

Surface Science: Foundations of Catalysis and Nanoscience
List of corrections to 3rd Edition
<http://courses.wcupa.edu/kkolasinski/surfacescience/c3e.pdf>

Special thanks to Dhananjay Kumar for pointing out errors in the LEED section and being persistent in getting me to correct them.

Chapter 1

In Table 1.1 under "bcc structure" the entry should read "Density of (110) / cm⁻² × 10⁻¹⁵".

Chapter 2

p. 74–75

It's Davisson not Davidson and de Broglie first proposed matter waves in 1923.

p. 77

Equations (2.5.15) and (2.5.16) should read

$$\mathbf{M} = \frac{1}{\det \mathbf{M}^*} \begin{pmatrix} m_{22}^* & -m_{21}^* \\ -m_{12}^* & m_{11}^* \end{pmatrix} \quad (2.5.15)$$

$$\mathbf{M}^* = \frac{1}{\det \mathbf{M}} \begin{pmatrix} m_{22} & -m_{21} \\ -m_{12} & m_{11} \end{pmatrix} \quad (2.5.16)$$

p 80

$$2M = \frac{12h^2}{mk_B} \left(\frac{\cos \varphi}{\lambda} \right)^2 \frac{T}{\theta_D^2}. \quad (2.5.23)$$

p. 108

2.14 Given LEED patterns (a)–(g) in Fig. 2.31

p. 109 Fig. 2.31(a) has an added row and the caption should be changed as below.

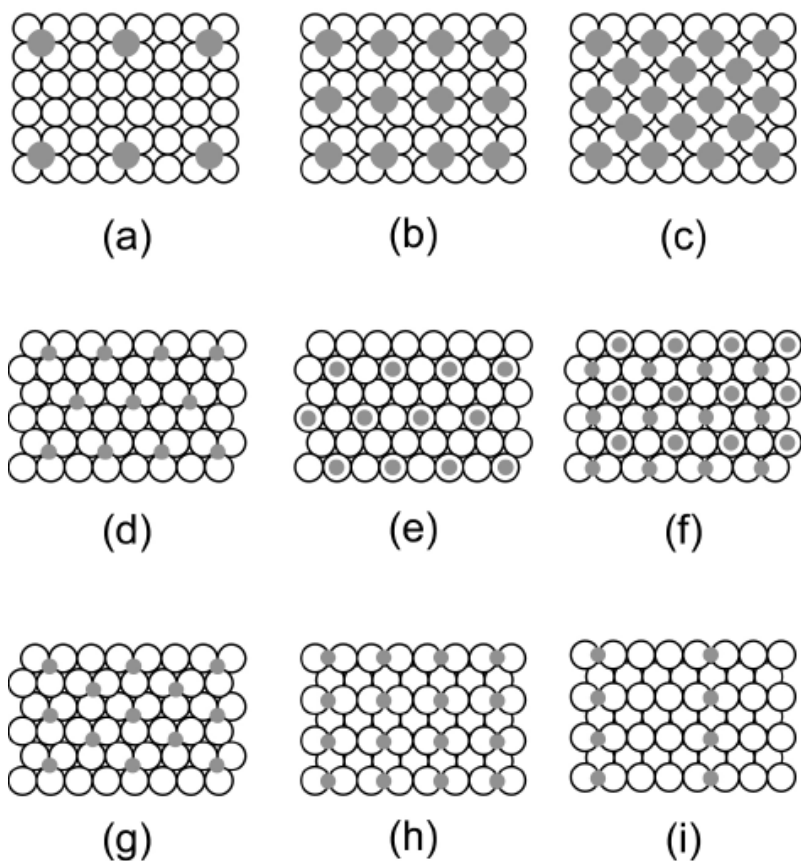


Fig. 2.31 Structures (a)-(i): see Exercise 2.12.

Figure 2.32 Low-energy electron diffraction (LEED) patterns (a)-(g): see Exercise 2.14

Chapter 4

p. 226 In Eq. (4.11.16), the right hand subscript should be a g.

$$\mu_a = \mu_g \quad (4.11.16)$$

Chapter 5

p. 257 $c^\circ = 1 \text{ mol dm}^{-3}$

p. 264 In exercise 5.10 it should say that the usual pre-exponential factor in electrochemistry is $1 \times 10^4 \text{ cm s}^{-1}$.

Chapter 6

p. 281 Equation (6.4.30) should read

$$\theta_* = \left(1 + K_1 \frac{P_{N_2}}{P_0} + \frac{P_{NH_3} P_0^{0.5}}{K_3 K_4 K_5 K_6 K_7^{1.5} P_{H_2}^{1.5}} + \frac{P_{NH_3}}{K_4 K_5 K_6 K_7 P_{H_2}} + \frac{P_{NH_3}}{K_5 K_6 K_7^{0.5} P_{H_2}^{0.5} P_0^{0.5}} + \frac{P_{NH_3}}{K_6 P_0} + K_7^{0.5} \frac{P_{H_2}^{0.5}}{P_0^{0.5}} \right)^{-1}$$

Here's a section that should have been added.

6.4.3 Counting sites in surface kinetics

All of the above has been derived for a gas-phase reaction. All of it is applicable to surface reactions; however, one must also keep in mind the single greatest differentiating factor of heterogeneous reaction kinetics as compared to kinetics in other phases: one must count sites. If the above reaction scheme were to be extended to a surface with I_1 , I_2 and R_2 present as adsorbed species (assuming that R_1 adsorbs dissociatively, and that it and P are so weakly bound as to have negligible coverage) then we would also have to keep track of the number of empty sites θ_* according to

$$\theta_* = 1 - \theta_{I_1} - \theta_{I_2} - \theta_{R_2} . \quad (6.4.17)$$

The necessity to count sites means that even for a simple reaction mechanism, there is not a unique relationship between the reaction order of gas phase species and the reaction rate. Consider a simple three-step reaction involving competitive adsorption of two species A and B to form a product that does not bind to the surface. The overall reaction



follows a Langmuir-Hinshelwood mechanism composed of the following three elementary steps.



In Exercise 4.12, we found that competitive absorption following Langmuir kinetics leads to equilibrium coverages of A and B described by

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad (6.4.22)$$

and

$$\theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B} \quad (6.4.23)$$

with $K_A = k_1/k_{-1}$ and $K_B = k_2/k_{-2}$. If the first two steps are equilibrated and the rate is determined by the surface reaction in the third step, the rate of reaction is given by

$$R = k_3 \vartheta_A \vartheta_B , \quad (6.4.24)$$

which upon substitution from Eqs. (6.4.22) and (6.4.23) yields

$$R = \frac{k_3 K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2} . \quad (6.4.25)$$

Eq. (6.4.25) does not represent a well-defined order for either p_A or p_B . Consider first the low-pressure limit in which $K_A p_A \ll 1$ and $K_B p_B \ll 1$. Thus,

$$R = k p_A p_B. \quad (6.4.26)$$

In this limit, the rate equation is now first-order in both p_A and p_B with an effective rate constant $k = k_3 K_A K_B$. Such kinetics is observed frequently as the conditions (reversible adsorption of the reactants, weakly interacting product and sufficiently low pressure) are broadly attainable. The oxidation of CO with O₂ to form CO₂ follows such kinetics at low pressure and sufficiently high temperature to ensure that both reactants are mobile and randomly adsorbed.

If B is strongly bound such that $K_B p_B \gg 1$ and it can block the adsorption of A, which is at low enough pressure such that $K_A p_A \ll 1$, then

$$R = k' p_A p_B^{-1}, \quad (6.4.27)$$

with effective rate constant $k' = k_3 K_A / K_B$. The rate law is now first-order in p_A but -1 order in p_B . In other words, B acts as an inhibitor because it blocks sites onto which A is attempting to adsorb. Such efficient site blocking means that the surface is starved for A and further increases in the pressure of B reduce the overall rate. This is exactly the scenario that was described in Section 3.14.1 in which CO acts as an inhibitor at high pressure because it is able to block O₂ dissociation. Therefore, we see that without any change in mechanism, site blocking engenders a change in effective reaction order with respect to the pressures of the reactants.

Chapter 8
p. 387

$$\Delta G^\ddagger = (\lambda + \Delta G^\circ)^2 / 4\lambda. \quad (8.4.4)$$

p. 387–388

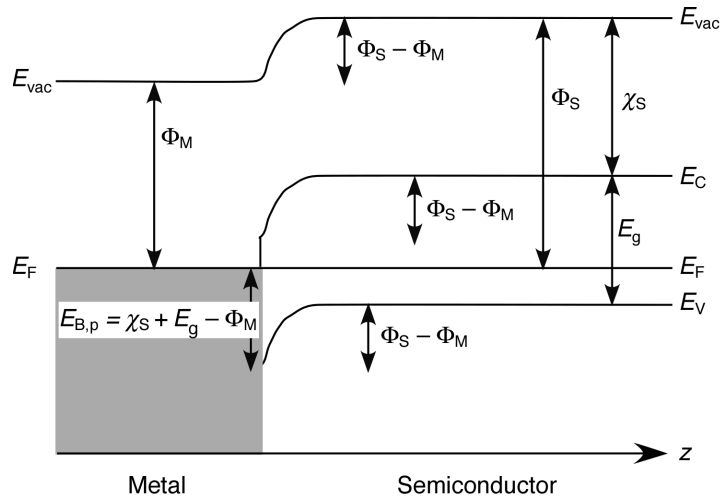
$$k = \frac{2\pi}{\hbar} |H_{DA}|^2 (4\pi\lambda k_B T)^{-1/2} \exp(-\Delta G^\ddagger / k_B T) \quad (8.4.6)$$

The coupling matrix element depends on orbital overlap and symmetry. Thus, it varies exponentially with distance according to

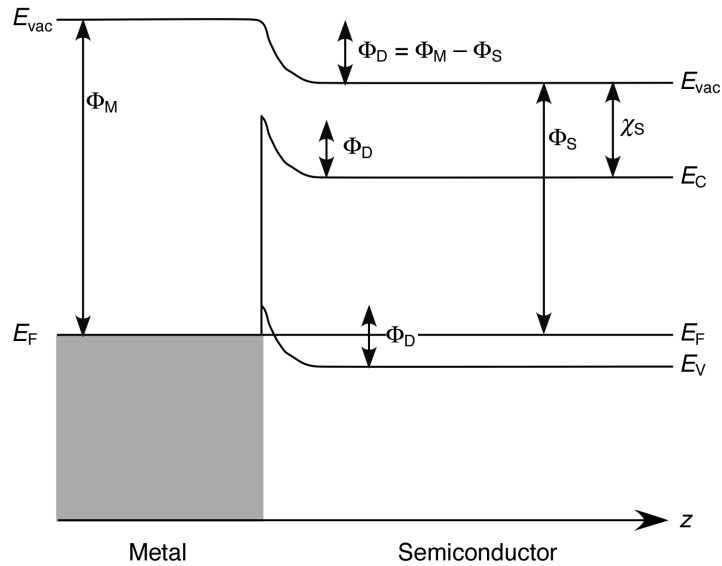
$$H_{DA} = \langle D | H | A \rangle = V_0 \exp[-\beta(R - R_0)/2] \quad (8.4.7)$$

where V_0 is the donor/acceptor coupling matrix element at the van der Waals separation R_0 , and β is a constant that typically lies in the range 0.8–1.2 Å⁻¹ [102]. Furthermore, for certain symmetry combinations, it may vanish or only be allowed due to vibronic mixing of non-totally-symmetric modes. Therefore, the electron transfer rate constant should exhibit a distance dependence that is determined by the exponential decay of H_{DA} according to $k = k_0 \exp[-\beta(R - R_0)]$.

Chapter 9



(a)



(b)

Figure Ex 1.10 Band bending for a p -type semiconductor. (a) Schottky barrier formation. (b) Ohmic contact

Chapter 10

p. 432

2.12 For structures (a)–(i) in Figure 2.31

p. 436

2.14 Given LEED patterns (a)–(g) in Figure 2.32

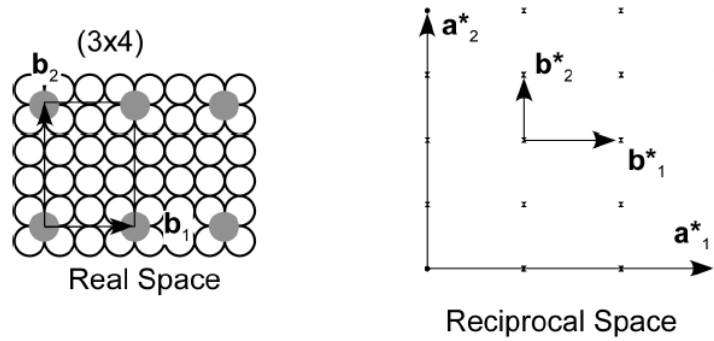


Fig.Ex 2.12(a)
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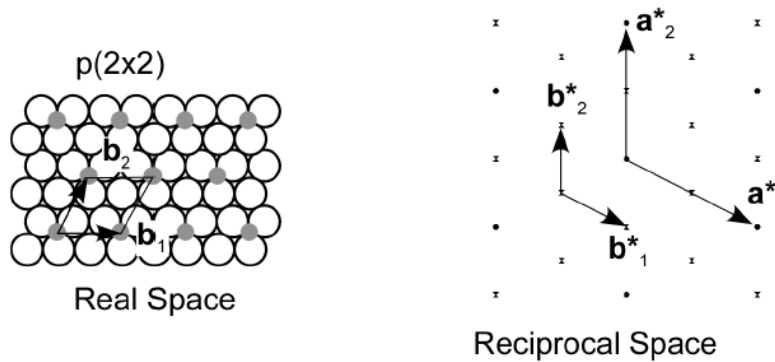


Fig.Ex 2.12(d)
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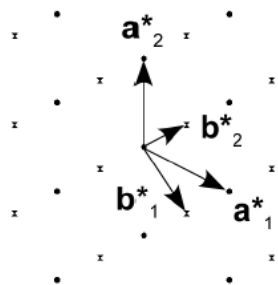
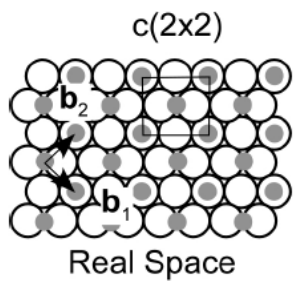


Fig.Ex 2.12(f)
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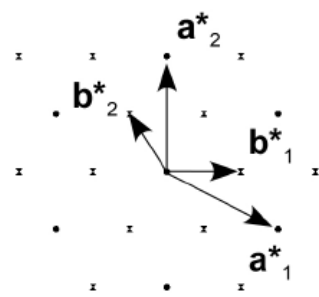
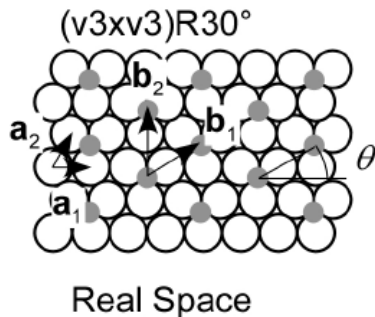


Fig.Ex 2.12(g)
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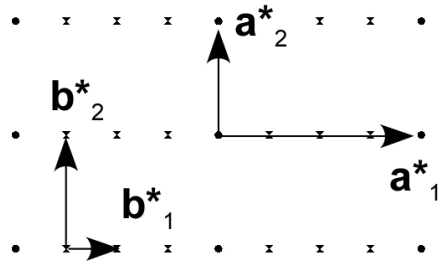
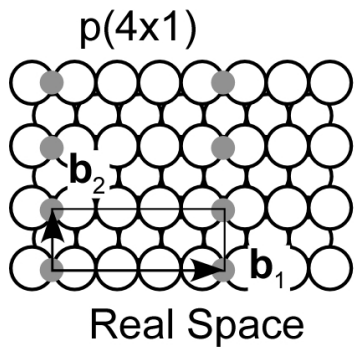


Fig.Ex 2.12(i)
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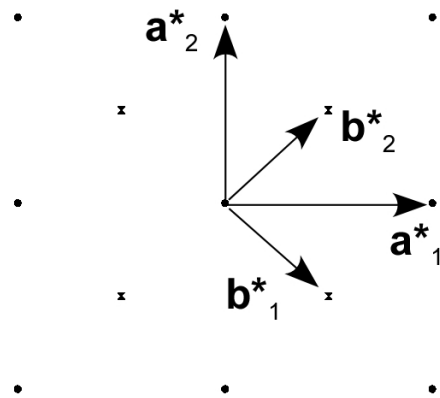
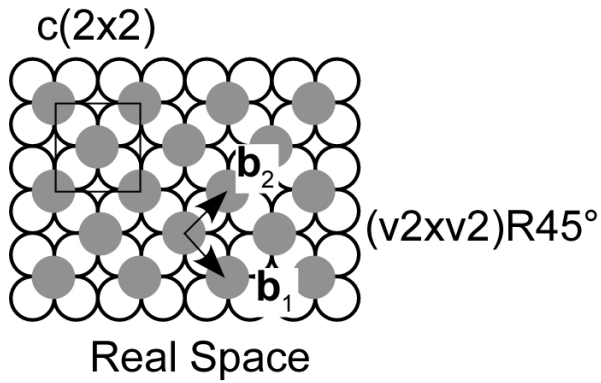


Fig.Ex 2.14(a)
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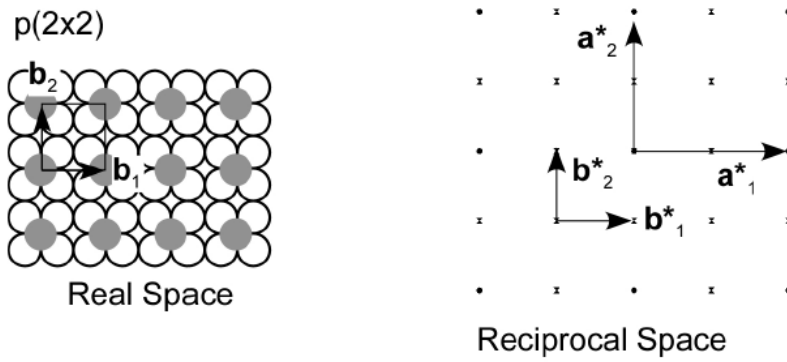


Fig.Ex 2.14(b)
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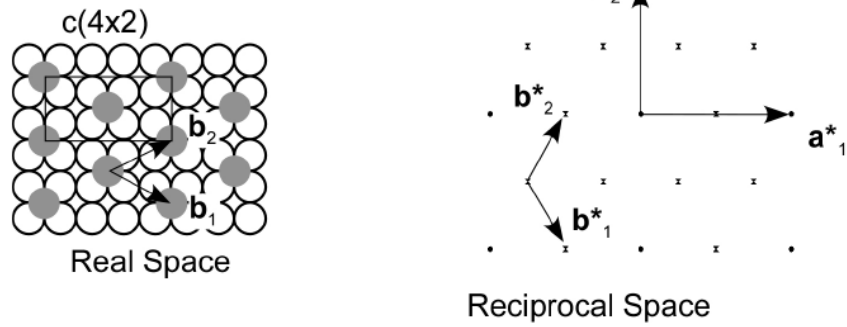


Fig.Ex 2.14(c)
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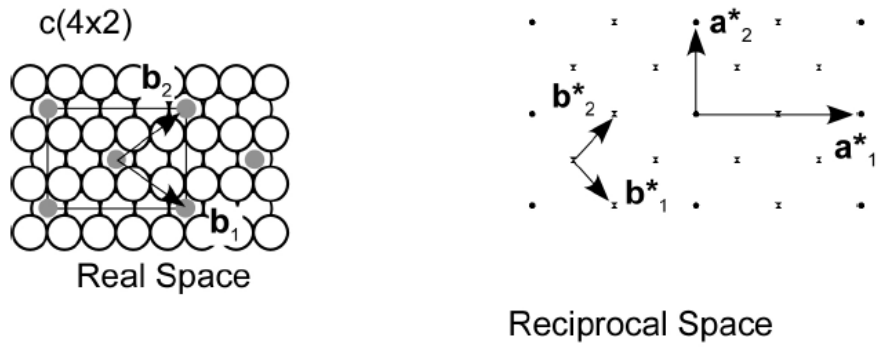


Fig. Ex 2.14(d)
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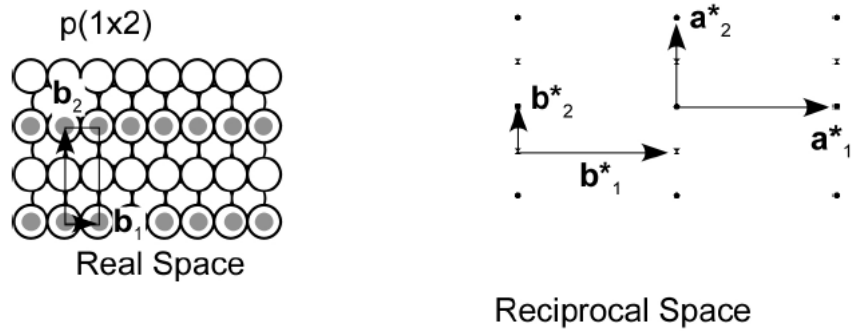


Fig. Ex 2.14(e)
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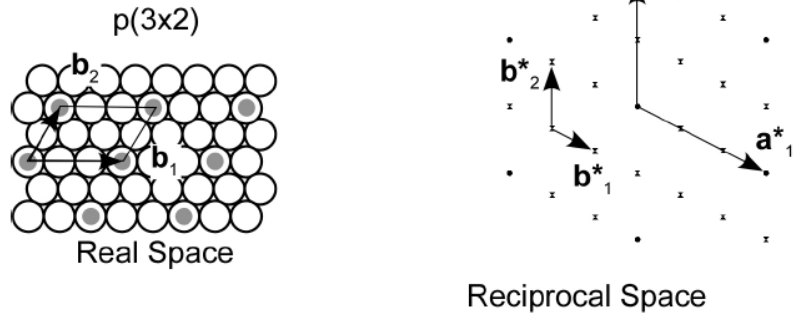


Fig.Ex 2.14(f)
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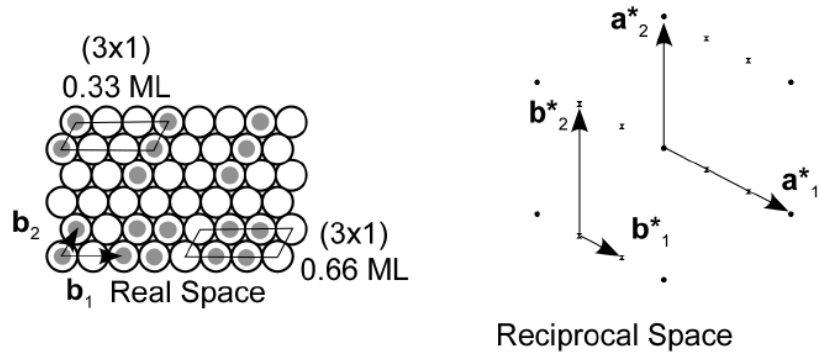


Fig.Ex 2.14(g)
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p. 472, Exercise 4.8: The last equation should read

$$A = s_0 \frac{k_B T}{h} \frac{q_{\ddagger}}{q_a} = 0.9 (7.0845 \times 10^{12} \text{ s}^{-1}) \frac{30870.6}{70.8151} = 2.8 \times 10^{15} \text{ s}^{-1}$$

p. 482, Exercise 4.24, in Eq. (4.11.16), the right hand subscript should be a g.

$$\mu_a = \mu_g \tag{4.11.16}$$

Chapter 13

p. 49 In exercise 5.10 it should say that the usual pre-exponential factor in electrochemistry is $1 \times 10^4 \text{ cm s}^{-1}$. The answer for $A_{\text{electrode}}$ is correct in units of cm s^{-1} .