E7.18(a)

$$R: \ Ag^+(aq) + e^- \rightarrow Ag(s) \qquad\quad +0.80\,V$$
$$L: \ AgI(s) + e^- \rightarrow Ag(s) + I^-(aq) \qquad -0.15\,V \ \Bigg\} \ E^\ominus = E_R^\ominus - E_L^\ominus = 0.9509\,V$$

Overall: $Ag^+(aq) + I^-(aq) \rightarrow AgI(s) \qquad \nu = 1.$
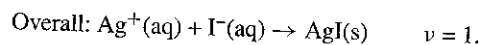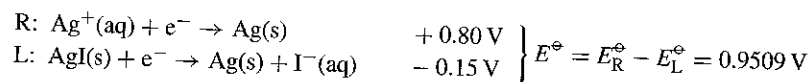
$$\ln K = \frac{\nu F E^\ominus}{RT}[7.30] = \frac{0.9509\,V}{25.693 \times 10^{-3}\,V} = 37.01\bar{0},$$
$$K = 1.1\bar{8} \times 10^{16}.$$

(a) $\quad K = \dfrac{a_{AgI(s)}}{a_{Ag^+(aq)} a_{I^-(aq)}} = \dfrac{1}{\left[Ag^+\right]\left[I^-\right]} = \dfrac{1}{\left[Ag^+\right]^2} = 1.1\bar{8} \times 10^{16}.$

(b) The solubility equilibrium is written as the reverse of the cell reaction. Therefore,
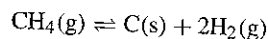
$$K_S = K^{-1} = 1/1.1\bar{8} \times 10^{16} = \boxed{8.5 \times 10^{-17}}.$$

In the above equation the activity of the solid equals 1 and, since the solution is extremely dilute, the activity coefficients of dissolved ions also equal 1. Solving for the molar ion concentration gives $[Ag^+] = [I^-] = 9.2 \times 10^{-9}$ M. AgI has a solubility equal to $\boxed{9.2 \times 10^{-9}\,M}$.

Solutions to problems

Solutions to numerical problems

P7.2 $\qquad CH_4(g) \rightleftharpoons C(s) + 2H_2(g)$

This reaction is the reverse of the formation reaction.

(a) $\qquad \Delta_r G^\ominus = -\Delta_f G^\ominus$

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$$
$$= -74850\,J\,mol^{-1} - 298\,K \times (-80.67\,J\,K^{-1}\,mol^{-1})$$
$$= -5.08 \times 10^4\,J\,mol^{-1}$$

$$\ln K = \frac{\Delta_r G^\ominus}{-RT}[7.8] = \frac{5.08 \times 10^4\,J\,mol^{-1}}{-8.314\,J\,K^{-1}\,mol^{-1} \times 298\,K} = -20.508$$
$$K = \boxed{1.24 \times 10^{-9}}$$

(b) $\qquad \Delta_r H^\ominus = -\Delta_f H^\ominus = 74.85\,kJmol^{-1}$

$$\ln K(50\,^\circ C) = \ln K(298\,K) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323\,K} - \frac{1}{298\,K}\right)[7.25]$$

$$= -20.508 - \left(\frac{7.4850 \times 10^4\,J\,mol^{-1}}{8.3145\,J\,K^{-1}\,mol^{-1}}\right) \times \left(-2.59\bar{7} \times 10^{-4}\right) = -18.17\bar{0}$$

$$K(50\,^\circ C) = \boxed{1.29 \times 10^{-8}}$$

(c) Draw up the equilibrium table

	$CH_4(g)$	$H_2(g)$
Amounts	$(1-\alpha)n$	$2\alpha n$
Mole fractions	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressures	$\left(\dfrac{1-\alpha}{1+\alpha}\right)p$	$\dfrac{2\alpha}{1+\alpha}$

$$K = \prod_J a_J^{v_J}\,[7.16] = \frac{\left(p_{H_2}/p^{\ominus}\right)^2}{\left(p_{CH_4}/p^{\ominus}\right)}$$

$$1.24 \times 10^{-9} = \frac{(2\alpha)^2}{1-\alpha^2}\left(\frac{p}{p^{\ominus}}\right) \approx 4\alpha^2 p \quad [\alpha \ll 1]$$

$$\alpha = \frac{1.24 \times 10^{-9}}{4 \times 0.010} = \boxed{1.8 \times 10^{-4}}$$

(d) Le Chatelier's principle provides the answers.

As pressure increases, α decreases, since the more compact state (less moles of gas) is favored at high pressures. As temperature increases the side of the reaction which can absorb heat is favored. Since $\Delta_r H^{\ominus}$ is positive, that is the right-hand side, hence α increases. This can also be seen from the results of parts (a) and (b), K increased from 25 °C to 50 °C, implying that α increased.

P7.4 $CO_2(g) \rightleftharpoons CO(g) + \tfrac{1}{2}O_2(g)$

Draw up the following equilibrium table

	CO_2	CO	O_2
Amounts	$(1-\alpha)n$	αn	$\dfrac{1}{2}\alpha n$
Mole fractions	$\dfrac{(1-\alpha)}{(1+(\alpha/2))}$	$\dfrac{\alpha}{(1+(\alpha/2))}$	$\dfrac{(1/2)\alpha}{(1+(\alpha/2))}$
Partial pressures	$\dfrac{(1-\alpha)p}{(1+(\alpha/2))}$	$\dfrac{\alpha p}{(1+(\alpha/2))}$	$\dfrac{\alpha p}{2(1+(\alpha/2))}$

$$K = \left(\prod_J a_J^{v_J}\right)_{equilibrium}\;[7.16] = \frac{\left(p_{CO}/p^{\ominus}\right) \times \left(p_{O_2}/p^{\ominus}\right)^{1/2}}{\left(p_{CO_2}/p^{\ominus}\right)}$$

$$= \frac{(\alpha)/((1+(\alpha/2)) \times ((\alpha/2))/(1+(\alpha/2))^{1/2} \times \left(p/p^{\ominus}\right)^{1/2}}{(1-\alpha)/(1+(\alpha/2))}$$

$$K \approx \frac{\alpha^{3/2}}{\sqrt{2}} \quad [\alpha \ll 1 \text{ at all the specified temperatures}]$$

$$\Delta_r G^{\ominus} = -RT \ln K \,[7.8]$$

The calculated values of K and $\Delta_r G$ are given in the table below. From any two pairs of K and T, $\Delta_r H$ may be calculated.

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\ [7.25]$$

Solving for $\Delta_r H^\ominus$

$$\Delta_r H^\ominus = \frac{R \ln\left(\dfrac{K_2}{K_1}\right)}{\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)}\ \text{[Exercise 7.10]} = \frac{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\dfrac{7.23 \times 10^{-6}}{1.22 \times 10^{-6}}\right)}{\left(\dfrac{1}{1395\,\text{K}} - \dfrac{1}{1498\,\text{K}}\right)}$$

$$= \boxed{3.00 \times 10^5\,\text{J mol}^{-1}}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T}$$

The calculated values of $\Delta_r S^\ominus$ are also given in the table.

T/K	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71
$K/10^{-6}$	1.22	2.80	7.23
$\Delta_r G^\ominus/(\text{kJ mol}^{-1})$	158	153	147
$\Delta_r S^\ominus/(\text{J K}^{-1}\,\text{mol}^{-1})$	102	102	102

COMMENT. $\Delta_r S^\ominus$ is essentially constant over this temperature range but it is much different from its value at 25 °C. $\Delta_r H^\ominus$, however, is only slightly different.

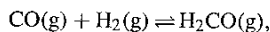*Question.* What are the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ at 25 °C for this reaction?

P7.6 $\Delta_r G^\ominus(\text{H}_2\text{CO, g}) = \Delta_r G^\ominus(\text{H}_2\text{CO, l}) + \Delta_{vap}G^\ominus(\text{H}_2\text{CO, l})$

For $\text{H}_2\text{CO(l)} \rightleftharpoons \text{H}_2\text{CO(g)}$, $K(\text{vap}) = \dfrac{p}{p^\ominus}$

$$\Delta_{vap}G^\ominus = -RT \ln K(\text{vap}) = -RT \ln \frac{p}{p^\ominus} \quad p^\ominus = 750\,\text{Torr}$$

$$= -(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times \ln\left(\frac{1500\,\text{Torr}}{750\,\text{Torr}}\right) = -1.72\,\text{kJ mol}^{-1}$$

Therefore, for the reaction

$$\text{CO(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{H}_2\text{CO(g)},$$

$$\Delta_r G^\ominus = (+28.95) + (-1.72)\,\text{kJ mol}^{-1} = +27.23\,\text{kJ mol}^{-1}$$

Hence, $K = e^{(-27.23 \times 10^3\,\text{J mol}^{-1})/(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})} = e^{-10.99} = \boxed{1.69 \times 10^{-5}}$

P7.8   Draw up the following table using $H_2(g) + I_2 \rightleftharpoons 2HI(g)$

	H_2	I_2	HI	Total
Initial amounts/mol	0.300	0.400	0.200	0.900
Change/mol	$-x$	$-x$	$+2x$	
Equilibrium amounts/mol	$0.300 - x$	$0.400 - x$	$0.200 + 2x$	0.900
Mole fraction	$(0.300 - x)/0.900$	$(0.400 - x)/0.900$	$(0.200 + 2x)/0.900$	1

$$K = \frac{\left(\dfrac{p(\text{HI})}{p^{\ominus}}\right)^2}{\left(\dfrac{p(\text{H}_2)}{p^{\ominus}}\right)\left(\dfrac{p(\text{I}_2)}{p^{\ominus}}\right)} = \frac{x(\text{HI})^2}{x(\text{H}_2)x(\text{I}_2)}[p(\text{J}) = x_{\text{J}}p] = \frac{(0.200 + 2x)^2}{(0.300 - x)(0.400 - x)} = 870 \text{ [given]}$$

Therefore,

$$(0.0400) + (0.800x) + 4x^2 = (870) \times (0.120 - 0.700x + x^2) \quad \text{or}$$

$$866x^2 - 609.80x + 104.36 = 0$$

which solves to $x = 0.293$ [$x = 0.411$ is excluded because x cannot exceed 0.300]. The final composition is therefore $\boxed{0.007 \text{ mol } H_2}$, 0.107 mol I_2, and $\boxed{0.786 \text{ mol HI}}$.

P7.10   If we knew $\Delta_r H^{\ominus}$ for this reaction, we could calculate $\Delta_f H^{\ominus}(\text{HClO})$ from

$$\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus}(\text{HClO}) - \Delta_f H^{\ominus}(\text{Cl}_2\text{O}) - \Delta_f H^{\ominus}(\text{H}_2\text{O})$$

We can find $\Delta_r H^{\ominus}$ if we know $\Delta_r G^{\ominus}$ and $\Delta_r S^{\ominus}$, since

$$\Delta_r G^{\ominus} = \Delta_r H - T\Delta_r S$$

And we can find $\Delta_r G^{\ominus}$ from the equilibrium constant.

$$K = \exp(-\Delta_r G^{\ominus}/RT) \quad \text{so} \quad \Delta_r G^{\ominus} = -RT\ln K,$$

$$\Delta_r G^{\ominus} = -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln 8.2 \times 10^{-2}$$

$$= 6.2 \text{ kJ mol}^{-1}$$

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

$$= 6.2 \text{ kJ mol}^{-1} + (298 \text{ K}) \times (16.38 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}),$$

$$\Delta_r H^{\ominus} = 11.1 \text{ kJ mol}^{-1}$$

Finally,

$$\Delta_f H^{\ominus}(\text{HClO}) = \frac{1}{2}[\Delta_r H^{\ominus} + \Delta_f H^{\ominus}(\text{Cl}_2\text{O}) + \Delta_f H^{\ominus}(\text{H}_2\text{O})],$$

$$\Delta_f H^{\ominus}(\text{HClO}) = \frac{1}{2}[11.1 + 77.2 + (-241.82)] \text{ kJ mol}^{-1}$$

$$= \boxed{76.8 \text{ kJ mol}^{-1}}$$

P7.16   **(a)** $E = E^{\ominus} - \dfrac{25.693\,\text{mV}}{\nu}\ln Q$ [*Illustration* 7.10, 25 °C]

$Q = a(\text{Zn}^{2+})a^2(\text{Cl}^-)$

$= \gamma_+\left(\dfrac{b}{b^{\ominus}}\right)(\text{Zn}^{2+})\gamma_-^2\left(\dfrac{b}{b^{\ominus}}\right)^2(\text{Cl}^-);\quad b(\text{Zn}^{2+}) = b;\quad b(\text{Cl}^-) = 2b;\quad \gamma_+\gamma_-^2 = \gamma_{\pm}^3$

Therefore, $Q = \gamma_{\pm}^3 \times 4b^3 \left[b \equiv \dfrac{b}{b^{\ominus}}\ \text{here and below}\right]$

and $E = E^{\ominus} - \dfrac{25.693\,\text{mV}}{2}\ln(4b^3\gamma_{\pm}^3) = E^{\ominus} - \left(\dfrac{3}{2}\right)\times(25.693\,\text{mV})\times\ln(4^{1/3}b\gamma_{\pm})$

$= \boxed{E^{\ominus} - (38.54\,\text{mV})\times\ln(4^{1/3}b) - (38.54\,\text{mV})\ln(\gamma_{\pm})}$

(b) $E^{\ominus}(\text{Cell}) = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} = E^{\ominus}(\text{Hg}_2\text{Cl}_2,\text{Hg}) - E^{\ominus}(\text{Zn}^{2+},\text{Zn})$

$= (0.2676\,\text{V}) - (-0.7628\,\text{V}) = \boxed{+1.0304\,\text{V}}$

(c) $\Delta_{\text{r}}G = -\nu FE = -(2)\times(9.6485\times10^4\,\text{C}\,\text{mol}^{-1})\times(1.2272\,\text{V}) = -236.81\,\text{kJ}\,\text{mol}^{-1}$

$\Delta_{\text{r}}G^{\ominus} = -\nu FE^{\ominus} = -(2)\times(9.6485\times10^4\,\text{C}\,\text{mol}^{-1})\times(1.0304\,\text{V}) = \boxed{-198.84\,\text{kJ}\,\text{mol}^{-1}}$

$\ln K = -\dfrac{\Delta_{\text{r}}G^{\ominus}}{RT} = \dfrac{1.9884\times10^5\,\text{J}\,\text{mol}^{-1}}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times(298.15\,\text{K})} = 80.211 \quad K = \boxed{6.84\times10^{34}}$

(d) From part (a)

$1.2272\,\text{V} = 1.0304\,\text{V} - (38.54\,\text{mV})\times\ln(4^{1/3}\times0.0050) - (38.54\,\text{mV})\times\ln\gamma_{\pm}$

$\ln\gamma_{\pm} = -\dfrac{(1.2272\,\text{V}) - (1.0304\,\text{V}) - (0.186\overline{4}\,\text{V})}{0.03854\,\text{V}} = -0.269\overline{8};\quad \gamma_{\pm} = \boxed{0.763}$

(e) $\log\gamma_{\pm} = -|z_-z_+|AI^{1/2}$ [5.69]

$I = \dfrac{1}{2}\sum_i z_i^2\left(\dfrac{b_i}{b^{\ominus}}\right)$ [5.70]

$b(\text{Zn}^{2+}) = b = 0.0050\,\text{mol}\,\text{kg}^{-1}\quad b(\text{Cl}^-) = 2b = 0.010\,\text{mol}\,\text{kg}^{-1}$

$I = \tfrac{1}{2}[(4)\times(0.0050) + (0.010)] = 0.015$

$\log\gamma_{\pm} = -(2)\times(0.509)\times(0.015)^{1/2} = -0.12\overline{5};\quad \gamma_{\pm} = \boxed{0.75}$

This compares remarkably well to the value obtained from experimental data in part (d).

(f) $\Delta_{\text{r}}S = -\left(\dfrac{\partial\Delta_{\text{r}}G}{\partial T}\right)_p$

$= \nu F\left(\dfrac{\partial E}{\partial T}\right)_p$ [7.39] $= (2)\times(9.6485\times10^4\,\text{C}\,\text{mol}^{-1})\times(-4.52\times10^{-4}\,\text{V}\,\text{K}^{-1})$

$= \boxed{-87.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}$

$\Delta_{\text{r}}H = \Delta_{\text{r}}G + T\Delta_{\text{r}}S = (-236.81\,\text{kJ}\,\text{mol}^{-1}) + (298.15\,\text{K})\times(-87.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})$

$= \boxed{-262.4\,\text{kJ}\,\text{mol}^{-1}}$
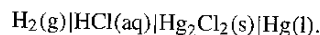
For HCl(aq), $b_+ = b_- = b$ and, if the activity coefficients are assumed equal, $a^2(H^+) = a^2(Cl^-)$; hence

$$Q = \frac{1}{a^2(H^+)a^2(Cl^-)} = \frac{1}{a^4(H^+)}.$$

Thus, $a(H^+) = \left(\frac{1}{Q}\right)^{1/4} = \left(\frac{1}{1.49 \times 10^8}\right)^{1/4} = 9 \times 10^{-3}$,

$pH = -\log a(H^+) = \boxed{2.0}$.

P7.17 $H_2(g)|HCl(aq)|Hg_2Cl_2(s)|Hg(l)$.

$E = E^\ominus - \frac{RT}{F} \ln a(H^+)a(Cl^-)$ [Section 7.8].

$a(H^+) = \gamma_+ b_+ = \gamma_+ b;\quad a(Cl^-) = \gamma_- b_- = \gamma_- b \left[b = \frac{b}{b^\ominus} \text{here and below}\right].$

$a(H^+)a(Cl^-) = \gamma_+\gamma_- b^2 = \gamma_\pm^2 b^2.$

$E = E^\ominus - \frac{2RT}{F} \ln b - \frac{2RT}{F} \ln \gamma_\pm.$ (a)

Converting from natural logarithms to common logarithms (base 10) in order to introduce the Debye–Hückel expression, we obtain

$$E = E^\ominus - \frac{(2.303) \times 2RT}{F} \log b - \frac{(2.303) \times 2RT}{F} \log \gamma_\pm$$

$$= E^\ominus - (0.1183 \text{ V})\log b - (0.1183 \text{ V})\log \gamma_\pm$$

$$= E^\ominus - (0.1183 \text{ V})\log b - (0.1183 \text{ V})\left[-|z_+ z_-|AI^{1/2}\right]$$

$$= E^\ominus - (0.1183 \text{ V})\log b + (0.1183 \text{ V}) \times A \times b^{1/2} \; [I = b].$$

Rearranging,

$$E + (0.1183 \text{ V})\log b = E^\ominus + \text{ constant } \times b^{1/2}.$$

Therefore, plot $E + (0.1183 \text{ V}) \log b$ against $b^{1/2}$, and the intercept at $b = 0$ is $E^\ominus/V$. Draw up the following table.

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$\left(\frac{b}{b^\ominus}\right)^{1/2}$	0.04010	0.05547	0.07100	0.08771	0.1046
$E/V + (0.1183)\log b$	0.27029	0.27109	0.27186	0.27260	0.27337

The points are plotted in Fig. 7.2. The intercept is at 0.26840, so $E^\ominus = +0.26840$ V. A least–squares best fit gives $E^\ominus = \boxed{+0.26843 \text{ V}}$ and a coefficient of determination equal to 0.99895.
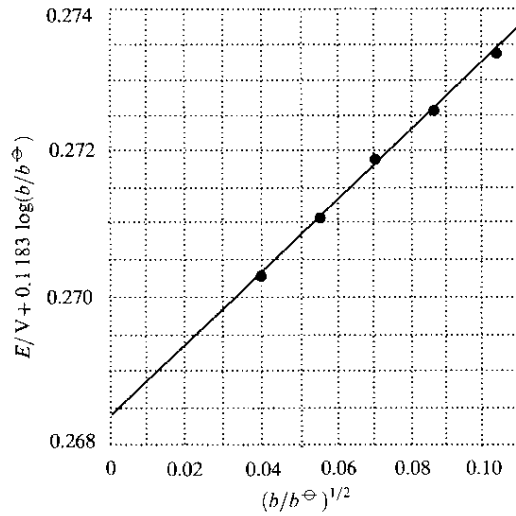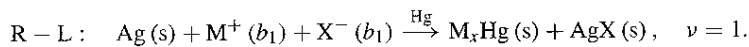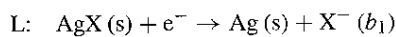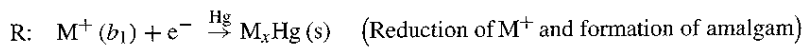
Figure 7.2

For the activity coefficients we obtain from equation (a)

$$\ln \gamma_{\pm} = \frac{E^{\ominus} - E}{2RT/F} - \ln \frac{b}{b^{\ominus}} = \frac{0.26843 - E/V}{0.05139} - \ln \frac{b}{b^{\ominus}}$$

and we draw up the following table.

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$\ln \gamma_{\pm}$	−0.3465	−0.05038	−0.6542	−0.07993	−0.09500
$\gamma_{\pm}$	0.9659	0.9509	0.9367	0.9232	0.9094

P7.19 The cells described in the problem are back-to-back pairs of cells each of the type

$$\text{Ag (s)} \,|\text{AgX (s)}\,|\text{MX } (b_1) \,|\text{M}_x\text{Hg (s)} \,.$$

R: $\text{M}^+ (b_1) + \text{e}^- \xrightarrow{\text{Hg}} \text{M}_x\text{Hg (s)}$ $\left(\text{Reduction of M}^+ \text{ and formation of amalgam}\right)$

L: $\text{AgX (s)} + \text{e}^- \rightarrow \text{Ag (s)} + \text{X}^- (b_1)$

R − L : $\text{Ag (s)} + \text{M}^+ (b_1) + \text{X}^- (b_1) \xrightarrow{\text{Hg}} \text{M}_x\text{Hg (s)} + \text{AgX (s)}, \quad \nu = 1.$

$$Q = \frac{a\left(\text{M}_x\text{Hg}\right)}{a\left(\text{M}^+\right) a\left(\text{X}^-\right)}.$$

$$E = E^{\ominus} - \frac{RT}{F} \ln Q.$$

P7.18 $\quad$ Pt$|$H$_2$(g)$|$NaOH(aq), NaCl(aq)$|$AgCl(s)$|$Ag(s)

$$H_2(s) + 2AgCl(s) \rightarrow 2Ag(s) + 2Cl^-(aq) + 2H^+(aq) \quad \nu = 2$$
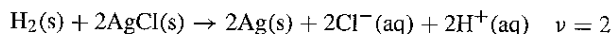
$$E = E^{\ominus} - \frac{RT}{2F}\ln Q, \quad Q = a(H^+)^2 a(Cl^-)^2 \quad [f/p^{\ominus} = 1]$$

$$= E^{\ominus} - \frac{RT}{F}\ln a(H^+)a(Cl) = E^{\ominus} - \frac{RT}{F}\ln\frac{K_w a(Cl^-)}{a(OH^-)} = E^{\ominus} - \frac{RT}{F}\ln\frac{K_w \gamma_{\pm} b(Cl^-)}{\gamma_{\pm} b(OH^-)}$$

$$= E^{\ominus} - \frac{RT}{F}\ln\frac{K_w b(Cl^-)}{b(OH^-)} = E^{\ominus} - \frac{RT}{F}\ln K_w - \frac{RT}{F}\ln\frac{b(Cl^-)}{b(OH^-)}$$

$$= E^{\ominus} + (2.303)\frac{RT}{F} \times pK_w - \frac{RT}{F}\ln\frac{b(Cl^-)}{b(OH^-)} \quad \left(pK_w = -\log K_w = \frac{-\ln K_w}{2.303}\right)$$

Hence, $pK_w = \dfrac{E - E^{\ominus}}{2.303RT/F} + \dfrac{\ln\left(\dfrac{b(Cl^-)}{b(OH^-)}\right)}{2.303} = \dfrac{E - E^{\ominus}}{2.303RT/F} + 0.05114$

$$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = E^{\ominus}(AgCl, Ag) - E^{\ominus}(H^+/H_2) = +0.22\,V - 0 \quad \text{[Table 7.2]}$$

We then draw up the following table with the more precise value for $E^{\ominus} = +0.2223$ V [See the solution to Problem 10.8, 7th edition]

$\theta/^{\circ}$C	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942
$\dfrac{(2.303RT/F)}{V}$	0.05819	0.05918	0.06018
pK_w	$\boxed{14.23}$	14.01	13.79

$$\frac{d\ln K_w}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2} \quad [7.23]$$

Hence, $\Delta_r H^{\ominus} = -(2.303)RT^2\dfrac{d}{dT}(pK_w)$

then with $\dfrac{d\,pK_w}{dT} \approx \dfrac{\Delta pK_w}{\Delta T}$

$$\Delta_r H^{\ominus} \approx -(2.303) \times (8.314\,J\,K^{-1}\,mol^{-1}) \times (298.15\,K)^2 \times \frac{13.79 - 14.23}{10\,K}$$

$$= \boxed{+74.9\,kJ\,mol^{-1}}$$

$$\Delta_r G^{\ominus} = -RT\ln K_w = 2.303\,RT \times pK_w = \boxed{+80.0\,kJ\,mol^{-1}}$$

$$\Delta_r S^{\ominus} = \frac{\Delta_r H^{\ominus} - \Delta_r G^{\ominus}}{T} = \boxed{-17.1\,J\,K^{-1}\,mol^{-1}}$$

See the original reference for a careful analysis of the precise data.