

19.2 Calculating Entropy Change

Entropy Change in the Surroundings

Consider the reaction $\text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) = 2\text{NO}(\text{g}) + 2\text{H}_2(\text{g})$
for which $\Delta H^\circ = 752.2 \text{ kJ}$ and $\Delta S^\circ = 351.6 \text{ J/K}$ at 298.15 K

- At 298.15 K is this reaction product or reactant favored?
- Is the answer to a) entropy or enthalpy driven?

$$\Delta S^\circ_{\text{UNIV}} = \Delta S^\circ_{\text{SYS}} + \Delta S^\circ_{\text{SURR}}$$

$$\Delta S^\circ_{\text{SYS}} = \Delta S^\circ_{\text{RXN}} = 351.6 \text{ J/K}$$

$$\begin{aligned}\Delta S^\circ_{\text{SURR}} &= -\frac{\Delta H^\circ_{\text{RXN}}}{T} \\ &= -\frac{752,200 \text{ J}}{298.15 \text{ K}} = -2522.8 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{\text{UNIV}} &= 351.6 - 2522.8 \\ &= -2171.2 \text{ J/K}\end{aligned}$$

a) $\Delta S^\circ_{\text{UNIV}} < 0$
Nonspontaneous, reactant favored.

b) $\Delta S^\circ_{\text{SYS}} > 0$
 $\Delta S^\circ_{\text{SURR}} < 0$... determined by ΔH°
Thus $\Delta S^\circ_{\text{UNIV}} < 0$ is enthalpy driven.

NOTE: To reduce the impact of $\Delta S^\circ_{\text{SURR}}$, then move away from standard temperature condition. Substantially increasing T would increase the effect of $\Delta S^\circ_{\text{SURR}}$ and one could find a T in which $\Delta S^\circ_{\text{SURR}}$ becomes > 0 .
This leads us to GIBBS FREE ENERGY.

19.3 Gibbs Free Energy

Gibbs Free Energy and Spontaneity

$$G = H - TS \quad G = \text{Gibbs Free Energy}$$
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad \text{for a spontaneous reaction.}$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$
$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$
$$\underbrace{-T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}}_{\Delta G_{\text{sys}}} < 0$$

$$\Delta G_{\text{sys}} < 0 \quad \text{for a spontaneous reaction.}$$

Gibbs Free Energy = the maximum work we can get from a reaction.

$\Delta G < 0$: spontaneous in the forward direction.

$\Delta G > 0$: nonspontaneous in the forward direction ... conversely spontaneous in the reverse direction.

$\Delta G = 0$: at equilibrium

19.3 Gibbs Free Energy

Standard Gibbs Free Energy

Two main methods to determine $\Delta G_{\text{RXN}}^{\circ}$

1.
$$\Delta G_{\text{RXN}}^{\circ} = \Delta H_{\text{RXN}}^{\circ} - T\Delta S_{\text{RXN}}^{\circ}$$

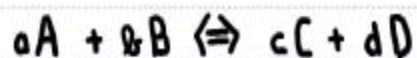
2.
$$\Delta G_{\text{RXN}}^{\circ} = \sum \Delta G_f^{\circ} (\text{products}) - \sum \Delta G_f^{\circ} (\text{reactants})$$

Similar to ΔH_f° are tabulated for a host of molecules.
Just like ΔH_f° for an element in its standard stat,
the ΔG_f° for an element in its standard state is zero.



19.3 Gibbs Free Energy

Free Energy, Standard Free Energy, and the Reaction Quotient



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$Q < K$: System not at equilibrium.
R \rightarrow P until $Q = K$

$Q > K$: System not at equilibrium.
P \rightarrow R until $Q = K$.

$Q = K$: System at equilibrium

$\Delta G < 0$: Reaction spontaneous in the forward direction,
Reactants \rightarrow Products

$\Delta G > 0$: Reaction spontaneous in the reverse direction,
Products \rightarrow Reactants.

$\Delta G = 0$: Reaction at equilibrium.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\hookrightarrow \Delta G^\circ = \sum \Delta G^\circ (\text{products}) - \sum \Delta G^\circ (\text{reactants})$$



19.3 Gibbs Free Energy

Free Energy, Standard Free Energy, and the Reaction Quotient

Consider the reaction



Calculate ΔG for this reaction at 298.15K if the pressure of each gas is 35.35 mm Hg.

ΔG°_f Values: $\text{CO(g)} = -137.2 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{COCl}_2\text{(g)} = -204.6 \text{ kJ}\cdot\text{mol}^{-1}$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\begin{aligned}\Delta G^\circ &= \Delta G^\circ_f \text{COCl}_2\text{(g)} - \Delta G^\circ_f \text{CO(g)} - \Delta G^\circ_f \text{Cl}_2\text{(g)} \\ &= -204.6 - (-137.2) - 0 \\ &= -67.4 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}p &= \frac{35.35 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \frac{1 \text{ atm}}{760 \text{ mm Hg}} \right. \\ &= 0.04615 \text{ atm}\end{aligned}$$

$$\begin{aligned}Q &= \frac{P_{\text{COCl}_2}}{P_{\text{CO}} P_{\text{Cl}_2}} \\ &= \frac{0.04615}{0.04615 (0.04615)} = 21.51\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -67,400 + 8.314 (298.15) \ln 21.51 \\ &= -67,400 + 7,606 \\ &= -59,794 \text{ J}\cdot\text{mol}^{-1} \\ &= -59.79 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$



19.3 Gibbs Free Energy

Standard Free Energy and the Equilibrium Constant

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When the system reaches equilibrium, then

$$\Delta G = 0 \text{ and } Q = K$$

$$0 = \Delta G^\circ + RT \ln K$$

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

Does this tie in with we already know?

$$K > 1$$

↳ product-favored

$$\ln K > 0$$

$$\Delta G^\circ < 0$$

↳ product-favored

$$K < 1$$

↳ reactant-favored

$$\ln K < 0$$

$$\Delta G^\circ > 0$$

↳ reactant-favored



19.3 Gibbs Free Energy

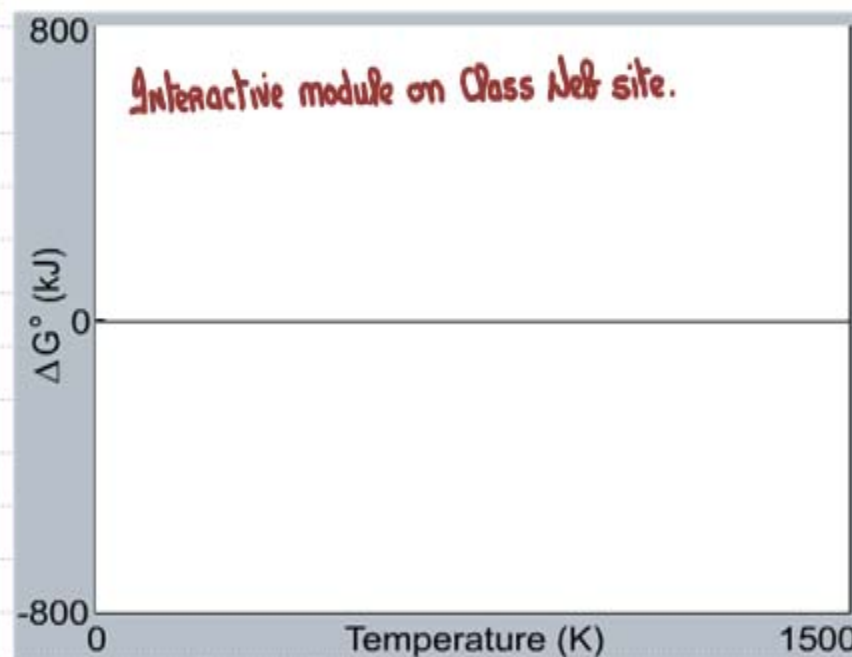
Gibbs Free Energy and Temperature

Free Energy and Temperature

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Temperature 0 K

- $2 \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{C}(\text{s}) \longrightarrow 3 \text{CO}_2(\text{g}) + 4 \text{Fe}(\text{s})$
- $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$
- $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$
- $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $2 \text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \longrightarrow 2 \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$



$$\Delta S^\circ = 561.00 \text{ J/K}\cdot\text{mol}$$

$$\Delta H^\circ = 468.00 \text{ kJ/mol}$$

$$\Delta G^\circ = 468.00 \text{ kJ/mol}$$

- i) $\Delta H^\circ > 0$, $\Delta S^\circ > 0$, $\Delta G^\circ = ?$
- ii) $\Delta H^\circ < 0$, $\Delta S^\circ < 0$, $\Delta G^\circ = ?$
- iii) $\Delta H^\circ > 0$, $\Delta S^\circ < 0$, $\Delta G^\circ > 0$
- iv) $\Delta H^\circ < 0$, $\Delta S^\circ > 0$, $\Delta G^\circ < 0$

