitely for a real system, but the peak in desorption rate (and subsequent collapse to zero desorption) is dictated by complete exhaustion of the adsorbate supply, not by the desorption rate equation. In other words, prediction of the temperature at which desorption is maximised lies outside the model, and equating our last equation to zero will yield no helpful insight.

If, on the other hand, we were to start with Eqn. 4.7 (Section 4.3) for second-order desorption

$$r_d = \nu\theta^2 \exp(-E_d/RT)$$

the result of differentiation with respect to temperature would be

$$\begin{aligned} \frac{dr_d}{dT} &= \nu \left( 2\theta \frac{d\theta}{dT} + \frac{\theta^2 E_d}{RT^2} \right) \exp(-E_d/RT) \\ &= \nu\theta \left( 2 \frac{d\theta}{dT} + \frac{\theta E_d}{RT^2} \right) \exp(-E_d/RT) \end{aligned}$$

which looks a little more promising.

Indeed, equating this expression to zero at  $T = T_m$  leads us to

$$\frac{E_d}{RT_m^2} = -\frac{2}{\theta_m} \left( \frac{d\theta}{dT} \right)_{T=T_m}$$

which differs from our equivalent deduction in the first-order case by an innocent factor of two.

Our problems begin, however, when we replace the temperature derivative with a time derivative, since we now obtain

$$\begin{aligned} \frac{E_d}{RT_m^2} &= -\frac{2}{\beta\theta_m} \left( \frac{d\theta}{dt} \right)_{T=T_m} = \frac{1}{\beta\theta_m} \cdot \nu\theta_m^2 \exp(-E_d/RT_m) \\ &= \theta_m \frac{\nu}{\beta} \exp(-E_d/RT_m) \end{aligned}$$

in which a factor of  $\theta_m$  still remains. The practical upshot of this is that the equation does not, in fact, uniquely link the values of  $\nu$  and  $E_d$  unless we can somehow find out the coverage at the moment of maximum desorption rate.

We can make progress, however, by noting that second-order TPD curves are very nearly symmetric, implying that  $\theta_m \approx \theta_i/2$ , with  $\theta_i$  being the initial coverage. Thus, we have

$$\frac{E_d}{RT_m^2} = \frac{\nu\theta_i}{2\beta} \exp(-E_d/RT_m)$$

and hence

$$\ln(\theta_i T_m^2) = \ln\left(\frac{2\beta E_d}{\nu R}\right) + \left(\frac{E_d}{R}\right) \frac{1}{T_m}$$

so that a plot of  $\ln(\theta_i T_m^2)$  against  $1/T_m$  (for a series of experiments with different starting coverages, but with a common heating rate) should yield a straight line of gradient  $E_d/R$ . A value for  $E_d$  could thus be extracted, and substitution of this back into the preceding equation would allow for  $\nu$  also to be obtained. All of this does, of course, pre-suppose that we are able to estimate different  $\theta_i$  values with reasonable accuracy.

It is possible, therefore, to ascertain the key desorption parameters,  $E_d$  and  $\nu$ , using only knowledge of the peak position,  $T_m$ , even for the second-order case, so long as we can measure initial coverage. But, unlike the first-order example, it will be necessary to conduct multiple experiments, with different known initial coverages, in order to do so.

One could, alternatively, simply treat the product  $\nu\theta_i$  as an unknown variable whose value may be guessed (just as the value of  $\nu$  must be guessed in the first-order case). Analysis could then be carried through based upon a single experiment, but whilst we can probably guess the initial coverage to within a factor of ten, it is rather harder to imagine what a reasonable attempt frequency should be for recombinative desorption. Estimates of  $E_d$  obtained in this way would, therefore, be subject to somewhat more uncertainty than those for a first-order process.

**4.3. Given the following data for first-order desorption at different heating rates, use the Redhead formula (Eqn. 4.9) to estimate the activation barrier for desorption (assuming some reasonable pre-exponential factor) for each heating rate separately. Then, use Eqn. 4.10 to obtain both the activation barrier and the pre-exponential factor, by plotting the data for different heating rates on a suitable graph. Comment on the discrepancy between the two methods.**

To apply the Redhead formula (Eqn. 4.9 from Section 4.3)

$$E_d = RT_m \left[ \ln \left( \frac{\nu T_m}{\beta} \right) - 3.64 \right]$$

it will be necessary for us to assume some appropriate value for the pre-exponential factor,  $\nu$ . As mentioned in the text, a value of  $\nu = 10^{13} \text{ s}^{-1}$  is often thought reasonable, so that is what we shall use here. Evaluating for each entry in the table of data, we get

$\beta$ (K.s <sup>-1</sup> )	0.5	1.0	2.0	5.0	10.0	15.0	25.0
$T_m$ (K)	450	455	463	475	485	490	495
$E_d$ (kJ.mol <sup>-1</sup> )	123.8	122.6	122.2	121.8	121.7	121.3	120.5

in which there is clearly a trend toward lower estimated adsorption heat at higher heating rates (as opposed to random noise in the estimated values). This is an indicator that the assumed pre-exponential factor is probably somewhat too low, whereas an increasing trend might suggest that the value used was too low.

One could, of course, proceed to use trial an error, in search of a guess for the pre-exponential factor that yields no strong trend either way, but a more systematic approach will be to make use of Eqn. 4.10 (Section 4.3) which takes the form

$$\ln \left( \frac{RT_m^2}{\beta} \right) = \left( \frac{E_d}{R} \right) \frac{1}{T_m} + \ln \left( \frac{E_d}{\nu} \right)$$

and permits a solution by graphical means.

Plotting  $\ln(RT_m^2/\beta)$  against  $1/T_m$  (see Fig. 1) we observe roughly linear correlation, indicating that Eqn. 4.10 holds reasonably well, aside from some experimental noise. Fitting a straight line to the data, we obtain a gradient of 17290 K and an intercept of  $-23.55$ . Clearly the slope should take the value  $E_d/R$ , implying that we must have

$$E_d = 17290 \times 8.314 = 143.8 \text{ kJ.mol}^{-1}$$

which is quite close to, but a little higher than, the values obtained from the Redhead formula.



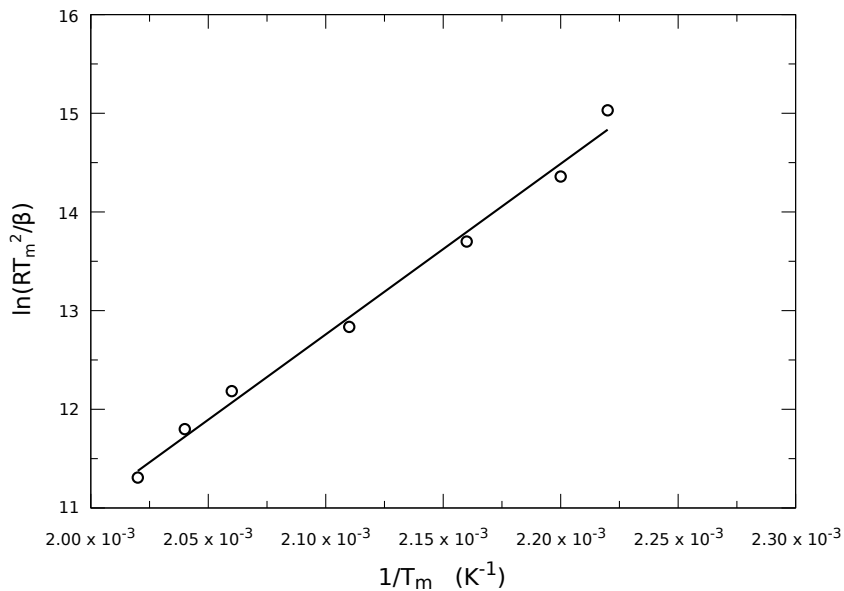


Figure 1: Plot of  $\ln(RT_m^2/\beta)$  against  $1/T_m$  to ascertain  $E_d$  and  $\nu$ .

Likewise, the intercept should take the value  $\ln(E_d/\nu)$ , so that we have

$$\nu = \frac{E_d}{\exp(-23.55)} = \frac{143750}{\exp(-23.55)} = 2.43 \times 10^{15} \text{ s}^{-1}$$

which clearly differs somewhat from the assumption of  $10^{13} \text{ s}^{-1}$  that we used in the Redhead formula above.

Indeed, had we used an estimate for  $\nu$  of  $2.5 \times 10^{15} \text{ s}^{-1}$  in the Redhead formula, instead of  $10^{13} \text{ s}^{-1}$ , we would have obtained the following results for each individual data point

$\beta$ ( $K.s^{-1}$ )	0.5	1.0	2.0	5.0	10.0	15.0	25.0
$T_m$ (K)	450	455	463	475	485	490	495
$E_d$ ( $\text{kJ.mol}^{-1}$ )	144.5	143.5	143.4	143.6	143.9	143.8	143.2

in which there is no clear trend, only a little noise, and the mean value of  $143.7 \text{ kJ.mol}^{-1}$  lies very close to the value of  $143.8 \text{ kJ.mol}^{-1}$  derived from Eqn. 4.10. It is notable, however, that even using a value for  $\nu$  that differed from our best estimate by a factor of almost 250, the adsorption heats obtained via the Redhead formula for individual data points lie only 14-16% below the value inferred from the whole dataset. Clearly the Redhead formula allows us to make a reasonable estimate of adsorption heat from a single experiment at some convenient heating rate, but a better estimate can generally be achieved if time permits to conduct several experiments at different heating rates.

**4.4. The surface-catalysed reaction  $A + B \rightarrow C$  proceeds via a Langmuir-Hinshelwood mechanism. Assuming that the surface coverages of all species follow the form given in Eqn. 1.43 (with non-dissociative adsorption throughout) write a general expression for the rate of forward reaction in terms of their gas-phase pressures,  $P_A$ ,  $P_B$ , and  $P_C$ . Comment upon the kinetics in circumstances where (i) one of the reactants adsorbs much more strongly than either the product or the other reactant; and (ii) the product adsorbs much more strongly than either reactant.**

We are told to make use of Eqn. 1.43 (from Section 1.7) which is

$$\theta_i = \frac{(b_i P_i)^{n_i}}{1 + \sum_j (b_j P_j)^{n_j}}$$

where the  $b_i$  and  $P_i$  represent the Langmuir coefficients and gas-phase partial pressures for species labelled  $i$ . The exponents  $n_i$  simply take the value of unity for non-dissociative adsorption.

Using this, we can write the following expressions for the relative coverages of species A, B, and C

$$\begin{aligned}\theta_A &= \frac{b_A P_A}{1 + b_A P_A + b_B P_B + b_C P_C} \\ \theta_B &= \frac{b_B P_B}{1 + b_A P_A + b_B P_B + b_C P_C} \\ \theta_C &= \frac{b_C P_C}{1 + b_A P_A + b_B P_B + b_C P_C}\end{aligned}$$

where it is clear that the numerators differ but the denominators do not.

For a Langmuir-Hinshelwood mechanism, the forward reaction rate ought to be proportional to the coverages of species A and B, and thus takes the general form

$$r = k \frac{b_A P_A b_B P_B}{(1 + b_A P_A + b_B P_B + b_C P_C)^2}$$

in which we introduce a rate constant,  $k$ .

Addressing the particular special cases raised in the question, the first specifies that one of the reactants (let us say species A) adsorbs much more strongly than either the product or the other reactant. We are therefore justified in expecting  $b_A P_A \gg b_B P_B$  and  $b_A P_A \gg b_C P_C$ , so that we obtain

$$r \approx k \frac{b_A P_A b_B P_B}{(1 + b_A P_A)^2}$$

in which the pressure of the product does not feature.

For a sufficiently low pressure of species A ( $b_A P_A \ll 1$ ) we may therefore expect a reaction that is first-order in both reactant pressures, with

$$r \approx k b_A P_A b_B P_B$$

in this case.

Once the product  $b_A P_A$  significantly exceeds unity, however, we find

$$r \approx k \frac{b_B P_B}{b_A P_A}$$

which implies a reaction rate that is inversely related to the pressure of species A (but still proportional to the pressure of species B). In effect, the strongly adsorbing reactant species (A) will tend to block sites that might otherwise accommodate the other reactant species (B). Since the reaction relies on both species being present on the surface, this results in a form of self-poisoning.

The second special case asks us to consider a situation where the product (C) binds much more strongly than either reactant, so that we should expect  $b_C P_C \gg b_A P_A$  and  $b_C P_C \gg b_B P_B$ . Our general expression then becomes

$$r \approx k \frac{b_A P_A b_B P_B}{(1 + b_C P_C)^2}$$

from which we deduce that the reaction would be strongly suppressed by any appreciable pressure of the product species (kinetic order approaching  $-2$  as the relevant partial pressure increases).

#### 4.5. How would your answers to the last question differ if the reaction proceeded via an Eley-Rideal mechanism?

If the reaction occurs via an Eley-Rideal mechanism, we can assume that one of our reactant species (let us say species B) no longer adsorbs appreciably on the surface at all. We may therefore modify our remaining coverage expressions (from the previous question) to the forms

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_C P_C}$$

$$\theta_C = \frac{b_C P_C}{1 + b_A P_A + b_C P_C}$$

and the general expression for the forward reaction rate is just

$$r = k \frac{b_A P_A P_B}{1 + b_A P_A + b_C P_C}$$

where the proportionality to  $P_B$  arises due to the flux of species B from the gas phase, and not from the coverage of species B on the surface.

Considering the special case where adsorption of species A dominates over that of species C (as well as that of species B) we set  $b_A P_A \gg b_C P_C$  and obtain

$$r \approx k \frac{b_A P_A P_B}{1 + b_A P_A}$$

in which the pressure of species C no longer features. In fact, for a sufficiently high partial pressure of species A, we will eventually find

$$r \approx k P_B$$

so that the rate depends only upon the gas-phase pressure of the non-adsorbing species.

Finally, if the product binds much more strongly than reactant A, we may set  $b_C P_C \gg b_A P_A$ , and the Eley-Rideal forward reaction rate becomes

$$r \approx k \frac{b_A P_A P_B}{1 + b_C P_C}$$

which is proportional to both of the reactant pressures. The rate will then be suppressed by increasing partial pressure of the product species, approaching a kinetic order of  $-1$  in the limit that this becomes high.

Crucially, the kinetic behaviour in different regimes will differ between the Langmuir-Hinshelwood and Eley-Rideal mechanisms, so that the two modes can potentially be determined through systematic experimental studies.