



**21.22a** The mobility of a chloride ion in aqueous solution at 25°C is  $7.91 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ , Calculate the molar ionic conductivity.

**21.23a** The mobility of a  $\text{Rb}^+$  ion in aqueous solution is  $7.92 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$  at 25°C. The potential difference between two electrodes placed in the solution is 35.0 V. If the electrodes are 8.00 mm apart, what is the drift speed of the  $\text{Rb}^+$  ion?

**21.24a** What fraction of the total current is carried by  $\text{Li}^+$  when current flows through an aqueous solution of  $\text{LiBr}$  at 25°C?

**21.24b** What fraction of the total current is carried by  $\text{Cl}^-$  when current flows through an aqueous solution of  $\text{NaCl}$  at 25°C?

**21.25a** The limiting molar conductivities of  $\text{KCl}$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$  are  $14.99 \text{ mS m}^2 \text{ mol}^{-1}$ ,  $14.50 \text{ mS m}^2 \text{ mol}^{-1}$ , and  $13.34 \text{ mS m}^2 \text{ mol}^{-1}$ , respectively (all at 25°C). What is the limiting molar conductivity of  $\text{AgCl}$  at this temperature?

**21.26a** At 25°C the molar ionic conductivities of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  are  $3.87 \text{ mS m}^2 \text{ mol}^{-1}$ ,  $5.01 \text{ mS m}^2 \text{ mol}^{-1}$ , and  $7.35 \text{ mS m}^2 \text{ mol}^{-1}$ , respectively. What are their mobilities?

**21.27a** The mobility of a  $\text{NO}_3^-$  ion in aqueous solution at 25°C is  $7.40 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ . Calculate its diffusion coefficient in water at 25°C.

**21.29a** Estimate the effective radius of a sucrose molecule in water 25°C given that its diffusion coefficient is  $5.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and that the viscosity of water is 1.00 cP.

**21.8** Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is  $76 \text{ mS m}^{-1}$  at 25°C and the conductivity of  $0.100 \text{ mol dm}^{-3} \text{ KCl(aq)}$  is  $1.1639 \text{ S m}^{-1}$ . A cell had a resistance of  $33.21 \Omega$  when filled with  $0.100 \text{ mol dm}^{-3} \text{ KCl(aq)}$  and  $300.0 \Omega$  when filled with  $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ . What is the molar conductivity of acetic acid at that concentration and temperature?

**21.9** The resistances of a series of aqueous  $\text{NaCl}$  solutions, formed by successive dilution of a sample, were measured in a cell with cell constant (the constant  $C$  in the relation  $\kappa = C/R$ ) equal to  $0.2063 \text{ cm}^{-1}$ . The following values were found:

$C / (\text{mol dm}^{-3})$	0.00050	0.00100	0.00500	0.01000	0.02000	0.05000
$R / \Omega$	3314.0	1669.0	342.1	174.1	89.1	37.1

Verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity. Determine the coefficient  $k$ . Use the value of  $k$  (which should depend only on the nature, not the identity of the ions) and the information that  $\lambda(\text{Na}^+) = 5.01 \text{ mS m}^2 \text{ mol}^{-1}$  and  $\lambda(\text{I}^-) = 7.68 \text{ mS m}^2 \text{ mol}^{-1}$  to predict (a) the molar conductivity, (b) the conductivity, (c) the resistance it would show in the cell, of  $0.010 \text{ mol dm}^{-3} \text{ NaI(aq)}$  at 25°C.

21.10 After correction for the water conductivity, the conductivity of a saturated aqueous solution of AgCl at 25°C was found to be 0.1887 mS m<sup>-1</sup>. What is the solubility of silver chloride at this temperature?

21.13 In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained aqueous KCl at a concentration of 0.021 mol dm<sup>-3</sup>. A steady current of 18.2 mA was passed, and the boundary advanced as follows:

$\Delta t$ /s	200	400	600	800	1000
x /mm	64	128	192	254	318

Find the transport number of K<sup>+</sup>, its mobility, and its ionic conductivity.

21.18 A concentrated sucrose solution is poured into a cylinder of diameter 5.0 cm. The solution consisted of 10 g of sugar in 5.0 cm<sup>3</sup> of water. A further 1.0 dm<sup>3</sup> of water is then poured very carefully on top of the layer, without disturbing the layer. Ignore gravitational effects, and pay attention only to diffusional processes. Find the concentration at 5.0 cm above the lower layer after a lapse of (a) 10 s, (b) 1.0 year.

21.20:1: A.K. Srivastava, R.A. Samant, and S.D. Patankar (J. Chem. Eng. Data 41,431 (1996)) measured the conductance of several salts in a binary solvent mixture of water and a dipolar aprotic solvent 1,3-dioxolan-2-one (ethylene carbonate). They report the following conductances at 25°C in a solvent 80 per cent 1,3-dioxolan-2-one by mass:

NaI:

c / (mmol dm <sup>-3</sup> )	32.02	20.28	12.06	8.64	2.85	1.24	0.83
$\Lambda_m$ / (S cm <sup>2</sup> mol <sup>-1</sup> )	50.26	51.99	54.01	55.75	57.99	58.44	58.67

KI:

c / (mmol dm <sup>-3</sup> )	17.68	10.8	7.19	2.67	1.28	0.83	0.19
$\Lambda_m$ / (S cm <sup>2</sup> mol <sup>-1</sup> )	42.45	45.91	47.53	51.81	54.09	55.78	57.42

Calculate  $\Lambda_m^\circ$ , for NaI and KI in this solvent and  $\lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{K}^+)$ . Compare your results to the analogous quantities in aqueous solution using Table 21.5 in the Data section.

**Table 21.5** Limiting ionic conductivities in water at 298 K,  $\lambda^\circ$ /(mS m<sup>2</sup> mol<sup>-1</sup>)

Cations		Anions	
Ba <sup>2+</sup>	12.72	Br <sup>-</sup>	7.81
Ca <sup>2+</sup>	11.90	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.09
Cs <sup>+</sup>	7.72	Cl <sup>-</sup>	7.635
Cu <sup>2+</sup>	10.72	ClO <sub>4</sub> <sup>-</sup>	6.73
H <sup>+</sup>	34.96	CO <sub>3</sub> <sup>2-</sup>	13.86
K <sup>+</sup>	7.350	(CO <sub>2</sub> ) <sub>2</sub> <sup>2-</sup>	14.82
Li <sup>+</sup>	3.87	F <sup>-</sup>	5.54
Mg <sup>2+</sup>	10.60	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	30.27
Na <sup>+</sup>	5.010	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	44.20
[N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ] <sup>+</sup>	3.26	HCO <sub>2</sub> <sup>-</sup>	5.46
[N(CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	4.49	I <sup>-</sup>	7.68
NH <sub>4</sub> <sup>+</sup>	7.35	NO <sub>3</sub> <sup>-</sup>	7.146
Rb <sup>+</sup>	7.78	OH <sup>-</sup>	19.91
Sr <sup>2+</sup>	11.89	SO <sub>4</sub> <sup>2-</sup>	16.00
Zn <sup>2+</sup>	10.56		

Data: KL, RS.

## Answers to “A)” and “B)” Exercises:

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- 21.1 (a) 9.975; (b) 1.  
 21.2 (a) 72 K; (b)  $9.5 \times 10^2 \text{ m s}^{-1}$ ; (c) No.  
 21.3  $p = 0.081 \text{ Pa}$ .  
 21.4  $\lambda = 9.7 \times 10^{-1} \text{ m}$ .  
 21.5 (a)  $z = 5 \times 10^{10} \text{ s}^{-1}$ ; (b)  $z = 5 \times 10^9 \text{ s}^{-1}$ ; (c)  $z = 5 \times 10^3 \text{ s}^{-1}$ .  
 21.6 (a) 6.7 nm; (b) 67 nm; (c) 6.7 cm.  
 21.7  $9.06 \times 10^{-3}$ .  
 21.8  $N = 1.9 \times 10^{20}$ .  
 21.9  $\Delta m = 104 \text{ mg}$ .  
 21.10  $M' = 43 \text{ g mol}^{-1}$ .  
 21.11  $t = 1.1 \times 10^5 \text{ s} = 30 \text{ h}$ .  
 21.12  $J_z = 4.1 \times 10^{-2} \text{ J m}^{-2} \text{ s}^{-1}$ .  
 21.13  $\sigma = 5.6 \times 10^{-20} \text{ m}^2$  or  $0.056 \text{ nm}^2$ .  
 21.14 17 W.  
 21.15  $\sigma = 1.42 \times 10^{-19} \text{ m}^2$  or  $0.142 \text{ nm}^2$ .  
 21.16 205 kPa.  
 21.17 (a)  $T = 273 \text{ K}$ : 130  $\mu\text{P}$ ; (b)  $T = 298 \text{ K}$ : 130  $\mu\text{P}$ ; (c)  $T = 1000 \text{ K}$ : 240  $\mu\text{P}$ .  
 21.18 (a) For Ar,  $\kappa = 5.4 \text{ m J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ , rate of flow = 8.1 m W;  
 (b) For He,  $\kappa = 29 \text{ m J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ , rate of flow = 44 m W.  
 21.19  $\eta(\text{CO}_2) = 1.38 \mu\text{P}$ ,  $d = 390 \text{ pm}$ .  
 21.20  $\kappa = 5.4 \times 10^{-3} \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ .  
 21.21 (a) At 1 Pa:  $D = 1.1 \text{ m}^2 \text{ s}^{-1}$ ,  $J = 4.4 \times 10^2 \text{ mol m}^{-2} \text{ s}^{-1}$ ;  
 (b) At 100 kPa:  $D = 1.1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ,  $J = 4.4 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ ;  
 (c) At 10 MPa:  $D = 1.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ,  $J = 4.4 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ .  
 21.22  $\lambda = 7.63 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ .  
 21.23  $s = 3.47 \times 10^{-4} \text{ m s}^{-1}$ , or  $347 \mu\text{m s}^{-1}$ .  
 21.24 0.331.  
 21.25  $\Lambda_m^\circ(\text{AgCl}) = 13.83 \text{ mS m}^2 \text{ mol}^{-1}$ .  
 21.26  $u(\text{Li}^+) = 4.01 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $u(\text{Na}^+) = 5.19 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  
 $u(\text{K}^+) = 7.62 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ .  
 21.27  $D = 1.90 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .  
 21.28  $t = 1.3 \times 10^3 \text{ s}$ .  
 21.29  $a = 420 \text{ pm}$ .  
 21.30  $s = 27 \text{ ps}$ .

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- 21.1 (a) 7.079; (b) 1.  
 21.2 (a)  $c = 4.75 \times 10^2 \text{ m s}^{-1}$ ; (b)  $\lambda = 4 \times 10^4 \text{ m}$ ; (c)  $z = 0.01 \text{ s}^{-1}$ .  
 21.3  $p = 2.4 \times 10^7 \text{ Pa}$ .  
 21.4  $\lambda = 4.1 \times 10^{-7} \text{ m}$ .  
 21.5  $z = 9.9 \times 10^8 \text{ s}^{-1}$ .  
 21.6 (a)  $\lambda = 3.7 \times 10^{-9} \text{ m}$ ; (b)  $\lambda = 5.5 \times 10^{-8} \text{ m}$ ; (c)  $\lambda = 4.1 \times 10^{-5} \text{ m}$ .  
 21.7  $F \approx 9.6 \times 10^{-2}$ .  
 21.8  $N = 5.3 \times 10^{21}$ .  
 21.9  $\Delta m = 4.98 \times 10^{-4} \text{ kg}$ .  
 21.10  $M_{\text{fluorocarbon}} = 554 \text{ g mol}^{-1}$ .  
 21.11  $t = 1.5 \times 10^4 \text{ s}$ .  
 21.12  $0.17 \text{ J m}^{-2} \text{ s}^{-1}$ .  
 21.13  $1.61 \times 10^{-19} \text{ m}^2$ .  
 21.14  $22 \text{ J s}^{-1}$ .  
 21.15  $3.00 \times 10^{-19} \text{ m}^2$ .  
 21.16  $1.00 \times 10^5 \text{ Pa}$ .  
 21.17 (a) At 273 K:  $\eta = 0.95 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ ;  
 (b) At 298 K:  $\eta = 0.99 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ ;  
 (c) At 1000 K:  $\eta = 1.81 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ .  
 21.18 (a)  $\kappa = 0.0114 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ ,  $0.017 \text{ J s}^{-1}$ ;  
 (b)  $\kappa = 9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ ,  $0.014 \text{ J s}^{-1}$ .  
 21.19  $52.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$ ,  $d = 923 \text{ pm}$ .  
 21.20  $\kappa = 9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ .  
 21.21 (a)  $D = 0.107 \text{ m}^2 \text{ s}^{-1}$ ,  $J = 0.87 \text{ mol m}^{-2} \text{ s}^{-1}$ ;  
 (b)  $D = 1.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ,  $J = 8.7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ ;  
 (c)  $D = 7.13 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ ,  $J = 5.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ .  
 21.22  $4.09 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ .  
 21.23  $4.81 \times 10^{-5} \text{ m V}^{-1} \text{ s}^{-1}$ .  
 21.24 0.604.  
 21.25  $\Lambda_m^\circ(\text{MgI}_2) = 25.96 \text{ mS m}^2 \text{ mol}^{-1}$ .  
 21.26  $\text{F}^-$ :  $u = 5.74 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ;  
 $\text{Cl}^-$ :  $u = 7.913 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ;  
 $\text{Br}^-$ :  $u = 8.09 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ .  
 21.27  $1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .  
 21.28  $4.1 \times 10^3 \text{ s}$ .

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- 21.2 (a) 2.8 km h<sup>-1</sup> East; (b) 86 km h<sup>-1</sup>; (c) 86 km h<sup>-1</sup>.
- 21.3 (a)  $\langle h \rangle = 1.89$  m; (b)  $\sqrt{\langle h^2 \rangle} = 1.89$  m.
- 21.4 9.1.
- 21.5  $p = 7.3 \times 10^{-3}$  Pa, or 7.3 mPa.
- 21.6 (a) 100 Pa; (b) 24 Pa.
- 21.7 (a) Cadmium:  $2 \times 10^{14}$  s<sup>-1</sup>; (b) Mercury:  $1 \times 10^{17}$  s<sup>-1</sup>.
- 21.8  $5.3 \times 10^{-4}$  mS m<sup>2</sup> mol<sup>-1</sup>.
- 21.9  $\Lambda_m^\circ = 12.6$  mS m<sup>2</sup> mol<sup>-1</sup>;  $\chi = 7.30$  mS m<sup>2</sup> mol<sup>-1</sup> M<sup>-1/2</sup>.  
(a)  $\Lambda_m = 11.96$  mS m<sup>2</sup> mol<sup>-1</sup>; (b)  $\kappa = 119.6$  mS m<sup>-1</sup>; (c)  $R = 172.5 \Omega$ .
- 21.10  $1.36 \times 10^{-5}$  M.
- 21.11  $s(\text{Li}^+) = 4.0 \times 10^{-3}$  cm s<sup>-1</sup>,  $s(\text{Na}^+) = 5.2 \times 10^{-3}$  cm s<sup>-1</sup>;  $s(\text{K}^+) = 7.6 \times 10^{-3}$  cm s<sup>-1</sup>.  $t(\text{Li}^+) = 250$  s,  $t(\text{Na}^+) = 190$  s,  $t(\text{K}^+) = 130$  s.  
(a)  $d(\text{Li}^+) = 1.3 \times 10^{-6}$  cm;  $d(\text{Na}^+) = 1.7 \times 10^{-6}$  cm;  $d(\text{K}^+) = 2.4 \times 10^{-6}$  cm.  
(b) 43, 55 and 81 solvent molecule diameters respectively.
- 21.12 0.82, 0.0028.
- 21.13  $t_+ = 0.48$  and  $t_- = 0.52$ .  $u_+ = 7.5 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>.  $\lambda_+ = 72$  S cm<sup>2</sup> mol<sup>-1</sup>.
- 21.14 In the first solution,  $t_+ = 0.278$ . In the second solution  $t_+ = 0.278$ .  $t_+ = 0.278$ .
- 21.15 (a)  $2.1 \times 10^{-20}$  N molecule<sup>-1</sup>; (b)  $2.8 \times 10^{-20}$  N molecule<sup>-1</sup>;  
(c)  $4.1 \times 10^{-20}$  N molecule<sup>-1</sup>.
- 21.17 9.3 kJ mol<sup>-1</sup>.
- 21.18 0, 0.063 M.
- 21.19  $1.2 \times 10^{-3}$  kg m<sup>-1</sup> s<sup>-1</sup>.
- 21.20 In solvent:  $\Lambda_m^\circ(\text{NaI}) = 60.7$  S cm<sup>2</sup> mol<sup>-1</sup> and  $\Lambda_m^\circ(\text{KI}) = 58.9$  S cm<sup>2</sup> mol<sup>-1</sup>,  
In water:  $\Lambda_m^\circ(\text{NaI}) = 126.9$  S cm<sup>2</sup> mol<sup>-1</sup> and  $\Lambda_m^\circ(\text{KI}) = 150.3$  S cm<sup>2</sup> mol<sup>-1</sup>.
- 21.21 (a)  $3.68 \times 10^{-10}$  m; (b)  $3.07 \times 10^{-10}$  m.
- 21.22  $a = 830$  pm.
- 21.25  $\langle v_x \rangle = 0.47 \langle v_x \rangle_{\text{initial}}$ .
- 21.26 (a) 39 per cent; (b) 61 per cent; (c) greater: 47 per cent, less than: 53 per cent.
- 21.27 
$$\frac{f(nc^*)}{f(c^*)} = \frac{(nc^*)^2 e^{-mn^2c^*/2kT}}{c^{*2} e^{-mc^*/2kT}} [24.4] = n^2 e^{-(n^2-1)mc^*/2kT} = n^2 e^{(1-n^2)mc^*/2kT},$$
  
$$\frac{f(3c^*)}{f(c^*)} = 3.02 \times 10^{-3}, \frac{f(4c^*)}{f(c^*)} = 4.9 \times 10^{-6}.$$
- 21.31 (a)  $p = 0$ ; (b)  $p = 0.016$ ; (c)  $p = 0.054$ .
- 21.32  $N > 60$ .
- 21.36  $D = 1.6 \times 10^{16}$  m<sup>2</sup> s<sup>-1</sup>,  $\kappa = 0.34$  J K<sup>-1</sup> m<sup>-1</sup> s<sup>-1</sup>.
- 21.37 The total energy density (translational plus rotational) =  $\rho T = 0.25$  J cm<sup>-3</sup>.
- 21.39  $t = 10^8$  s.
- 21.40  $1.7 \times 10^{-2}$  s.