

Announcements – Lecture XXII – Tuesday, Apr 24th

1. iClicker:



Pick any letter a-e

2. Quiz 9:

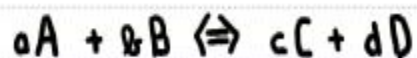
Place in basket on the front bench.

3. Owl:

All remaining Owls for Exam III are now up. The due dates for some are different, based on projected coverage. *Just wanted to give you a heads up on the remaining Owls in this course as we quickly approach the end of the semester.*

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

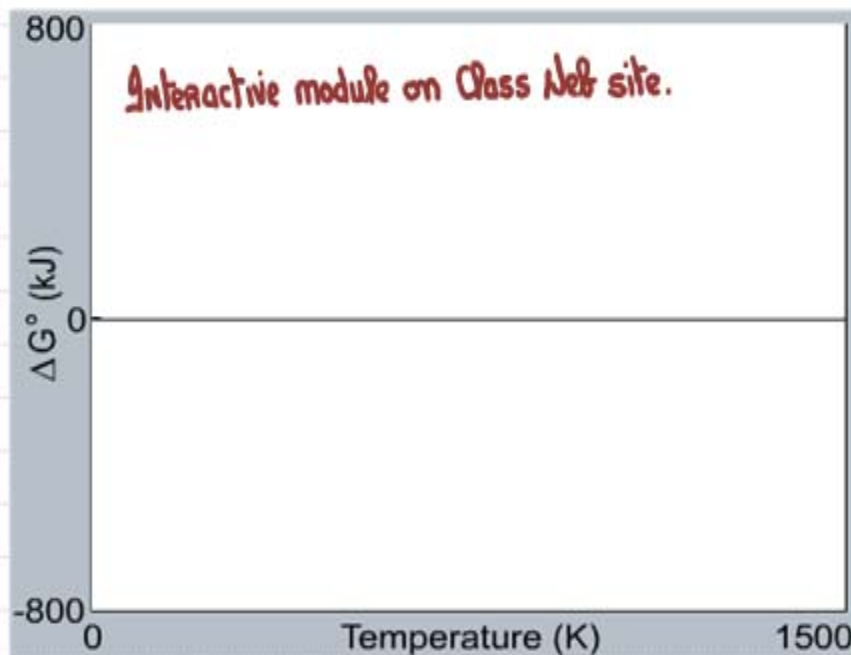
Gibbs Free Energy and Temperature

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) $\Delta H^\circ < 0, \Delta S^\circ > 0, \Delta G^\circ < 0$



19.3 Gibbs Free Energy

Gibbs Free Energy and Temperature

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

i) $\Delta H^\circ > 0$... endothermic
 $\Delta S^\circ > 0$... $-T\Delta S^\circ < 0$

Reaction at low T expected to have a $\Delta G^\circ > 0$.
However at a certain high value of T could expect
 $-T\Delta S^\circ$ to become large enough that ΔG° becomes < 0 .

iii) $\Delta H^\circ > 0$... endothermic
 $\Delta S^\circ < 0$... $-T\Delta S^\circ > 0$

Since both $\Delta H^\circ > 0$ and $-T\Delta S^\circ > 0$, then ΔG° will
always be > 0 .
Nonspontaneous, react-favored at all values of T.

ii) $\Delta H^\circ < 0$... exothermic
 $\Delta S^\circ < 0$... $-T\Delta S^\circ > 0$

Reaction at low T expected to have a $\Delta G^\circ < 0$.
However at a certain high value of T could expect
 $-T\Delta S^\circ$ to become large enough that ΔG° becomes > 0 .

iv) $\Delta H^\circ < 0$... exothermic
 $\Delta S^\circ > 0$... $-T\Delta S^\circ < 0$

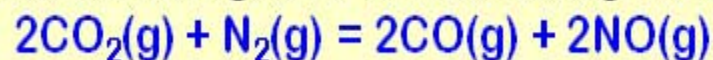
Since both $\Delta H^\circ < 0$ and $-T\Delta S^\circ < 0$, then ΔG° will
always be < 0 .
Spontaneous, product-favored at all values of T



19.3 Gibbs Free Energy

Gibbs Free Energy and Temperature

Without doing any calculations, match the following thermodynamic properties with their appropriate numerical sign for the following **endothermic reaction**.



a) ΔH_{rxn}

b) ΔS_{rxn}

c) ΔG_{rxn}

d) ΔS_{univ}



1. >0

2. <0

3. $=0$

4. >0 low T, <0 high T

5. <0 low T, >0 high T

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

a) 1. Reaction is endothermic.

b) 1. 3 gas molecules \rightarrow 4 gas molecules.
 $\Delta S_{\text{rxn}} = S(\text{products}) - S(\text{reactants})$.

c) 4. $\Delta H_{\text{rxn}} > 0$; $-T\Delta S < 0$.

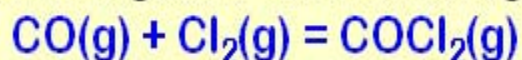
d) 5. ΔS_{univ} the reverse of ΔG .
Spontaneous $\Delta G < 0$; $\Delta S_{\text{univ}} > 0$.



19.3 Gibbs Free Energy

Gibbs Free Energy and Temperature

Without doing any calculations, match the following thermodynamic properties with their appropriate numerical sign for the following **exothermic reaction**.



a) ΔH_{rxn}

b) ΔS_{rxn}

c) ΔG_{rxn}

d) ΔS_{univ}



1. >0

2. <0

3. $=0$

4. >0 low T, <0 high T

5. <0 low T, >0 high T

a) 2. Reaction is exothermic.

b) 2. 2 gas molecules \rightarrow 1 gas molecule.
 $\Delta S = S(\text{products}) - S(\text{reactants})$.

c) 5. $\Delta H_{\text{rxn}} < 0$; $-T\Delta S_{\text{rxn}} > 0$

d) 4. ΔS_{univ} the universe of ΔG .
Spontaneous $\Delta G < 0$; $\Delta S_{\text{univ}} > 0$.

