Statistical Molecular Thermodynamics

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Video 13.5

Ionic Free Energies of Formation

Thermodynamic Values for Ions

Recall convention: $\frac{1}{2}H_{2(g)} \leftrightarrows H^+_{(aq)} + e^- \qquad E^o = 0.000\ V$

thus

$$E^o = -\frac{\Delta G^o_r}{nF} \quad \Rightarrow \quad \Delta G^o_r = 0$$

zero because pure "elements"

but, we also have

$$\Delta G^o_r = \Delta G^o_f\left[H^+_{(aq)}\right] + \Delta G^o_f\left(e^-\right) - \frac{1}{2}\Delta G^o_f\left[H_{2(g)}\right]$$

$$= \Delta G^o_f\left[H^+_{(aq)}\right] \quad \Rightarrow \quad \Delta G^o_f\left[H^+_{(aq)}\right] = 0$$

consequence of adopting $E^o = 0$ for SHE

Once one ion is set (H^+), all the rest can be determined from cell voltages that relate back to that ion.

Thermochemistry in Solution

E.g.,

$$\frac{1}{2}\mathrm{H_{2(g)}} + \frac{1}{2}\mathrm{Cl_{2(g)}} \leftrightarrows \mathrm{H^{+}_{(aq)}} + \mathrm{Cl^{-}_{(aq)}} \qquad E^{o} = 0.000_{\mathrm{SHE}} + 1.361_{\mathrm{Cl_2,red}}\ \mathrm{V} = 1.361\ \mathrm{V}$$

$$-nFE^{o} = \Delta G^{o}_{r} = \Delta G^{o}_{f}\left[\mathrm{H^{+}_{(aq)}}\right] + \Delta G^{o}_{f}\left[\mathrm{Cl^{-}_{(aq)}}\right] - \frac{1}{2}\Delta G^{o}_{f}\left[\mathrm{H_{2(g)}}\right] - \frac{1}{2}\Delta G^{o}_{f}\left[\mathrm{Cl_{2(g)}}\right]$$

and so

$$-(1)\left(96{,}485\ \mathrm{C\ mol^{-1}}\right)(1.361\ \mathrm{V}) = \Delta G^{o}_{f}\left[\mathrm{Cl^{-}_{(aq)}}\right] \Rightarrow \Delta G^{o}_{f}\left[\mathrm{Cl^{-}_{(aq)}}\right] = -131.2\ \mathrm{kJ\ mol^{-1}}$$

Considering temperature dependence lets us assign entropies and enthalpies to ions in solution as well (continuing to adopt the convention that the proton has a value of 0 for all quantities); this provides everything that is needed to move thermochemistry from the gas phase to solution, using the same techniques we considered for gaseous equilibria and taking advantage of enormous compilations of heats, entropies, and free energies of formation.

Big Tables...

Summary of the Apparent Standard Partial Molal Gibbs Free Energies of Formation of Aqueous Species, Minerals, and Gases at Pressures 1 to 5000 Bars and Temperatures 25 to 1000 °C

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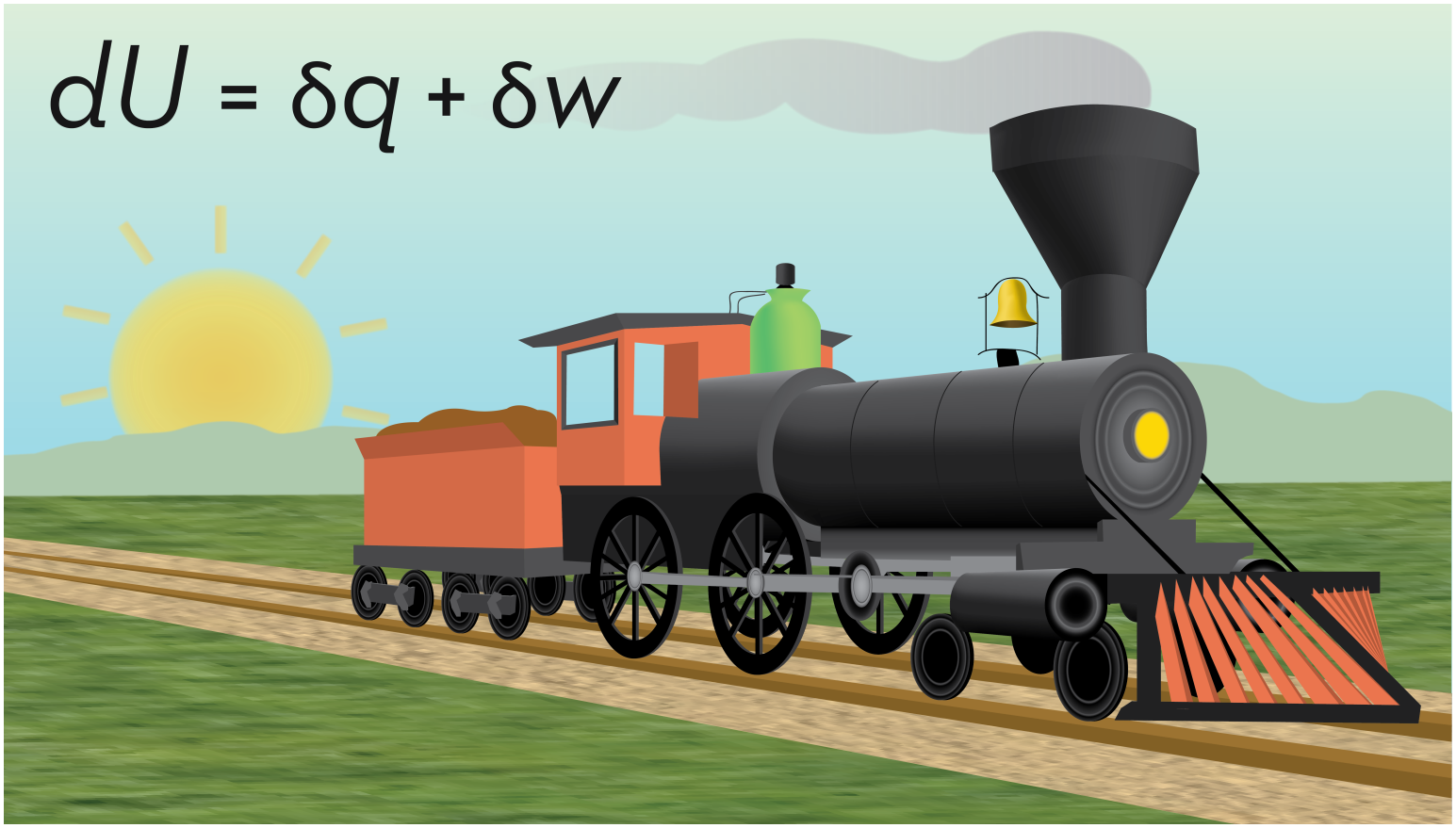

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