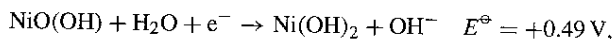
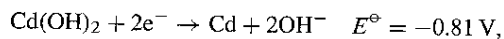


**CHEM 402—Physical Chemistry**  
**Chapter 25 Homework Solutions**

**E25.31(a)** The cell half-reactions are



Therefore the standard cell potential is  $\boxed{+1.30 \text{ V}}$ . If the cell is working reversibly yet producing 100 mA, the power it produces is

$$P = I E = (100 \times 10^{-3} \text{ A}) \times (1.3 \text{ V}) = \boxed{0.13 \text{ W}}.$$

**E25.32(a)**

$$\frac{(1.0 \text{ A m}^{-2}) \times (3.16 \times 10^7 \text{ s yr}^{-1})}{9.65 \times 10^4 \text{ C mol}^{-1}} = 327 \text{ mol e}^- \text{ m}^{-2} \text{ yr}^{-1} = 164 \text{ mol Fe m}^{-2} \text{ yr}^{-1}$$

$$\frac{(164 \text{ mol m}^{-2} \text{ yr}^{-1}) \times (55.85 \text{ g mol}^{-1})}{7.87 \times 10^6 \text{ g m}^{-3}} = 1.2 \times 10^{-3} \text{ m yr}^{-1} = \boxed{1.2 \text{ mm yr}^{-1}}$$

## Solutions to problems

### Solutions to numerical problems

**P25.2**

$$\begin{aligned} Z_W &= \frac{p}{(2\pi mkT)^{1/2}} \quad [25.1a] \\ &= \frac{p/\text{Pa}}{[(2\pi) \times (32.0) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})]^{1/2}} \\ &= (2.69 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}) \times p/\text{Pa} = (2.69 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}) \times p/\text{Pa} \end{aligned}$$

(a) At 100 kPa,  $Z_W = \boxed{2.69 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}}$

(b) At 1.000 Pa,  $Z_W = \boxed{2.69 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}}$

The nearest neighbor in titanium is 291 pm, so the number of atoms per  $\text{cm}^2$  is approximately  $1.4 \times 10^{15}$  (the precise value depends on the details of the packing, which is hcp, and the identity of the surface). The number of collisions per exposed atom is therefore  $Z_W/(1.4 \times 10^{15} \text{ cm}^{-2})$ .

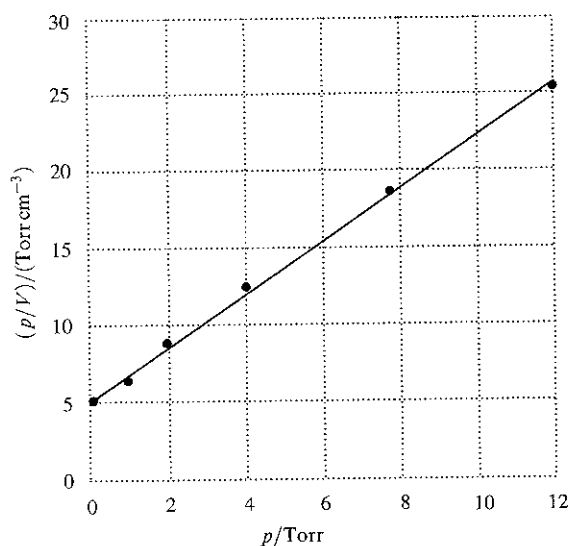
(a) When  $p = 100 \text{ kPa}$ ,  $Z_{\text{atom}} = \boxed{2.0 \times 10^8 \text{ s}^{-1}}$

(b) When  $p = 1.000 \text{ Pa}$ ,  $Z_{\text{atom}} = \boxed{2.0 \times 10^3 \text{ s}^{-1}}$

**P25.4** We follow Example 25.1 and draw up the following table (with pressures converted to Torr)

$p/\text{Torr}$	0.19	0.97	1.90	4.05	7.50	11.95
$(p/V)/(\text{Torr cm}^{-3})$	4.52	5.95	8.60	12.6	18.3	25.4

$p/V$  is plotted against  $p$  in Figure 25.1.



**Figure 25.1**

The low-pressure points fall on a straight line with intercept 4.7 and slope 1.8. It follows that  $1/V_\infty = 1.8 \text{ Torr cm}^{-3}/\text{Torr} = 1.8 \text{ cm}^{-3}$ , or  $V_\infty = 0.57 \text{ cm}^3$  and  $1/KV_\infty = 4.7 \text{ Torr cm}^{-3}$ . Therefore,

$$K = \frac{1}{(4.7 \text{ Torr cm}^{-3}) \times (0.57 \text{ cm}^3)} = \boxed{0.37 \text{ Torr}^{-1}} = \boxed{0.0028 \text{ Pa}^{-1}}$$

**COMMENT.** It is unlikely that low-pressure data can be used to obtain an accurate value of the volume corresponding to complete coverage. See Problem 25.6 for adsorption data at higher pressures.

**P25.6** We assume that the data fit the Langmuir isotherm; to confirm this we plot  $p/V$  against  $p$  and expect a straight line [Example 25.1]. We draw up the following table

$p/\text{atm}$	0.050	0.100	0.150	0.200	0.250
$p/V/(10^{-2} \text{ atm cm}^{-3})$	4.1	7.52	11.5	14.7	17.9

The data are plotted in Figure 25.2.

They fit closely to a straight line with slope  $0.720 \text{ dm}^{-3}$ . Hence

$$V_\infty = \boxed{1.39 \text{ cm}^{-3}} = 1.39 \times 10^{-3} \text{ dm}^{-3} \approx V_{\text{mon}}$$

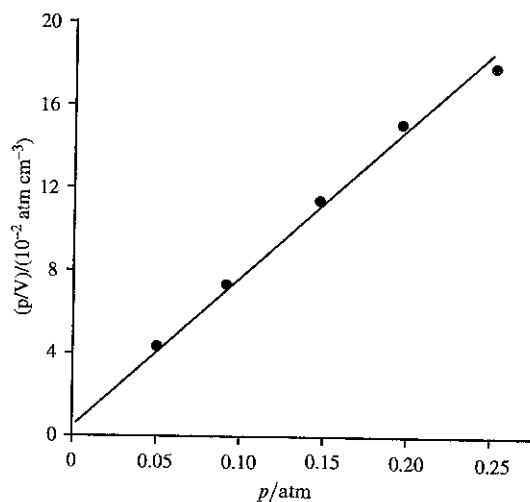


Figure 25.2

The number of  $\text{H}_2$  molecules corresponding to this volume is

$$N_{\text{H}_2} = \frac{pVN_A}{RT} = \frac{(1.00 \text{ atm}) \times (1.39 \times 10^{-3} \text{ dm}^3) \times (6.02 \times 10^{23} \text{ mol}^{-1})}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = 3.73 \times 10^{19}$$

The area occupied is the number of molecules times the area per molecule. The area per molecule can be estimated from the density of the liquid

$$\begin{aligned} A &= \pi \left( \frac{3V}{4\pi} \right)^{2/3} \left[ V = \text{volume of molecule} = \frac{M}{\rho N_A} \right] \\ &= \pi \left( \frac{3M}{4\pi \rho N_A} \right)^{2/3} = \pi \left( \frac{3 \times (2.02 \text{ g mol}^{-1})}{4\pi \times (0.0708 \text{ g cm}^{-3}) \times (6.02 \times 10^{23} \text{ mol}^{-1})} \right)^{2/3} \\ &= 1.58 \times 10^{-15} \text{ cm}^2 \end{aligned}$$

$$\text{Area occupied} = (3.73 \times 10^{19}) \times (1.58 \times 10^{-15} \text{ cm}^2) = (5.9 \times 10^4 \text{ cm}^2) = \boxed{5.9 \text{ m}^2}$$

**COMMENT.** The value for  $V_\infty$  calculated here may be compared to the value obtained in Problem 25.4. The agreement is not good and illustrates the point that these kinds of calculations provide only rough value surface areas.

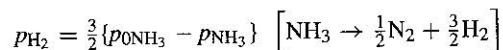
**P25.8** We assume that the Langmuir isotherm applies.

$$\theta = \frac{Kp}{1 + Kp} \quad [25.4] \quad \text{and} \quad 1 - \theta = \frac{1}{1 + Kp}$$

For a strongly adsorbed species,  $Kp \gg 1$  and  $1 - \theta = 1/Kp$ . Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{dp_{\text{NH}_3}}{dt} = -k_c p_{\text{NH}_3} (1 - \theta) \approx -\frac{k_c p_{\text{NH}_3}}{k p_{\text{H}_2}}$$

To solve the rate law, we write



from which it follows that, with  $p = p_{\text{NH}_3}$

$$\frac{-dp}{dt} = \frac{kp}{p_0 - p}, \quad k = \frac{2k_c}{3K}$$

This equation integrates as follows

$$\int_{p_0}^p \left(1 - \frac{p_0}{p}\right) dp = k \int_0^t dt$$

$$\text{or } \boxed{\frac{p - p_0}{t} = k + \frac{p_0}{t} \ln \frac{p}{p_0}}$$

We write  $F' = (p_0/t) \ln (p/p_0)$ ,  $G = (p - p_0)/t$

and obtain  $G = k + F' = p_0 F$

Hence, a plot of  $G$  against  $F'$  should give a straight line with intercept  $k$  at  $F' = 0$ . Alternatively, the difference  $G - F'$  should be a constant,  $k$ . We draw up the following table (with pressures converted to Torr)

$t/\text{s}$	0	30	60	100	160	200	250
$p/\text{Torr}$	100	88	84	80	77	74	72
$G/(\text{Torr s}^{-1})$		-0.40	-0.27	-0.20	-0.14	-0.13	-0.11
$F'/(\text{Torr s}^{-1})$		-0.43	-0.29	-0.22	-0.16	-0.15	-0.13
$(G - F')/(\text{Torr s}^{-1})$		0.03	0.02	0.02	0.02	0.02	0.02

Thus, the data fit the rate law, and we find  $\boxed{k = 0.02 \text{ Torr s}^{-1}} = \boxed{0.05 \text{ kPa s}^{-1}}$ .

**P25.10** Application of the van't Hoff equation [25.7] to adsorption equilibria yields

$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta = \frac{-\Delta_{\text{ad}}H^\ominus}{RT^2} \quad \text{or} \quad \left(\frac{\partial \ln K}{\partial(1/T)}\right)_\theta = \frac{-\Delta_{\text{ad}}H^\ominus}{R}$$

Hence, a plot (Figure 25.3) of  $\ln K$  against  $1/T$  should be a straight line with slope  $-\Delta_{\text{ad}}H^\ominus/R$ . The transformed data and plot follow

$T/\text{K}$	28.3	298	308	318
$10^{-11}K$	2.642	2.078	1.286	1.085
$1000 \text{ K}/T$	3.53	3.36	3.25	3.14
$\ln K$	26.30	26.06	25.58	25.41

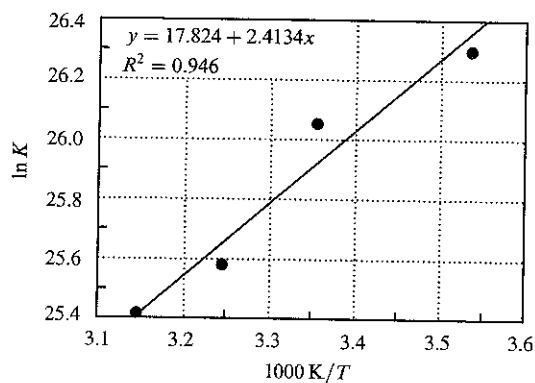


Figure 25.3

The plot is not the straightest of lines. Still, we can extract

$$\begin{aligned}
 -\Delta_{\text{ad}}H^{\ominus} &= -(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (2.41 \times 10^3 \text{ K}) \\
 &= -20.0 \times 10^3 \text{ J mol}^{-1} = \boxed{-20.1 \text{ kJ mol}^{-1}}
 \end{aligned}$$

The Gibbs energy for absorption is

$$\begin{aligned}
 -\Delta_{\text{ad}}G^{\ominus} &= -\Delta_{\text{ad}}H^{\ominus} - T\Delta_{\text{ad}}S^{\ominus} = -20.1 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (0.146 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\
 &= \boxed{63.6 \text{ kJ mol}^{-1}}
 \end{aligned}$$

**P25.12** For the Langmuir adsorption isotherm we must alter eqn 25.4 so that it describes adsorption from solution. This can be done with the transforms

$p \rightarrow$  concentration,  $c$

$V \rightarrow$  amount adsorbed per gram adsorbent,  $s$

Langmuir isotherm and regression analysis:

$$\frac{c}{s} = \frac{c}{s_{\infty}} + \frac{1}{Ks_{\infty}}$$

$$\frac{1}{s_{\infty}} = 0.163 \text{ g mmol}^{-1}, \text{ standard deviation} = 0.017 \text{ g mmol}^{-1}$$

$$\frac{1}{Ks_{\infty}} = 35.6 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1}),$$

$$\text{standard deviation} = 5.9 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})$$

$$\boxed{R (\text{Langmuir}) = 0.973}$$

$$K = \frac{0.163 \text{ g mmol}^{-1}}{35.6 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})} = 0.0046 \text{ dm}^3 \text{ mmol}^{-1}$$

Freundlich isotherm and regression analysis:

$$s = c_1 c^{1/c_2}$$

$$c_1 = 0.139, \quad \text{standard deviation} = 0.012$$

$$\frac{1}{c_2} = 0.539, \quad \text{standard deviation} = 0.003$$

$$R (\text{Freundlich}) = 0.99994$$

Temkin isotherm and regression analysis:

$$s = c_1 \ln(c_2 c)$$

$$c_1 = 1.08, \quad \text{standard deviation} = 0.14$$

$$c_2 = 0.074, \quad \text{standard deviation} = 0.023$$

$$R (\text{Temkin}) = 0.9590$$

The correlation coefficients and standard deviations indicate that the **Freundlich isotherm** provides the best fit of the data.

**P25.14**  $E = E^\ominus + (RT/zF) \ln a(M^+)$

Deposition may occur when the potential falls to below  $E$  and so simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by

$$E^\ominus(\text{Sn}, \text{Sn}^{2+}) + \frac{RT}{2F} \ln a(\text{Sn}^{2+}) = E^\ominus(\text{Pb}, \text{Pb}^{2+}) + \frac{RT}{2F} \ln a(\text{Pb}^{2+})$$

$$\text{or } \ln \frac{a(\text{Sn}^{2+})}{a(\text{Pb}^{2+})} = \left( \frac{2F}{RT} \right) \{E^\ominus(\text{Pb}, \text{Pb}^{2+}) - E^\ominus(\text{Sn}, \text{Sn}^{2+})\} = \frac{(2) \times (-0.126 + 0.136) \text{ V}}{0.0257 \text{ V}} = 0.78$$

That is, we require  $a(\text{Sn}^{2+}) \approx 2.2a(\text{Pb}^{2+})$

**P25.16**  $E' = E - IR_s - \frac{2RT}{zF} \ln g(I)$  [25.64a]

$$g = \frac{(I/A\bar{j})^{2z}}{[(1 - (I/Aj_{\text{lim,L}})) \times (1 - (I/Aj_{\text{lim,R}}))]^{1/2}}$$

with  $j_{\text{lim}} = cRT\lambda/zF\delta$  [25.57b] =  $a\lambda$

$$R_s = \frac{l}{\kappa A} = \frac{1}{cA\Lambda_m} \quad \text{with } \Lambda_m = \lambda_+ + \lambda_-$$

Therefore,  $E' = E - \frac{lI}{cA\Lambda_m} - \frac{2RT}{zF} \ln g(I)$

$$\text{with } g(I) = \frac{(I^2/A^2 j_{\text{L,O}} j_{\text{R,O}})^z}{[1 - (I/Aa_L\lambda_{L+})]^{1/2} [1 - (I/Aa_R\lambda_{R+})]^{1/2}}$$

with  $a_L = RTc_L/z_L F\delta_L$  and  $a_R = RTc_R/z_R F\delta_R$

$$(a) \frac{2}{1.24 \times 10^{-15} \text{ cm}^2} = \boxed{1.61 \times 10^{15} \text{ cm}^{-2}}$$

$$(b) \frac{2}{1.75 \times 10^{-15} \text{ cm}^2} = \boxed{1.14 \times 10^{15} \text{ cm}^{-2}}$$

$$(c) \frac{4}{2.15 \times 10^{-15} \text{ cm}^2} = \boxed{1.86 \times 10^{15} \text{ cm}^{-2}}$$

For the collision frequencies calculated in Exercise 25.1(a), the frequency of collision per atom is calculated by dividing the values given there by the number densities just calculated. We can therefore draw up the following table.

$Z/(\text{atom}^{-1} \text{ s}^{-1})$	Hydrogen		Propane	
	100 Pa	$10^{-7}$ Torr	100 Pa	$10^{-7}$ Torr
(100)	$6.8 \times 10^5$	$8.7 \times 10^{-2}$	$1.4 \times 10^5$	$1.9 \times 10^{-2}$
(110)	$9.6 \times 10^5$	$1.2 \times 10^{-1}$	$2.0 \times 10^5$	$2.7 \times 10^{-2}$
(111)	$5.9 \times 10^5$	$7.5 \times 10^{-2}$	$1.2 \times 10^5$	$1.7 \times 10^{-2}$

**P25.5**

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \left[ 25.8, \text{ BET isotherm, } z = \frac{p}{p^*} \right].$$

This rearranges to

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}.$$

Therefore a plot of the left-hand side against  $z$  should result in a straight line if the data obeys the BET isotherm. We draw up the following tables.

(a)  $0^\circ\text{C}$ ,  $p^* = 3222$  Torr.

$p/\text{Torr}$	105	282	492	594	620	755	798
$10^3 z$	32.6	87.5	152.7	184.4	192.4	234.3	247.7
$10^3 z/(1-z)(V/\text{cm}^3)$	3.04	7.10	12.1	14.1	15.4	17.7	20.0

(b)  $18^\circ\text{C}$ ,  $p^* = 6148$  Torr.

$p/\text{Torr}$	39.5	62.7	108	219	466	555	601	765
$10^3 z$	6.4	10.2	17.6	35.6	75.8	90.3	97.8	124.4
$10^3 z/(1-z)(V/\text{cm}^3)$	0.70	1.05	1.74	3.27	6.36	7.58	8.09	10.8

The points are plotted in Fig. 25.3, but we analyse the data by a least-squares procedure.

The intercepts are at (a) 0.466 and (b) 0.303. Hence

$$\frac{1}{cV_{\text{mon}}} = (a) 0.466 \times 10^{-3} \text{ cm}^{-3}, \quad (b) 0.303 \times 10^{-3} \text{ cm}^{-3}.$$

The slopes of the lines are (a) 76.10 and (b) 79.54. Hence

$$\frac{c^{-1}}{cV_{\text{mon}}} = \text{(a)} 76.10 \times 10^{-3} \text{ cm}^{-3}, \quad \text{(b)} 79.54 \times 10^{-3} \text{ cm}^{-3}.$$

Solving the equations gives

$$c - 1 = \text{(a)} 163.\bar{3}, \quad \text{(b)} 262.\bar{5}$$

and hence

$$c = \text{(a)} \boxed{164}, \quad \text{(b)} \boxed{264}; \quad V_{\text{mon}} = \text{(a)} \boxed{13.1 \text{ cm}^3}, \quad \text{(b)} \boxed{12.5 \text{ cm}^3}.$$

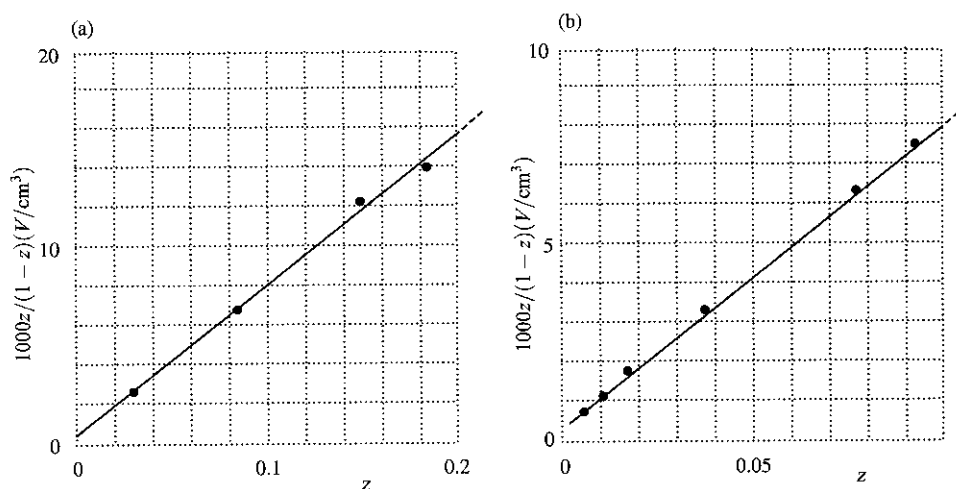


Figure 25.3

P25.7

$$\theta = c_1 p^{1/c_2}.$$

We adapt this isotherm to a liquid by noting that  $w_a \propto \theta$  and replacing  $p$  by  $[A]$ , the concentration of the acid. Then  $w_a = c_1 [A]^{1/c_2}$  (with  $c_1, c_2$  modified constants), and hence

$$\log w_a = \log c_1 + \frac{1}{c_2} \times \log[A].$$

We draw up the following table.

$[A]/(\text{mol dm}^{-3})$	0.05	0.10	0.15	0.20	0.25
$\log([A]/\text{mol dm}^{-3})$	-1.30	-1.00	-0.30	-0.00	0.18
$\log(w_a/\text{g})$	-1.40	-1.22	-0.92	-0.80	-0.72