Use thermodynamic data to calculate $K_{sp}$ of $\text{PbCl}_2(s)$ at 25°C.

Given $\Delta H_{\text{rxn}}$ and $\Delta S_{\text{rxn}}$:

$$\text{PbCl}_2(s) \rightarrow \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$$

$$\Delta G_{\text{rm}}^0 = \left[ 1(-24.3) + 2(-131.17) \right] - [1(-314)]$$

$$\Delta G^0 = +27.36 \text{ kJ}$$

$$\Delta G^0 = -RT \ln K$$

$$\ln K = -\frac{\Delta G^0}{RT}$$

$$\ln K = -\frac{(27.36 \text{ kJ}) \left(\frac{1000 \text{ J}}{\text{kJ}}\right)}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}} = -11.04$$

$$K_{sp} = e^{-11.04} = 1.6 \times 10^{-5}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = -RT \ln K$$

Get $K$ at several $T$

Plot $\ln K$ vs. $1/T$

slope = $-\frac{\Delta H^0}{R}$

$y$-int. = $\frac{\Delta S^0}{R}$
\[ \ln K = -\frac{\Delta H^o}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^o}{R} \]

\[ \ln \frac{K_2}{K_1} = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{(obtainable from above)} \]

\[ \ln K_1 = -\frac{\Delta H^o}{R} \left( \frac{1}{T_1} \right) + \frac{\Delta S^o}{R} \]

\[ \ln K_2 = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} \right) + \frac{\Delta S^o}{R} \]

\[ \ln K_2 - \ln K_1 = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} \right) - \left( -\frac{\Delta H^o}{R} \left( \frac{1}{T_1} \right) \right) + \frac{\Delta S^o}{R} - \frac{\Delta S^o}{R} \]

\[ \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{eqn. 17.10} \]

van't Hoff eqn.
Chapter 21
Electrochemistry

Review: Reduction-Oxidation Reactions (See Chapter 4)

Driving force: transfer/shift of electrons

- LEO the lion says GER
  Loss of Electrons is Oxidation; Gain of Electrons is Reduction
- OIL RIG
  Oxidation Is Loss; Reduction Is Gain
- ELMO
  Electron Loss Means Oxidation

The substance that is oxidized ≡ the reducing agent.
The substance that is reduced ≡ the oxidizing agent.

A reaction is a “redox reaction” if the oxidation numbers of one or more atoms changes. e.g.,

\[ 2\text{Zn(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO(s)} \]

ON of Zn changes from 0 to +2
ON of O changes from 0 to 2

∴ This is a redox reaction,
and
Zn was oxidized and was the reducing agent,
and
O\textsubscript{2} was reduced and was the oxidizing agent.

---

**Electrochemistry**

- the study of interchange of chemical and electrical energy
- involves redox reactions

Goal: to be able to do useful things (work) by generating an electric current.

Much of the experimental evidence for thermodynamic concepts arose from electrochemical experiments!

Experimentally, this reaction is spontaneous (i.e., \( \Delta G^0 \) is negative): \( \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \)

\( \text{Zn oxidized, Cu}^{2+} \text{ reduced} \)

The problem is that the electron transfer occurs at the interface between the substances. To do useful electrical work, we need to force the electrons to travel through a wire; i.e., the reduction and oxidation processes must be separated!
We need to add an apparatus that will allow electrical neutrality to be maintained in both beakers without allowing the contents of the beakers to mix.

- **Salt bridge**
  - allows ions to flow, maintaining electrical neutrality
  - contains a **strong electrolyte** in a gelatinous matrix or a porous/absorbent substance saturated with a strong electrolytes solution, with the ends closed with a glass frit.
  - is an “external source” of ions.

- **Porous disk**
  - prevents solutions from mixing significantly but allows ions to cross, maintaining charge balance.
  - is an “internal source” of ions.

**Voltaic (galvanic) cell**: device in which chemical energy is converted to electrical energy

**Electrodes**: metallic conductors that make electrical contact with contents of half-cells.

- **Anode**: electrode at which oxidation occurs e.g. Zn
- **Cathode**: electrode at which reduction occurs e.g. Cu

In the salt bridge:
- Anions flow toward/into anode compartment
- Cations flow toward/into cathode compartment
Cell Potential, \( E^\circ \) (\( E^\circ \))

measured in volts  
1 volt = 1 joule energy per coulomb charge transferred \([1 \text{ V} = 1 \text{ J} \cdot \text{C}^{-1}]\)

\[
E^\circ_{\text{CELL}} = E^\circ_{\text{OVERALL}} = E^\circ_{\text{OXIDATION}} + E^\circ_{\text{REDUCTION}} = E^\circ_{\text{CATHODE}} - E^\circ_{\text{ANODE}}
\]

\[E^\circ_{\text{OXIDATION}} = -E^\circ_{\text{ANODE}}\]

\[E^\circ_{\text{REDUCTION}} = E^\circ_{\text{CATHODE}}\]

\[
\text{e.g., the two tabulated reductions } \text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad E^\circ_{\text{RED}} = -0.76 \text{ V}
\]

\[
\text{and } \quad \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E^\circ_{\text{RED}} = +0.34 \text{ V}
\]

Reverse Zn half-reaction: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad E^\circ_{\text{OX}} = +0.76 \text{ V} \quad (\quad --E^\circ_{\text{ANODE}} = --(-0.76 \text{ V})\quad)
\]

Add to Cu half-reaction: \( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E^\circ_{\text{RED}} = +0.34 \text{ V} \quad (\quad --E^\circ_{\text{CATHODE}}\quad)
\]

For \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+} \):

\[E^\circ_{\text{CELL}} = +1.10 \text{ V}\]

We need a reference to measure half-cell \( E^\circ \)’s…

“Standard Hydrogen Electrode” (SHE) (really a half-cell)

\[\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^- \quad \text{anode} \quad \text{OR} \quad 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \]

\[\text{Pt(s)} \quad \text{cathode} \]

**Cell Shorthand Notation**

<table>
<thead>
<tr>
<th>anode</th>
<th>species oxidized, if different</th>
<th>oxidation product</th>
<th>species reduced</th>
<th>reduction product</th>
<th>cathode solid, if different</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[\star\text{e.g.,} \quad \text{For } \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) : \quad \text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)} \]

\[\text{e.g.,} \quad \text{For } 2\text{H}^+(\text{aq}) + \text{Fe(s)} \rightarrow \text{H}_2(\text{g}) + \text{Fe}^{2+}(\text{aq}) : \quad \text{Fe(s)} | \text{Fe}^{2+}(\text{aq}) || \text{H}^+(\text{aq}) | \text{H}_2(\text{g}) | \text{Pt(s)} \]

\[\text{OR: } \quad \text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \]

\[\text{red: } 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \]

\[\text{Fe}^{2+}(\text{aq}, 0.10 \text{ m}) \]

\[E^\circ \text{ and Reaction Spontaneity—or—Predicting Redox Reactions} \]

\[\star\text{ Redox reactions that have a positive overall } E^\circ \text{ are spontaneous as written.} \]

\[\Delta G = -nFE^\circ \]

\[n = \text{moles e}^- \text{ transferred} \]

\[F = \text{Faraday constant} \]

\[96,485 \text{ coul/mol e}^- \]

\[\Delta G^\circ = -nFE^\circ \]

\[n, F \text{ always positive} \]

\[\therefore \Delta G, \Delta G^\circ \text{ negative} \]

\[\text{if } E, E^\circ \text{ positive} \]
E.g. What is $\Sigma^0$ of this reaction (at 298K)?

\[
\text{Cr(s)} + 3\text{Ag}^+(aq) \rightarrow \text{Cr}^{3+}(aq) + 3\text{Ag}(s)
\]

From Table

\[
\begin{align*}
\text{Ag}^+(aq) + e^- &\rightleftharpoons \text{Ag(s)} & +0.80 \\
\text{Cr}^{3+}(aq) + 3e^- &\rightleftharpoons \text{Cr(s)} & -0.74 \\
\end{align*}
\]

\[
\begin{align*}
3\text{Ag}^+ + 3e^- &\rightarrow 3\text{Ag} & \Sigma^0_{\text{cathode}} = +0.80 \text{V} \\
\text{Cr}(s) &\rightarrow 3e^- + \text{Cr}^{3+} & \Sigma^0_{\text{anode}} = -( -0.74 \text{V}) \\
3\text{Ag}^+ + \text{Cr} &\rightarrow \text{Cr}^{3+} + 3\text{Ag} & \Sigma^0_{\text{cell}} = +1.54 \text{V} \\
\end{align*}
\]

\* Do not triple \( 0.80 \text{V} \) (I will find you)

Spontaneous: \( \Sigma^0_{\text{cell}} \oplus (\Delta G^0_{\Theta}) \)