

## 20.5 Answers:

The rate of effusion of Germanium is:

$$r_e = \frac{\Delta m}{M \Delta t} N_A$$

and the cross-sectional area is:

$$A_0 = \pi r^2$$

According to Graham's Law of effusion,  $r_e = \frac{p A_0 N_A}{\sqrt{2\pi M R T}}$ , we can get the vapor pressure is:

$$p = \frac{\Delta m}{r^2 \Delta t} \sqrt{\frac{2 R T}{\pi M}}$$

the parameters with SI units are replaced by the data given in the question and then the vapor pressure of Ge at 1000 C is:

$$p_{1273K}(Ge) = \frac{43 \times 10^{-6} \text{ kg}}{0.25 \times 10^{-6} \text{ m}^2 \times 7200 \text{ s}} \times \sqrt{\frac{2 \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot 1273 \text{ K}}{3.14 \times 72.64 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}}} = 7.277 \text{ Pa}$$

## 20.6 Answers:

According to Graham's Law of effusion,  $r_e = \frac{p A_0 N_A}{\sqrt{2\pi M R T}}$ , and the relative parameters

are substituted by the data in the question, then we can get:

for (a) cadmium,  $M=0.1124 \text{ kg/mol}$ ,  $T=380\text{K}$ ,  $A_0=10^{-7}\text{m}^2$ ,  $p=0.13\text{Pa}$ , so the atomic current  $r_e=1.657\text{E}14 \text{ s}^{-1}$ ;

for (b) mercury,  $M=0.2006$ ,  $p=12\text{Pa}$ , similarly we can get the atomic current  $r_e=1.145\text{E}16 \text{ s}^{-1}$ .

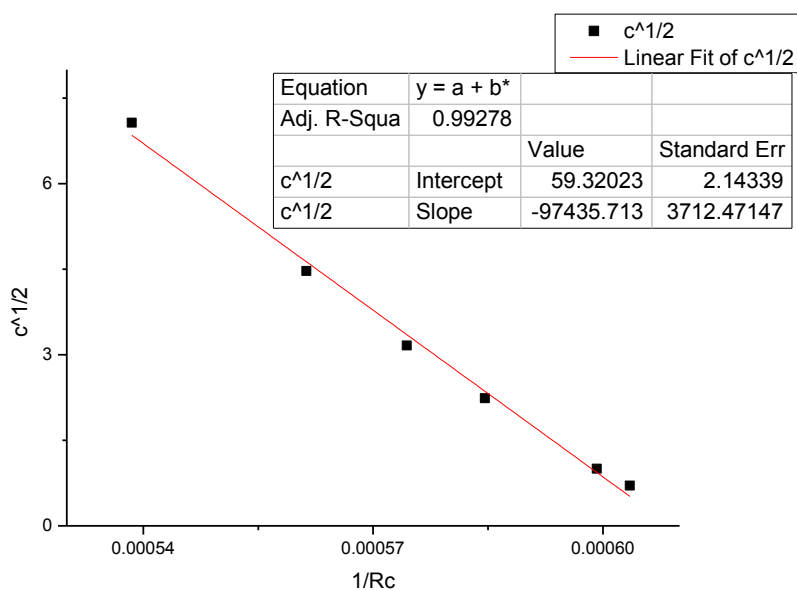
## 20.8 Answers:

Assuming the molar conductivity follows the Kohlrausch law, we can get:

$$\Lambda_m = \frac{C}{Rc} = \Lambda_m^0 - \kappa \sqrt{c}$$

$$\Rightarrow \sqrt{c} = \Lambda_m^0 / \kappa - \frac{C}{\kappa} \times \frac{1}{Rc}$$

that is, if the assumption is correct, the  $\sqrt{c}$  will changed linearly with  $\frac{1}{Rc}$ , and the intercept and the slope are  $\Lambda_m^0 / \kappa$  and  $-\frac{C}{\kappa}$  respectively. The following is the figure(using SI standard units) of  $\sqrt{c} \square \frac{1}{Rc}$ . From the figure we know that the relative coefficient  $R=0.993$ . It is believed that the assumption is plausible. So the molar conductivity follows the Kohlrausch law.



the intercept is:  $\Lambda_m^0 / \kappa = 59.32$

and the slope is:  $-\frac{C}{\kappa} = -97435.71$

finally we get:  $\kappa = 0.2117 \text{ mS} / \text{m}$ ,  $\Lambda_m^0 = 12.56 \text{ mS} \square \text{m}^2 / \text{mol}$

For NaI in solution,



According to the law of independent migration of ions,

$$\Lambda_m^0(\text{NaI}) = \lambda(\text{Na}^+) + \lambda(\text{I}^-)$$

so the limiting molar conductivity is:

$$\Lambda_m^0(\text{NaI}) = (5.01 + 7.68 = 12.69) \text{ mS m}^2 \text{ mol}^{-1};$$

According to the Kohlrausch law, we can get:  $\Lambda_m = \Lambda_m^0 - \kappa\sqrt{c}$ , so the molar conductivity of  $0.010 \text{ mol dm}^{-3}$  NaI(aq) is  $12.02 \text{ mS m}^2 \text{ mol}^{-1}$ ;

and then the conductivity can be easily got by the molar conductivity multiplied by the concentration of the NaI solution. Finally, the conductivity is  $0.1202 \text{ S/m}$ ;

so the resistance  $R = C/k = 171.63 \Omega$ .

## 20.10 Answers:

The mobilities of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  are 4.01, 5.19, 7.62 ( $10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ) respectively according to data section. The drift speed  $s$  is proportional to the electric field of magnitude  $E$ , that is:

$$s = uE = u \frac{V}{l}$$

so  $s(\text{Li}^+) = 0.0401 \text{ mm/s}$ ,  $s(\text{Na}^+) = 0.0519 \text{ mm/s}$ ,  $s(\text{K}^+) = 0.0762 \text{ mm/s}$ .

the time for the ion to move from one electrode to another one is:  $t = l/s$ , so we get the time for each ion is: 249.4s, 192.7s, 131.2s respectively.

The time of a half cycle of 1.0 kHz alternating potential is 0.5ms, so the displacement( $x=st$ ) of each ion is:  $2.005 \times 10^{-6} \text{ cm}$ ,  $2.595 \times 10^{-6} \text{ cm}$ ,  $3.810 \times 10^{-6} \text{ cm}$  respectively, or 66.8 (300pm), 86.5 (300pm), 127 (300pm) respectively.

## 20.20 Answers:

According to Maxwell distribution of speeds,

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT}\right)$$

At the point of the most probable speed, the function  $f(v)$  becomes maximum and

$$\left(\frac{\partial f}{\partial v}\right)_{p,T} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \left(2v \exp\left(-\frac{Mv^2}{2RT}\right) - v^2 \exp\left(-\frac{Mv^2}{2RT}\right) \frac{2Mv}{2RT}\right) = 0$$

the solution of the equation above is:  $v = \sqrt{\frac{2RT}{M}}$ , known as the most probable speed

of a gas at a temperature  $T$ .

for one single molecule whose speed is the interval  $[v, v+dv]$ , the probability is  $f(v)dv$ ,

and give the assumption that the mass of the single molecule is  $m$ , so the translational

kinetic energy of the molecule is  $E_k = \frac{1}{2}mv^2$ . Considering the probability, the

average energy is  $E_k f(v)dv$ . Taking all the speed distribution from zero to  $\infty$  into

account, we can get the average kinetic energy is:

$$\langle E_k \rangle = \int_0^\infty \frac{1}{2}mv^2 f(v)dv$$

As Gauss integral is known to us, we can calculate the integral above is  $\frac{3}{2}kT$ , which

is consistent with model of molecules motion.

## 20.20 Answers:

For the reaction  $AB \rightleftharpoons A^+ + B^-$ , the equilibrium constant is:

$$K = \frac{[B^-][A^+]}{[AB]} = \frac{\alpha c \times \alpha c}{(1-\alpha)c} = \frac{\alpha^2}{1-\alpha}c$$

In fact,  $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$ , then we get:

$$K = \frac{\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2}{1 - \frac{\Lambda_m}{\Lambda_m^0}} c$$

From the equation above, we can get:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{c}{K} \frac{\Lambda_m}{(\Lambda_m^0)^2}$$

Considering the equilibrium constant, the factor  $c/k$  is replaced, and then we get:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{1-\alpha}{\alpha^2} \frac{\Lambda_m}{(\Lambda_m^0)^2}$$

From the equation above, we know that the molar conductivity of weak electrolyte is related to its degree of ionization.

The conductance in the electrolyte is resulting from the mobility of ions contained in the solution. As a consequence, the total conductivity is the sum of individual conductivity of each ion. As for weak electrolyte, the proportion that has been disassociated can be regarded as strong solute which applies to Kohlrausch's Law.

That is:

$$\Lambda_m = \Lambda_m^0 - \kappa \sqrt{\alpha c}$$