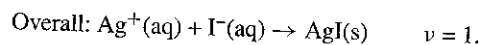
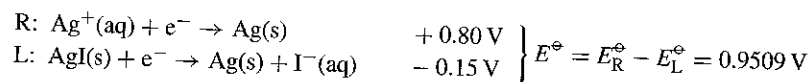


E7.18(a)



$$\ln K = \frac{\nu F E^\ominus}{RT} [7.30] = \frac{0.9509 \text{ V}}{25.693 \times 10^{-3} \text{ V}} = 37.01\bar{0},$$

$$K = 1.1\bar{8} \times 10^{16}.$$

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

(b) The solubility equilibrium is written as the reverse of the cell reaction. Therefore,

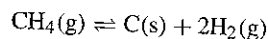
$$K_S = K^{-1} = 1/1.1\bar{8} \times 10^{16} = \boxed{8.5 \times 10^{-17}}.$$

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 $[\text{Ag}^+] = [\text{I}^-] = 9.2 \times 10^{-9} \text{ M}$. AgI has a solubility equal to $\boxed{9.2 \times 10^{-9} \text{ M}}$.

Solutions to problems

Solutions to numerical problems

P7.2



This reaction is the reverse of the formation reaction.

$$(a) \quad \Delta_{\text{r}}G^\ominus = -\Delta_{\text{f}}G^\ominus$$

$$\Delta_{\text{f}}G^\ominus = \Delta_{\text{f}}H^\ominus - T\Delta_{\text{f}}S^\ominus$$

$$= -74850 \text{ J mol}^{-1} - 298 \text{ K} \times (-80.67 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= -5.08 \times 10^4 \text{ J mol}^{-1}$$

$$\ln K = \frac{\Delta_{\text{r}}G^\ominus}{-RT} [7.8] = \frac{5.08 \times 10^4 \text{ J mol}^{-1}}{-8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = -20.508$$

$$K = \boxed{1.24 \times 10^{-9}}$$

$$(b) \quad \Delta_{\text{r}}H^\ominus = -\Delta_{\text{f}}H^\ominus = 74.85 \text{ kJ mol}^{-1}$$

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

$$= -20.508 - \left(\frac{7.4850 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-2.597 \times 10^{-4}) = -18.17\bar{0}$$

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

(c) Draw up the equilibrium table

	CH ₄ (g)	H ₂ (g)
Amounts	(1 - α)n	2αn
Mole fractions	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressures	$\left(\frac{1 - \alpha}{1 + \alpha}\right)p$	$\frac{2\alpha}{1 + \alpha}$

$$K = \prod_j a_j^{\nu_j} [7.16] = \frac{(p_{H_2}/p^\ominus)^2}{(p_{CH_4}/p^\ominus)}$$

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

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

(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 Δ_rH° 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



Draw up the following equilibrium table

	CO ₂	CO	O ₂
Amounts	(1 - α)n	αn	$\frac{1}{2}\alpha n$
Mole fractions	$\frac{(1 - \alpha)}{(1 + (\alpha/2))}$	$\frac{\alpha}{(1 + (\alpha/2))}$	$\frac{(1/2)\alpha}{(1 + (\alpha/2))}$
Partial pressures	$\frac{(1 - \alpha)p}{(1 + (\alpha/2))}$	$\frac{\alpha p}{(1 + (\alpha/2))}$	$\frac{\alpha p}{2(1 + (\alpha/2))}$

$$K = \left(\prod_j a_j^{\nu_j} \right)_{\text{equilibrium}} [7.16] = \frac{(p_{CO}/p^\ominus) \times (p_{O_2}/p^\ominus)^{1/2}}{(p_{CO_2}/p^\ominus)}$$

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

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

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

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

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

Solving for $\Delta_r H^\ominus$

$$\begin{aligned} \Delta_r H^\ominus &= \frac{R \ln \left(\frac{K_2}{K_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad [\text{Exercise 7.10}] = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{7.23 \times 10^{-6}}{1.22 \times 10^{-6}} \right)}{\left(\frac{1}{1395 \text{ K}} - \frac{1}{1498 \text{ K}} \right)} \\ &= \boxed{3.00 \times 10^5 \text{ J mol}^{-1}} \end{aligned}$$

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

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?

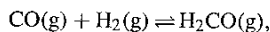
P7.6

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

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

$$\begin{aligned} \Delta_{\text{vap}} G^\ominus &= -RT \ln K(\text{vap}) = -RT \ln \frac{p}{p^\ominus} \quad p^\ominus = 750 \text{ Torr} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{1500 \text{ Torr}}{750 \text{ Torr}} \right) = -1.72 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, for the reaction



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

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

P7.8 Draw up the following table using $\text{H}_2(\text{g}) + \text{I}_2 \rightleftharpoons 2\text{HI}(\text{g})$

	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

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

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

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

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) $E = E^\ominus - \frac{25.693 \text{ mV}}{\nu} \ln Q$ [Illustration 7.10, 25 °C]
 $Q = a(\text{Zn}^{2+})a^2(\text{Cl}^-)$
 $= \gamma_+ \left(\frac{b}{b^\ominus}\right) (\text{Zn}^{2+}) \gamma_-^2 \left(\frac{b}{b^\ominus}\right)^2 (\text{Cl}^-)$; $b(\text{Zn}^{2+}) = b$; $b(\text{Cl}^-) = 2b$; $\gamma_+ \gamma_-^2 = \gamma_\pm^3$

Therefore, $Q = \gamma_\pm^3 \times 4b^3 \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right]$
 and $E = E^\ominus - \frac{25.693 \text{ mV}}{2} \ln(4b^3 \gamma_\pm^3) = E^\ominus - \left(\frac{3}{2}\right) \times (25.693 \text{ mV}) \times \ln(4^{1/3} b \gamma_\pm)$
 $= \boxed{E^\ominus - (38.54 \text{ mV}) \times \ln(4^{1/3} b) - (38.54 \text{ mV}) \ln(\gamma_\pm)}$

(b) $E^\ominus(\text{Cell}) = E_R^\ominus - E_L^\ominus = E^\ominus(\text{Hg}_2\text{Cl}_2, \text{Hg}) - E^\ominus(\text{Zn}^{2+}, \text{Zn})$
 $= (0.2676 \text{ V}) - (-0.7628 \text{ V}) = \boxed{+1.0304 \text{ V}}$

(c) $\Delta_r G = -\nu FE = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.2272 \text{ V}) = -236.81 \text{ kJ mol}^{-1}$
 $\Delta_r G^\ominus = -\nu FE^\ominus = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.0304 \text{ V}) = \boxed{-198.84 \text{ kJ mol}^{-1}}$
 $\ln K = -\frac{\Delta_r G^\ominus}{RT} = \frac{1.9884 \times 10^5 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 80.211 \quad K = \boxed{6.84 \times 10^{34}}$

(d) From part (a)

$$1.2272 \text{ V} = 1.0304 \text{ V} - (38.54 \text{ mV}) \times \ln(4^{1/3} \times 0.0050) - (38.54 \text{ mV}) \times \ln \gamma_\pm$$

$$\ln \gamma_\pm = -\frac{(1.2272 \text{ V}) - (1.0304 \text{ V}) - (0.1864 \text{ V})}{0.03854 \text{ V}} = -0.2698; \quad \gamma_\pm = \boxed{0.763}$$

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

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

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

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

$$\log \gamma_\pm = -(2) \times (0.509) \times (0.015)^{1/2} = -0.125; \quad \gamma_\pm = \boxed{0.75}$$

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

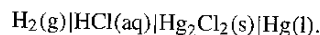
(f) $\Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_p$
 $= \nu F \left(\frac{\partial E}{\partial T}\right)_p$ [7.39] $= (2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (-4.52 \times 10^{-4} \text{ V K}^{-1})$
 $= \boxed{-87.2 \text{ J K}^{-1} \text{ mol}^{-1}}$
 $\Delta_r H = \Delta_r G + T \Delta_r S = (-236.81 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-87.2 \text{ J K}^{-1} \text{ mol}^{-1})$
 $= \boxed{-262.4 \text{ kJ mol}^{-1}}$

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

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

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

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

P7.17

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

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

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

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

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

$$\begin{aligned} E &= E^\ominus - \frac{(2.303) \times 2RT}{F} \log b - \frac{(2.303) \times 2RT}{F} \log \gamma_{\pm} \\ &= E^\ominus - (0.1183 \text{ V}) \log b - (0.1183 \text{ V}) \log \gamma_{\pm} \\ &= E^\ominus - (0.1183 \text{ V}) \log b - (0.1183 \text{ V}) \left[-|z_+ z_-| A I^{1/2} \right] \\ &= E^\ominus - (0.1183 \text{ V}) \log b + (0.1183 \text{ V}) \times A \times b^{1/2} \quad [I = b]. \end{aligned}$$

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
$E/\text{V} + (0.1183) \log b$	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 $E^\ominus = +0.26840 \text{ V}$. A least-squares best fit gives $E^\ominus = \boxed{+0.26843 \text{ V}}$ and a coefficient of determination equal to 0.99895.

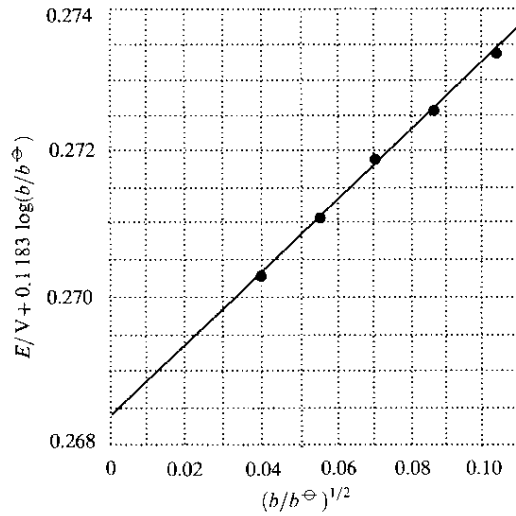


Figure 7.2

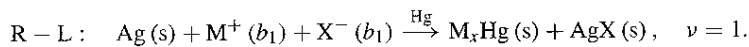
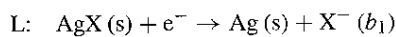
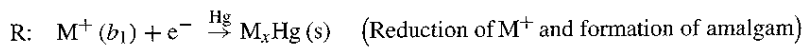
For the activity coefficients we obtain from equation (a)

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

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
γ_{\pm}	0.9659	0.9509	0.9367	0.9232	0.9094

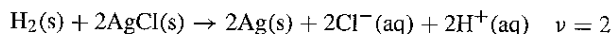
P7.19 The cells described in the problem are back-to-back pairs of cells each of the type



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

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

P7.18 Pt|H₂(g)|NaOH(aq), NaCl(aq)|AgCl(s)|Ag(s)



$$\begin{aligned} E &= E^\ominus - \frac{RT}{2F} \ln Q, \quad Q = a(\text{H}^+)^2 a(\text{Cl}^-)^2 \quad [f/p^\ominus = 1] \\ &= E^\ominus - \frac{RT}{F} \ln a(\text{H}^+) a(\text{Cl}) = E^\ominus - \frac{RT}{F} \ln \frac{K_w a(\text{Cl}^-)}{a(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln \frac{K_w \gamma_{\pm} b(\text{Cl}^-)}{\gamma_{\pm} b(\text{OH}^-)} \\ &= E^\ominus - \frac{RT}{F} \ln \frac{K_w b(\text{Cl}^-)}{b(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \\ &= E^\ominus + (2.303) \frac{RT}{F} \times \text{p}K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \quad \left(\text{p}K_w = -\log K_w = \frac{-\ln K_w}{2.303} \right) \end{aligned}$$

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

$$E^\ominus = E_R^\ominus - E_L^\ominus = E^\ominus(\text{AgCl, Ag}) - E^\ominus(\text{H}^+/\text{H}_2) = +0.22 \text{ V} - 0 \text{ [Table 7.2]}$$

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

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

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

$$\text{Hence, } \Delta_r H^\ominus = -(2.303)RT^2 \frac{d}{dT}(\text{p}K_w)$$

$$\text{then with } \frac{d \text{p}K_w}{dT} \approx \frac{\Delta \text{p}K_w}{\Delta T}$$

$$\begin{aligned} \Delta_r H^\ominus &\approx -(2.303) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})^2 \times \frac{13.79 - 14.23}{10 \text{ K}} \\ &= \boxed{+74.9 \text{ kJ mol}^{-1}} \end{aligned}$$

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

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

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