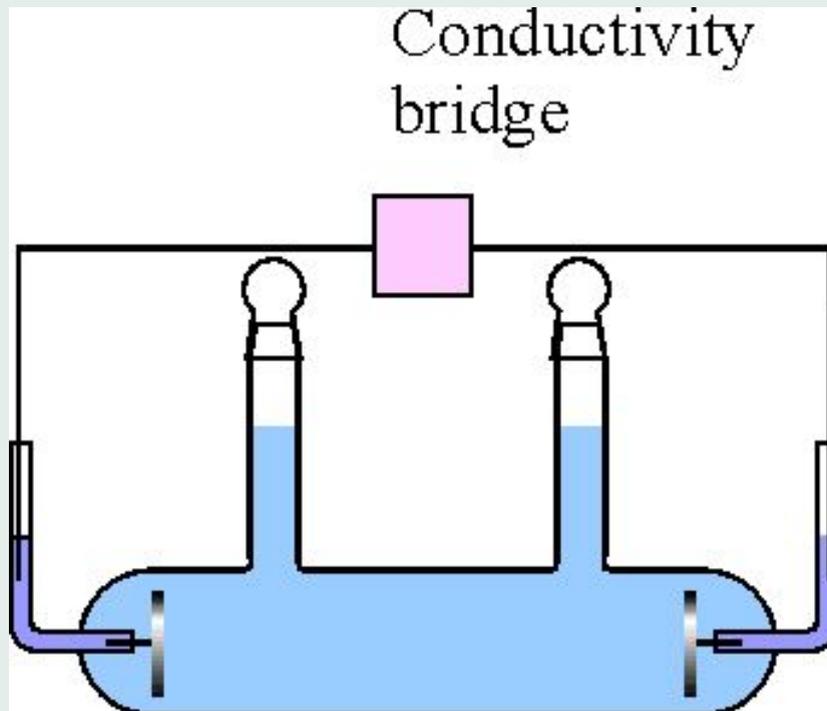


## CHM2S1-B Electrochemistry

- This lecture course will closely follow the Textbook  
*Atkins, Elements of Physical Chemistry, Chapter 9*
- The Examples (worked questions) and part of the Self-tests in the Textbook will be treated in the lecture.
- You are encouraged to read the Textbook and attempt the Self-tests along with the lectures.
- Basic knowledge of A-level Electrochemistry will be assumed.  
(See, for example, S-Cool AS & A2 Level Chemistry Revision Guide,  
[http://www.s-cool.co.uk/topic\\_index.asp?subject\\_id=7](http://www.s-cool.co.uk/topic_index.asp?subject_id=7) )
- You don't need to bring the Textbook to the lecture room because the necessary materials will be displayed on the screen.

**Fig 9.1**



**Fig 9.1** A typical conductivity cell. The cell is made part of a 'bridge' and its resistance is measured. The conductivity is normally determined by comparison of its resistance to that of a solution of known conductivity. An alternating current is used to avoid the formation of decomposition products at the electrodes.

### Example 9.1

*Determining the acidity constant from the conductivity of a weak acid*

The molar conductivity of 0.010 M  $\text{CH}_3\text{COOH}(\text{aq})$  is  $1.65 \text{ mS m}^2 \text{ mol}^{-1}$ . What is the acidity constant of the acid?

(Use  $\lambda_{\text{H}_3\text{O}^+} = 34.96$ ,  $\lambda_{\text{CH}_3\text{CO}_2^-} = 4.09 \text{ mS m}^2 \text{ mol}^{-1}$  from Table 9.1.)

*Strategy* Because acetic acid is a weak electrolyte, it is only partly deprotonated in aqueous solution. Only the fraction of acid molecules present as ions contributes to the conduction, so we need to express  $\Lambda_m$  in terms of the fraction deprotonated. Set up an equilibrium table, find the molar concentration of  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{CO}_2^-$  ions, and relate those concentrations to the observed molar conductivity.

Self-test 9.1

The molar conductivity of 0.0250 M  $\text{HCOOH}(\text{aq})$  is  $4.61 \text{ mS m}^2 \text{ mol}^{-1}$ . What is the  $\text{p}K_a$  of formic acid?

( $\lambda_{\text{HCO}_2^-} = 5.46 \text{ mS m}^2 \text{ mol}^{-1}$ )

---

Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

## Example 9.1

*Determining the acidity constant from the conductivity of a weak acid*

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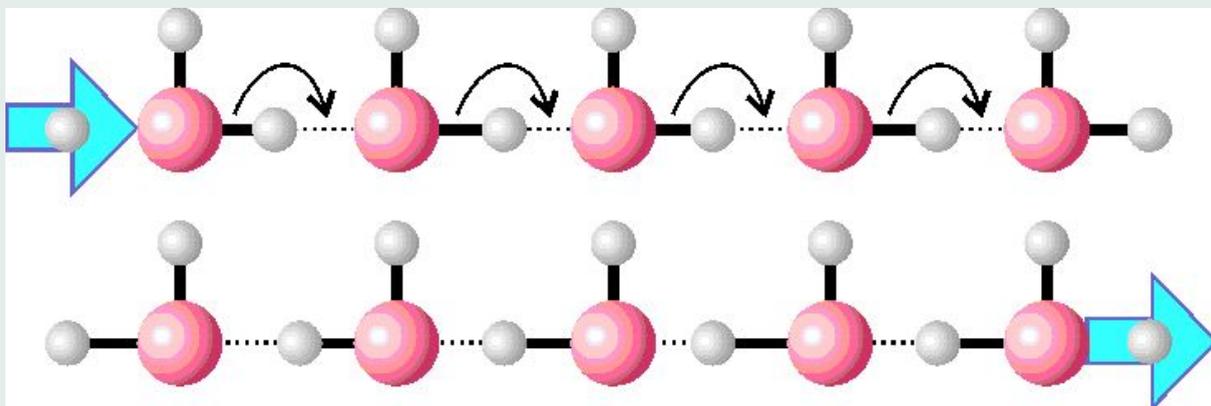
**Table 9.2**

*Ionic mobilities in water at 298 K,  $u/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$*

Cations		Anions	
H <sup>+</sup>	36.23	OH <sup>-</sup>	20.64
Li <sup>+</sup>	4.01	F <sup>-</sup>	5.74
Na <sup>+</sup>	5.19	Cl <sup>-</sup>	7.92
K <sup>+</sup>	7.62	Br <sup>-</sup>	8.09
Rb <sup>+</sup>	8.06	I <sup>-</sup>	7.96
Cs <sup>+</sup>	8.00	CO <sub>3</sub> <sup>2-</sup>	7.18
Mg <sup>2+</sup>	5.50	NO <sub>3</sub> <sup>-</sup>	7.41
Ca <sup>2+</sup>	6.17	SO <sub>4</sub> <sup>2-</sup>	8.29
Sr <sup>2+</sup>	6.16		
NH <sub>4</sub> <sup>+</sup>	7.62		
[N(CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	4.65		
[N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ] <sup>+</sup>	3.38		

Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

**Fig 9.2**



**Fig 9.2** A simplified version of the ‘Grotthuss mechanism’ of proton conduction through water. The proton leaving the chain on the right is not the same as the proton entering the chain on the left.

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

## Example 9.2

### *Determining the isoelectric point*

The speed with which bovine serum albumin (BSA) moves through water under the influence of an electric field was monitored at several values of pH, and the data are listed below. What is the isoelectric point of the protein?

pH	4.20	4.56	5.20	5.65	6.30	7.00
Velocity/ $(\mu\text{m s}^{-1})$	0.50	0.18	-0.25	-0.60	-0.95	-1.20

*Strategy* The macromolecule is not influenced by the electric field when it is uncharged. Therefore, the isoelectric point is the pH at which it does not migrate in an electric field. We should therefore plot speed against pH and find by interpolation the pH at which the speed is zero.

### Self-test 9.2

The following data were obtained for another protein.

pH	4.5	5.0	5.5	6.0
Velocity/ $(\mu\text{m s}^{-1})$	-0.10	-0.20	-0.30	-0.35

## Example 9.2

### *Determining the isoelectric point*

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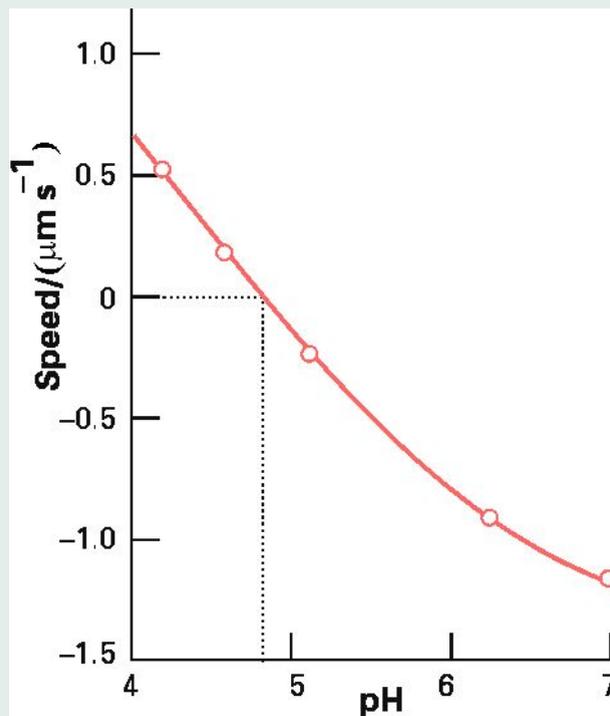
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### Self-test 9.2

The following data were obtained for another protein.

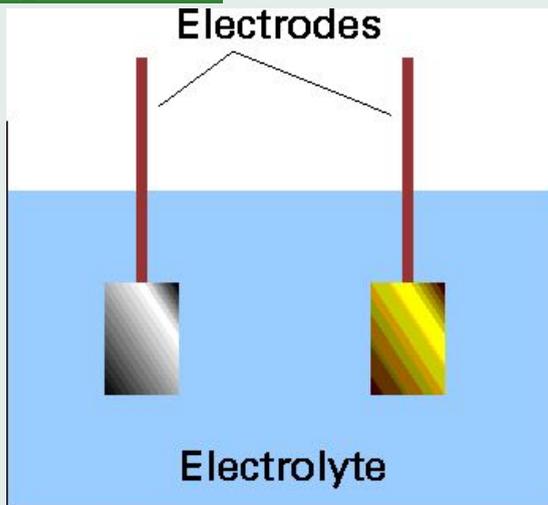
pH	4.5	5.0	5.5	6.0
Velocity/ $(\mu\text{m s}^{-1})$	-0.10	-0.20	-0.30	-0.35

**Fig 9.3**

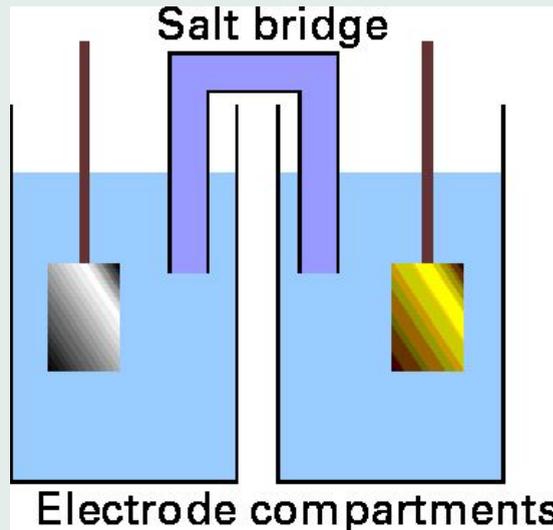


**Fig 9.3** The plot of the speed of a moving macromolecule against pH allows the isoelectric point to be detected as the pH at which the speed is zero.

**Fig 9.4, 9.5**

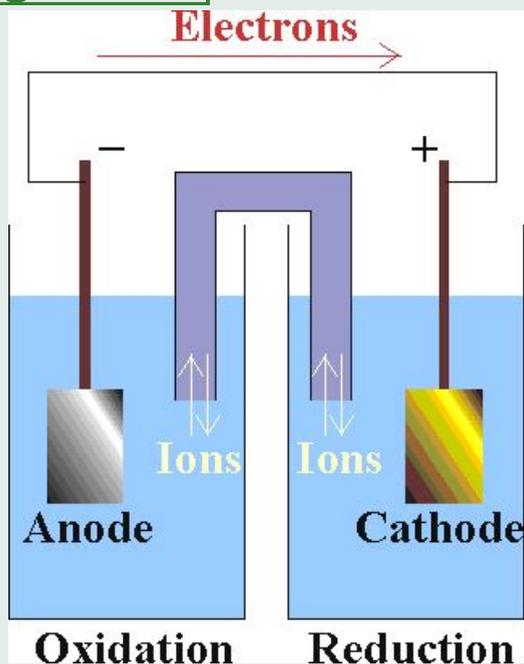


**Fig 9.4** The arrangement for an electrochemical cell in which the two electrodes share a common electrolyte.

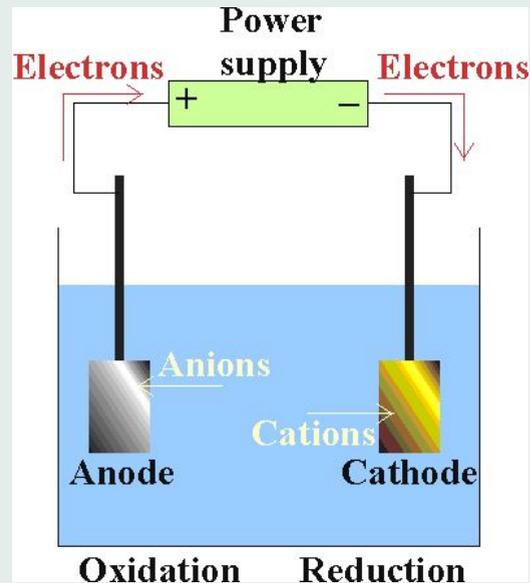


**Fig 9.5** When the electrolytes in the electrode compartments of a cell are different, they need to be joined so that ions can travel from one compartment to another. One device for joining the two compartments is a salt bridge.

**Fig 9.6, 9.7**

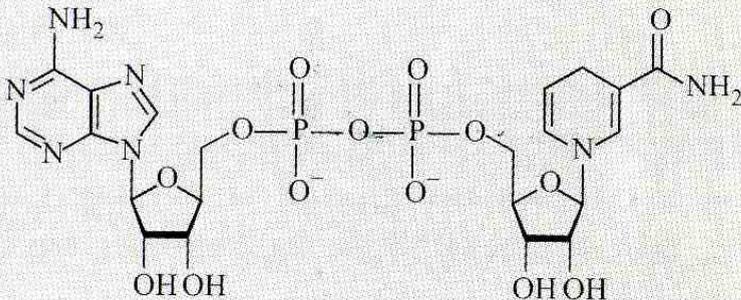


**Fig 9.6** The flow of electrons in the external circuit is from the anode of a galvanic cell, where they have been lost in the oxidation reaction, to the cathode, where they are used in the reduction reaction. Electrical neutrality is preserved in the electrolytes by the flow of cations and anions in opposite directions through the salt bridge.

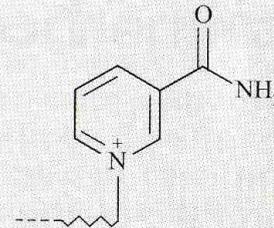


**Fig 9.7** The flow of electrons and ions in an electrolytic cell. An external supply forces electrons into the cathode, where they are used to bring about a reduction, and withdraws them from the anode, which results in an oxidation reaction at that electrode. Cations migrate towards the negatively charged cathode and anions migrate towards the positively charged anode. An electrolytic cell usually consists of a single compartment, but a number of industrial versions have two compartments.

# NADH / NAD<sup>+</sup>



**1** Nicotinamide adenine dinucleotide, reduced form (NADH)



**2** Nicotinamide adenine dinucleotide (NAD<sup>+</sup>)

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

**Self-test 9.3** Identify the species that have undergone oxidation and reduction in the reaction  $\text{CuS (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{Cu (s)} + \text{SO}_2 \text{ (g)}$ .

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

### Example 9.3

#### *Expressing a reaction in terms of half-reactions*

Express the oxidation of NADH (nicotinamide adenine dinucleotide), which participates in the chain of oxidations that constitutes respiration, to  $\text{NAD}^+$  by oxygen, when the latter is reduced to  $\text{H}_2\text{O}_2$ , in aqueous solution as the difference of two reduction half-reactions. The overall reaction is  $\text{NADH}(\text{aq}) + \text{O}_2(\text{g}) + \text{H}^+(\text{aq}) \rightarrow \text{NAD}^+(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$ .

*Strategy* To decompose a reaction into reduction half-reactions, identify one reactant species that undergoes reduction, its corresponding reduction product, and write the half-reaction for this process. To find the second half-reaction, subtract the overall reaction from this half-reaction and rearrange the species so that all the stoichiometric coefficients are positive and the equation is written as a reduction.

#### Self-test 9.4

Express the formation of  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$  in acidic solution as the difference of two reduction half-reactions.

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Express the formation of  $\text{H}_2\text{O}$  from  $\text{H}_2$  and  $\text{O}_2$  in acidic solution as the difference of two reduction half-reactions.

### Example 9.4

#### *Writing the half-reaction for a gas electrode*

Write the half-reaction and the reaction quotient for the reduction of oxygen to water in acidic solution.

*Strategy* Write the chemical equation for the half-reaction. Then express the reaction quotient in terms of the activities and the corresponding stoichiometric numbers, with products in the numerator and reactants in the denominator. Pure (and nearly pure) solids and liquids do not appear in  $Q$ ; nor does the electron. The activity of a gas is set equal to the numerical value of its partial pressure.

#### Self-test 9.5

Write the half-reaction and the reaction quotient for a chlorine gas electrode.

---

Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

### Example 9.4

#### *Writing the half-reaction for a gas electrode*

Write the half-reaction and the reaction quotient for the reduction of oxygen to water in acidic solution.

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#### Self-test 9.5

Write the half-reaction and the reaction quotient for a chlorine gas electrode.

---

Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

### Example 9.5

#### *Writing the half-reaction for an insoluble-salt electrode*

Write the half-reaction and the reaction quotient for the lead-lead-sulfate electrode of the lead-acid battery, in which Pb(II), as lead(II) sulfate, is reduced to metallic lead in the presence of hydrogensulfate ions in the electrolyte.

*Strategy* Begin by identifying the species that is reduced, and writing the half-reaction. Balance that half-reaction by using H<sub>2</sub>O molecules if O atoms are required, hydrogen ions (because the solution is acidic) if H atoms are needed, and electrons for the charge. Then write the reaction quotient in terms of the stoichiometric coefficients and activities of the species present. Products appear in the numerator, reactants in the denominator.

#### Self-test 9.6

Write the half-reaction and the reaction quotient for the calomel electrode, Hg(l) — Hg<sub>2</sub>Cl<sub>2</sub>(s) — Cl<sup>-</sup>(aq), in which mercury(I) chloride (calomel) is reduced to mercury metal in the presence of chloride ions. This electrode is a component of instruments used to measure pH, as explained later.

### Example 9.5

#### *Writing the half-reaction for an insoluble-salt electrode*

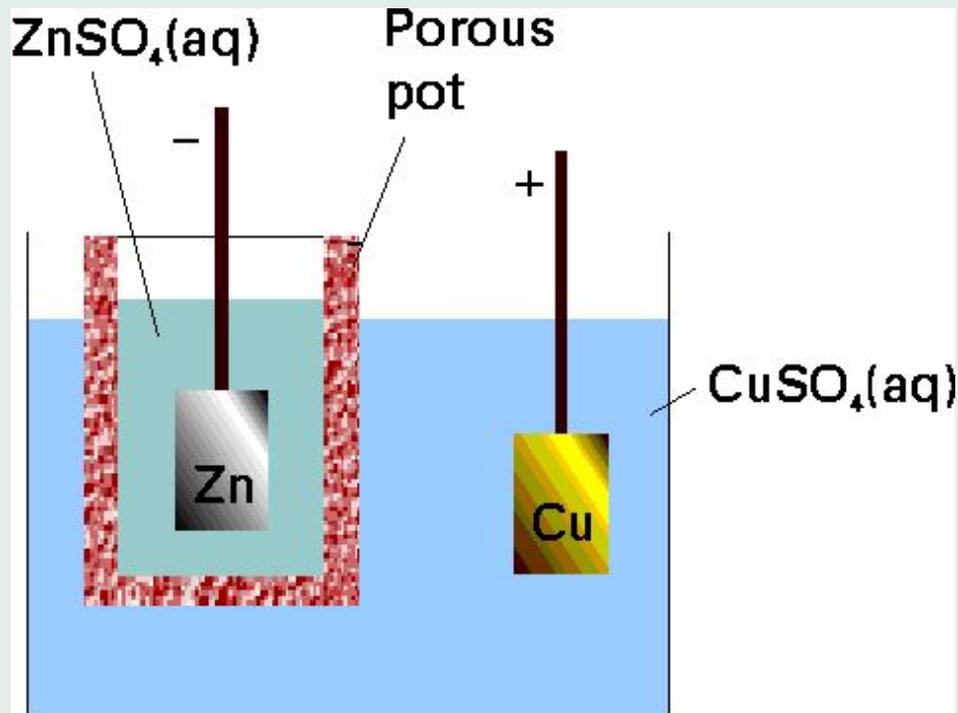
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#### Self-test 9.6

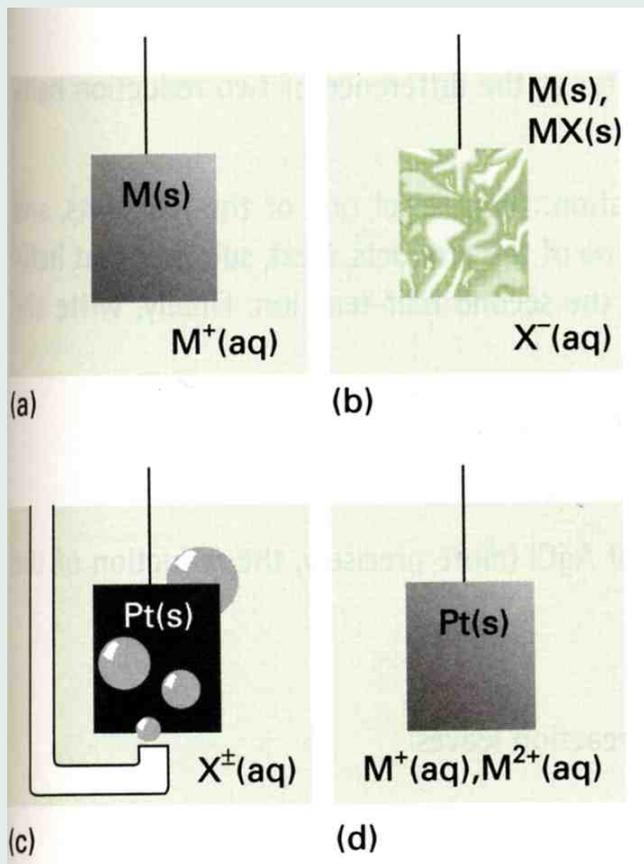
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**Fig 9.11**



**Fig 9.11** A Daniell cell consists of copper in contact with copper(II) sulfate solution and zinc in contact with zinc sulfate solution; the two compartments are in contact through the porous pot that contains the zinc sulfate solution.

## Typical Electrode Types



(a) metal/metal ion; (b) metal/insoluble salt; (c) gas; (d) redox

**Self-test 9.7** Give the notation for a cell in which the oxidation of NADH by oxygen could be studied (recall Example 9.3).

**Self-test 9.8** Write the chemical equation for the reaction in the cell  $\text{Ag(s)} \mid \text{AgBr(s)} \mid \text{NaBr(aq)} \parallel \text{NaCl(aq)} \mid \text{Cl}_2(\text{g}) \mid \text{Pt(s)}$ .

## Derivation 4.4 (p.97)

### Maximum non-expansion work

At **constant temperature**  $T$ ,

$$dG = dH - TdS$$

And **constant pressure**  $p$ ,

$$dG = dU + pdV - TdS$$

Using  $dU = dw + dq$  (work + heat),

$$dG = dw + dq + pdV - TdS$$

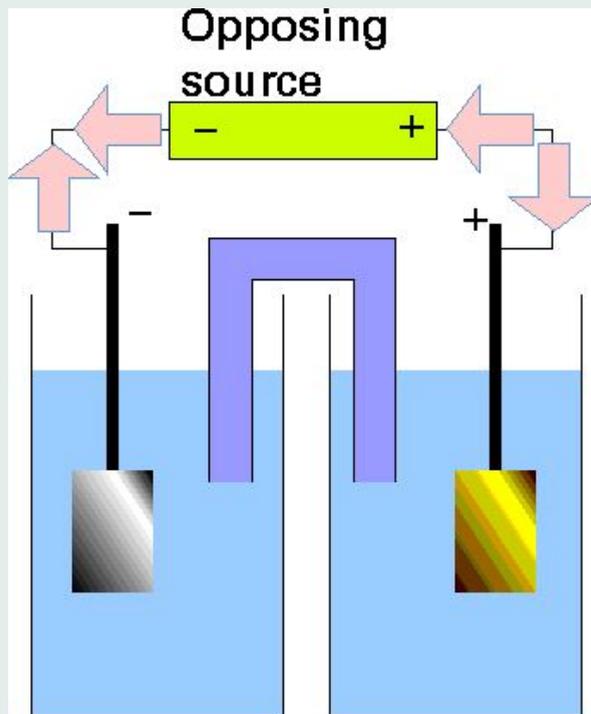
Work = expansion + non-expansion parts,  $dw = -p_{ex}dV + dw'$

$$dG = -p_{ex}dV + dw' + dq + pdV - TdS$$

In a **reversible** change,  $p_{ex} = p$  and  $dq = TdS$ , therefore,

$$dG = dw' \quad (\text{reversible, non-expansion})$$

**Fig 9.12**

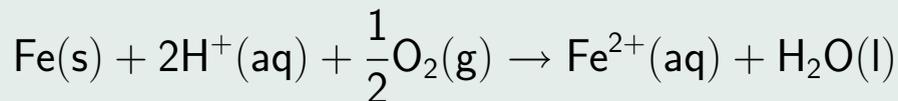


**Fig 9.12** The zero-current cell potential is measured by balancing the cell against an external potential that opposes the reaction in the cell. When there is no current flow, the external potential difference is equal to the cell potential.

### Example 9.6

#### *Identifying the spontaneous direction of a reaction*

One of the reactions important in corrosion in an acidic environment is



Does the equilibrium constant favour the formation of  $\text{Fe}^{2+}(\text{aq})$ ?  
(Use the standard potentials  $E^\ominus(\text{H}^+, \text{O}_2, \text{H}_2\text{O}) = +1.23 \text{ V}$ ,  $E^\ominus(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$ .)

*Strategy* We need to decide whether  $E^\ominus$  for the reaction is positive or negative:  $K > 1$  if  $E^\ominus > 0$ . We express the overall reaction as the difference of reduction half-reactions, look up the standard potentials of the two couples, and take their difference.

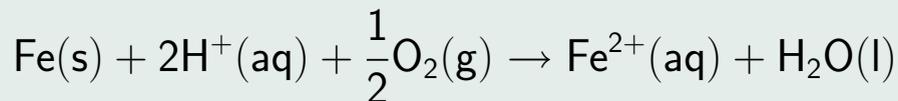
#### Self-test 9.9

Is the equilibrium constant for the displacement of lead from lead(II) solutions by copper greater or less than 1?  
(Use  $E^\ominus(\text{Pb}^{2+}, \text{Pb}) = -0.13 \text{ V}$ ,  $E^\ominus(\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V}$ .)

### Example 9.6

#### Identifying the spontaneous direction of a reaction

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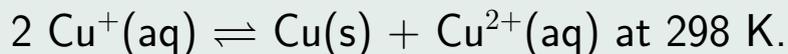
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### Example 9.7

#### *Calculating an equilibrium constant*

Calculate the equilibrium constant for the disproportionation reaction



*Strategy* The aim is to find the values of  $E^\ominus$  and  $\nu$  corresponding to the reaction, for then we can use eqn 9.14. To do so, we express the equation as the difference of two reduction half-reactions. The stoichiometric number of the electron in these matching half-reactions is the value of  $\nu$  we require. We then look up the standard potentials for the couples corresponding to the half-reactions and calculate their difference to find  $E^\ominus$ . In calculations of this kind a useful value is  $RT/F = 25.69 \text{ mV}$ .

Self-test 9.10

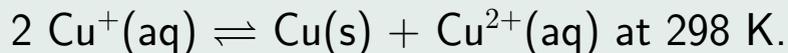
Calculate the equilibrium constant for the reaction



### Example 9.7

#### *Calculating an equilibrium constant*

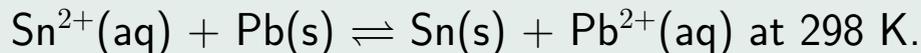
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#### Self-test 9.10

Calculate the equilibrium constant for the reaction



**Example 9.8***Converting a standard potential to a biological standard value*

Estimate the biological standard potential of the  $\text{NAD}^+/\text{NADH}$  couple at  $25\text{ }^\circ\text{C}$  (Example 9.3). The reduction half-reaction is



*Strategy* We write the Nernst equation for the potential, and express the reaction quotient in terms of the activities of the species. All species except  $\text{H}^+$  are in their standard states, so their activities are all equal to 1. The remaining task is to express the hydrogen ion activity in terms of the pH, exactly as was done in the text, and set  $\text{pH} = 7$ .

Self-test 9.11

Calculate the biological standard potential of the half-reaction



at  $25\text{ }^\circ\text{C}$  given its value  $+1.23 \text{ V}$  under thermodynamic standard conditions.

### Example 9.8

### Converting a standard potential to a biological standard value

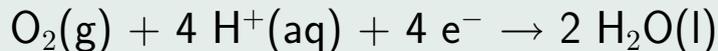
Estimate the biological standard potential of the  $\text{NAD}^+/\text{NADH}$  couple at  $25\text{ }^\circ\text{C}$  (Example 9.3). The reduction half-reaction is



*Strategy* We write the Nernst equation for the potential, and express the reaction quotient in terms of the activities of the species. All species except  $\text{H}^+$  are in their standard states, so their activities are all equal to 1. The remaining task is to express the hydrogen ion activity in terms of the pH, exactly as was done in the text, and set  $\text{pH} = 7$ .

### Self-test 9.11

Calculate the biological standard potential of the half-reaction

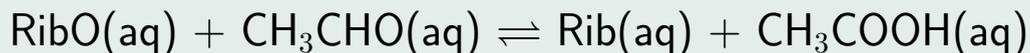


at  $25\text{ }^\circ\text{C}$  given its value  $+1.23 \text{ V}$  under thermodynamic standard conditions.

### Example 9.9

### Calculating a biological equilibrium constant

The reduced and oxidized forms of riboflavin form a couple with  $E^{\oplus} = -0.21$  V and the acetate/acetaldehyde couple has  $E^{\oplus} = -0.60$  V under the same conditions. What is the equilibrium constant for the reduction of riboflavin (Rib) by acetaldehyde in neutral solution at 25 °C ? The reaction is



where RibO is the oxidized form of riboflavin and Rib is the reduced form.

*Strategy* The procedure is the same as before: we express the overall reaction as the difference of two half-reactions, and identify the value of  $\nu$  required to match them. The standard potential for the reaction is then the difference of the two standard potentials for the half-reactions.

#### Self-test 9.12

What is the equilibrium constant for the reduction of riboflavin with rubredoxin, a bacterial iron-sulfur protein, in the reaction

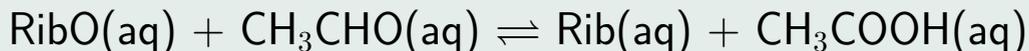


given the biological standard potential of the rubredoxin couple is  $-0.06$  V ?

## Example 9.9

### Calculating a biological equilibrium constant

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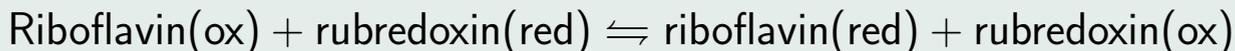


where RibO is the oxidized form of riboflavin and Rib is the reduced form.

*Strategy* The procedure is the same as before: we express the overall reaction as the difference of two half-reactions, and identify the value of  $\nu$  required to match them. The standard potential for the reaction is then the difference of the two standard potentials for the half-reactions.

#### Self-test 9.12

What is the equilibrium constant for the reduction of riboflavin with rubredoxin, a bacterial iron-sulfur protein, in the reaction



given the biological standard potential of the rubredoxin couple is -0.06 V ?

**Section 9.11** The determination of pH

Write the cell reaction equation and the reaction quotient for



Show that the Nernst equation can be converted to a form linear in pH,

$$E = E' + \frac{RT \ln 10}{F} \times \text{pH}$$

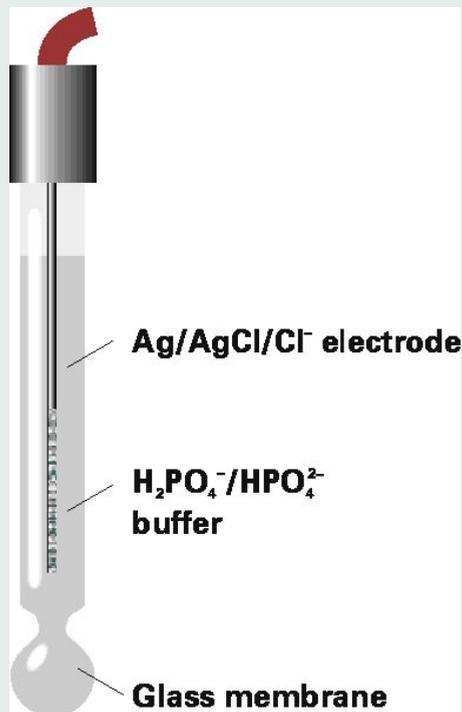
**Self-test 9.13**

What range should a voltmeter have (in volts) to display changes of pH from 1 to 14 at 25 °C if it is arranged to give a reading of 0 when pH = 7 ?

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

**Fig 9.13**



**Fig 9.13** A glass electrode has a potential that varies with the hydrogen ion concentration in the medium in which it is immersed. It consists of a thin glass membrane containing an electrolyte and a silver chloride electrode. The electrode is used in conjunction with a calomel (Hg<sub>2</sub>Cl<sub>2</sub>) electrode that makes contact with the test solution through a salt bridge.

## The electrochemical series

Spontaneous reaction  $\Leftrightarrow E^{\ominus} > 0 \Leftrightarrow \Delta G^{\ominus} < 0$

**Self-test 9.14** Does acidified dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) have a thermodynamic tendency to oxidize mercury metal to mercury(I) ?

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford

**Example 9.10***Calculating a standard potential from two others*

Given the standard potentials  $E^\ominus(\text{Cu}^{2+}, \text{Cu}) = +0.340 \text{ V}$  and  $E^\ominus(\text{Cu}^+, \text{Cu}) = +0.522 \text{ V}$ , calculate  $E^\ominus(\text{Cu}^{2+}, \text{Cu}^+)$ .

*Strategy*

We need to convert the  $E^\ominus$  values to  $\Delta_r G^\ominus$  values by using eqn 9.13,

$$E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F}$$

adding them appropriately, and converting the overall  $\Delta_r G^\ominus$  so obtained to the required  $E^\ominus$  by using eqn 9.13 again. Because the  $F$ s cancel at the end of the calculation, carry them through. Self-test 9.15

Given the standard potentials  $E^\ominus(\text{Fe}^{3+}, \text{Fe}) = -0.04 \text{ V}$  and  $E^\ominus(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$ , calculate  $E^\ominus(\text{Fe}^{3+}, \text{Fe}^{2+})$ .

### Example 9.10

#### *Calculating a standard potential from two others*

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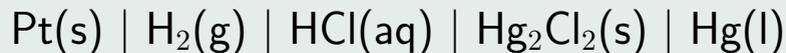
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Given the standard potentials  $E^\ominus(\text{Fe}^{3+}, \text{Fe}) = -0.04 \text{ V}$  and  $E^\ominus(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$ , calculate  $E^\ominus(\text{Fe}^{3+}, \text{Fe}^{2+})$ .

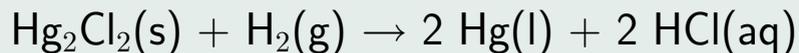
**Example 9.11**

*Using the temperature dependence of the cell potential*

The standard potential of the cell



was found to be +0.2699 V at 293 K and +0.2669 V at 303 K. Evaluate the standard Gibbs energy, enthalpy and entropy at 298 K of the reaction



*Strategy* We find the standard reaction Gibbs energy from the standard potential by using eqn 9.13 and making a linear interpolation between the two temperatures (in this case, we take the mean  $E^\ominus$  because 298 K lies midway between 293 K and 303 K). The standard reaction entropy is obtained by substituting the data into eqn 9.19

$$\Delta_r S^\ominus = \frac{\nu F (E^\ominus - E^{\ominus'})}{T - T'}$$

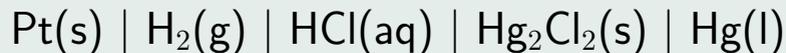
Then the standard reaction enthalpy is obtained by combining these two quantities by using eqn 9.20.

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus$$

**Example 9.11**

*Using the temperature dependence of the cell potential*

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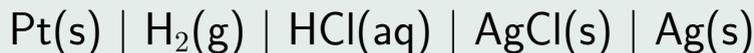
$$\Delta_r S^\ominus = \frac{\nu F (E^\ominus - E^{\ominus'})}{T - T'}$$

Then the standard reaction enthalpy is obtained by combining these two quantities by using eqn 9.20.

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus$$

**Self-test 9.16**

Predict the standard potential of the Harned cell



at 303 K from tables of thermodynamic data for 298 K. Use the following data:

	AgCl(s)	Ag(s)	HCl(aq)	H <sub>2</sub> (g)
$\Delta_f H^\ominus$	-127.07	0	-167.16	0
$\Delta_f G^\ominus$	-109.79	0	-131.23	0

(in kJ mol<sup>-1</sup>)

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Atkins, *Elements of Physical Chemistry*, 3rd Ed, Oxford