Statistical Molecular Thermodynamics

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Video 12.5

Reaction Quotient Redux

Utility of the Reaction Quotient

Cf. video 12.2:

any arbitrary pressures

In general: $\Delta_r G = \Delta_r G^\circ(T) + RT \ln Q_P$ $\quad Q_P = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)$

At equilibrium: $\Delta_r G^\circ(T) = -RT \ln K_P$ $\quad K_P = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq}$ *

$(\Delta_r G = 0)$

the *equilibrium* pressures

substitute: $\Delta_r G = -RT \ln K_P + RT \ln Q_P$

$$\Delta_r G = RT \ln \frac{Q_P}{K_P}$$

reaction quotient (Q_P)

equilibrium constant (K_P)

Reaction Quotient Dictates Direction

$$\nu_A \mathrm{A(g)} + \nu_B \mathrm{B(g)} \rightleftharpoons \nu_Y \mathrm{Y(g)} + \nu_Z \mathrm{Z(g)}$$

$$\Delta_r G = RT \ln \frac{Q_P}{K_P} \qquad Q_P = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right) \quad K_P = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq} *$$

- At equilibrium, $\Delta_r G = 0$ and $Q_P = K_P$.

- If $Q_P < K_P$ then Q_P must *increase* to proceed toward equilibrium. This means the pressure of the products will *increase* and the pressure of the reactants will *decrease*, and the reaction will go to the *right*.

- If $Q_P > K_P$ then Q_P must *decrease* to proceed toward equilibrium. This means the pressure of the products will *decrease* and the pressure of the reactants will *increase* and the reaction will go to the *left*.

Self-assessment

Consider the reaction below, for which K_P = 10 at 960 K:

$$2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$$

Given 960 K starting partial pressures of 1.0 x 10^{-3}, 0.20, and 1.0 x 10^{-4} bar for SO_2, O_2, and SO_3, respectively, predict the direction in which the reaction will spontaneously proceed and the overall $\Delta_r G$

Self-assessment Explained

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad K_P = 10 \text{ at } 960 \text{ K}$$

Given 960 K starting partial pressures of 1.0 x 10^{-3}, 0.20, and 1.0 x 10^{-4} bar for SO_2, O_2, and SO_3, respectively, predict the direction in which the reaction will spontaneously proceed and the overall $\Delta_r G$

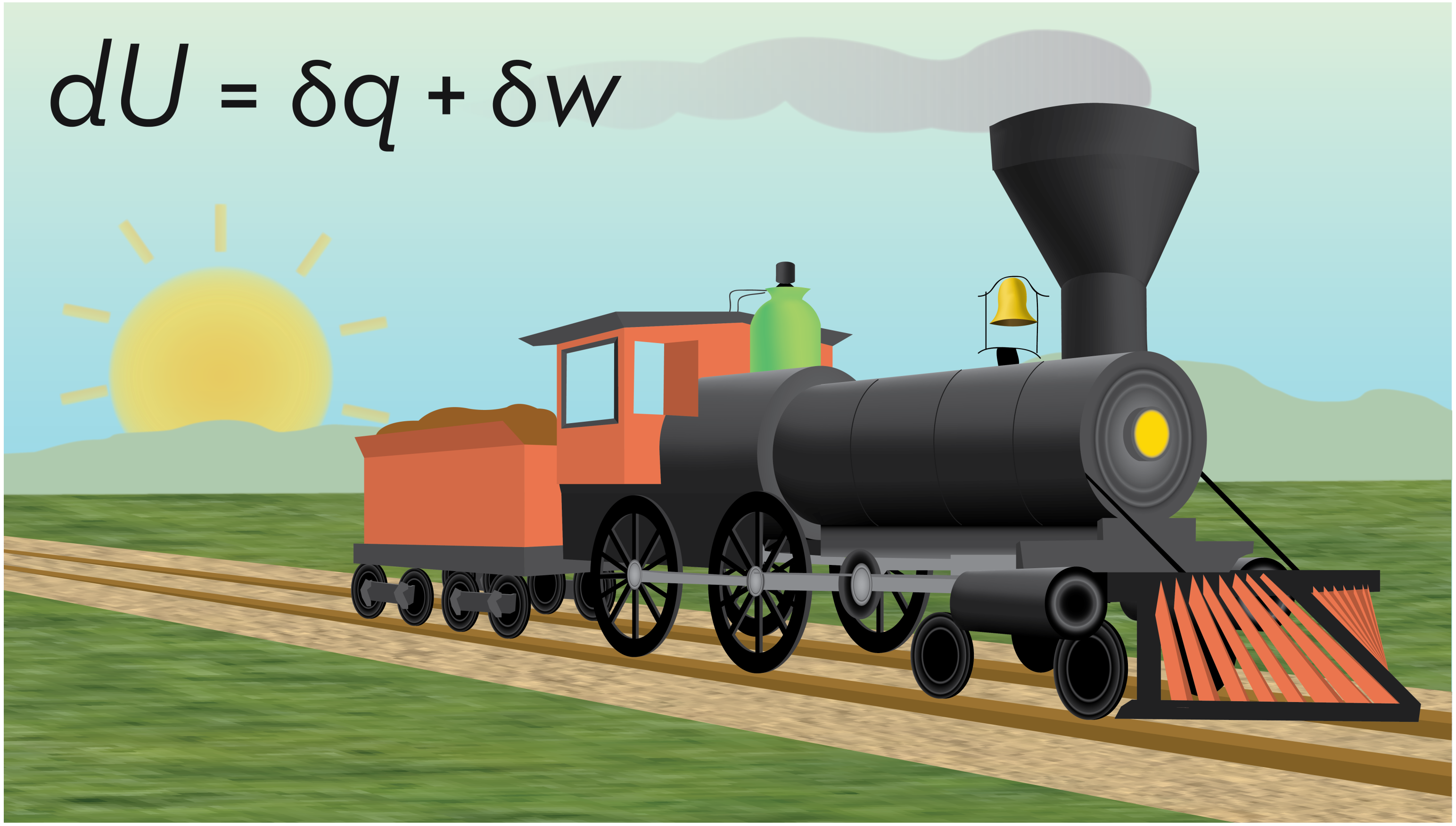
To begin, $$Q_P = \frac{P_{SO_3}^2}{P_{O_2} P_{SO_2}^2} = \frac{(0.0001)^2}{(0.001)^2(0.2)} = 0.05$$

as $Q_P < K_P$, the reaction will proceed to the right

And, $$\Delta_r G = RT \ln \frac{Q_P}{K_P}$$

$$= (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(960 \text{ K}) \ln\left(\frac{0.05}{10}\right)$$

$$= -42.3 \text{ kJ mol}^{-1}$$



Next: Temperature Dependence of K