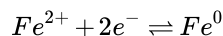


## 17.17: Combining two Half-cell Equations to Obtain a new Half-cell Equation

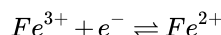
The same chemical species can be a reactant or product in many different half-cells. Frequently, data on two different half-cells can be combined to give information about a third half-cell. Let us consider two half-cells that involve the ferrous ion,  $Fe^{2+}$ . Ferrous ion and elemental iron form a redox couple. The half-cell consists of a piece of pure iron in contact with aqueous ferrous ion at unit activity. Our notation for this half-cell and its potential are  $Fe | Fe^{2+}$  and  $\mathcal{E}_{Fe|Fe^{2+}}$ . The corresponding half-reaction and its potential are



and

$$\mathcal{E}_{Fe|Fe^{2+}} = \mathcal{E}_{Fe|Fe^{2+}}^{\circ} - \frac{RT}{2\mathcal{F}} \ln \frac{1}{\tilde{a}_{Fe^{2+}}}$$

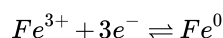
Ferrous ion can also give up an electron at an inert electrode, forming ferric ion,  $Fe^{3+}$ . This process is reversible. Depending on the potential of the half-cell with which it is paired, the inert electrode can either accept an electron from the external circuit and deliver it to a ferric ion, or take an electron from a ferrous ion and deliver it to the external circuit. Thus, ferrous and ferric ions form a redox couple. Platinum metal functions as an inert electrode in this reaction. The half-cell consists of a piece of pure platinum in contact with aqueous ferrous and ferric ions, both present at unit activity. Our notation for this half-cell and potential are  $Pt | Fe^{2+}, Fe^{3+}$  and  $\mathcal{E}_{Pt|Fe^{2+}, Fe^{3+}}$ . The corresponding half-reaction and its potential are



and

$$\mathcal{E}_{Pt|Fe^{2+}, Fe^{3+}} = \mathcal{E}_{Pt|Fe^{2+}, Fe^{3+}}^{\circ} - \frac{RT}{\mathcal{F}} \ln \frac{\tilde{a}_{Fe^{2+}}}{\tilde{a}_{Fe^{3+}}}$$

We can add these two half-reactions, to obtain



The Nernst equation for this half-reaction is

$$\mathcal{E}_{Fe|Fe^{3+}} = \mathcal{E}_{Fe|Fe^{3+}}^{\circ} - \frac{RT}{3\mathcal{F}} \ln \frac{1}{\tilde{a}_{Fe^{3+}}}$$

From our past considerations, both of these equations are clearly correct. However, in this case, the Nernst equation of the sum is not the sum of the Nernst equations. Nor should we expect it to be. The half-cell Nernst equations are really shorthand notation for the behavior of the half-cell when it is operated against a S.H.E. Adding half-cell Nernst equations corresponds to creating a new system by connecting the two S.H.E. electrodes of two separate full cells, as we illustrate in Figure 8. In the present instance, we are manipulating two half-reactions to obtain a new half-reaction; this manipulation does not correspond to any possible way of interconnecting the corresponding half-cells.

Nevertheless, if we know the standard potentials for the first two reactions ( $\mathcal{E}_{Fe|Fe^{2+}}^{\circ}$  and  $\mathcal{E}_{Pt|Fe^{2+}, Fe^{3+}}^{\circ}$ ), we can obtain the standard potential for their sum ( $\mathcal{E}_{Fe|Fe^{3+}}^{\circ}$ ). To do so, we exploit the relationship we found between electrical potential and Gibbs free energy. The first two reactions represent sequential steps that jointly achieve the same net change as the third reaction. Therefore, the sum of the Gibbs free energy changes for the first two reactions must be the same as the Gibbs free energy change for the third reaction. The standard potentials are not additive, but the Gibbs free energy changes are. We have

$$\begin{array}{rcl} Fe^{3+} + e^- \rightleftharpoons Fe^{2+} & \Delta G_{Fe^{3+} \rightarrow Fe^{2+}}^{\circ} = \mathcal{F} \mathcal{E}_{Pt|Fe^{2+}, Fe^{3+}}^{\circ} & \\ Fe^{2+} + 2e^- \rightleftharpoons Fe^0 & \Delta G_{Fe^{2+} \rightarrow Fe^0}^{\circ} = 2\mathcal{F} \mathcal{E}_{Fe|Fe^{2+}}^{\circ} & \\ \hline Fe^{3+} + 3e^- \rightleftharpoons Fe^0 & \Delta G_{Fe^{3+} \rightarrow Fe^0}^{\circ} = 3\mathcal{F} \mathcal{E}_{Fe|Fe^{3+}}^{\circ} & \end{array}$$

Since also

$$\Delta G_{Fe^{3+} \rightarrow Fe^{2+}}^{\circ} + \Delta G_{Fe^{2+} \rightarrow Fe^0}^{\circ} = \Delta G_{Fe^{3+} \rightarrow Fe^0}^{\circ}$$

we have

$$\mathcal{F}\mathcal{E}_{Pt|Fe^{2+},Fe^{3+}}^o + 2\mathcal{F}\mathcal{E}_{Fe|Fe^{2+}}^o = 3\mathcal{F}\mathcal{E}_{Fe|Fe^{3+}}^o$$

and

$$\mathcal{E}_{Fe|Fe^{3+}}^o = \frac{\mathcal{E}_{Pt|Fe^{2+},Fe^{3+}}^o + 2\mathcal{E}_{Fe|Fe^{2+}}^o}{3}$$

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