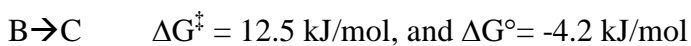
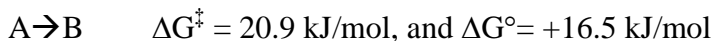


For a hypothetical reaction

The thermodynamic parameters were found to be as follows:



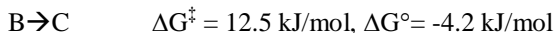
Draw a reaction energy diagram for this series of two equilibria. What are the values of ΔG^\ddagger and ΔG° for:

- the overall reaction $A \rightarrow C$?
- the overall reaction $C \rightarrow A$?
- the reaction $C \rightarrow B$?
- the reaction $B \rightarrow A$?

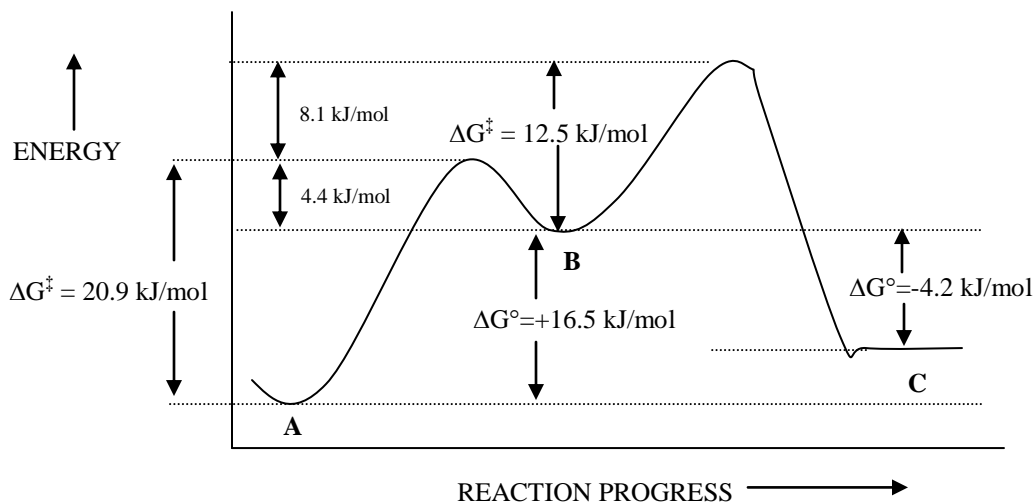
Note:

ΔG^\ddagger = the **activation energy** change for the reaction (also denoted in textbooks as E_a or E_{act})

ΔG° = the **standard free energy** change for the reaction

SAMPLE ANSWER FOR REACTION ENERGY DIAGRAM**Given:**

The first step in answering this type of questions is to draw a very accurate energy flow diagram. This will help you see all the energy changes from reactant to product and be able to calculate for any questions about 'return/reverse reactions'.



Sample Gibbs Free Energy Answers:

- 4.a To calculate the **activation energy ΔG^\ddagger for $A \rightarrow C$** , you must look for this highest point in the reaction series. Note that it is NOT simply the sum the individual activation energies of the individual reactions because you must take into account that the energy level might not return to the base level for A when product B is formed. In this case, you use the ΔG° for reaction $A \rightarrow B$ and add to it the activation energy for reaction $B \rightarrow C$ to get the value of the high point in the energy flow diagram.

Thus:

$$\Delta G^\ddagger = (+16.5 \text{ kJ/mol}) + (+12.5 \text{ kJ/mol}) = \mathbf{29.0 \text{ kJ/mol}}$$

- 4.a In most textbooks, you will find the **standard free energy ΔG°** (at 1 atm & 25° C) for a reaction described as being equal to the sum of the standard free energy values per mole of each product, each multiplied by the corresponding coefficient in the balanced equation (in this case n=1), less the corresponding sum of the reactants:

$$\Delta G^\circ_r = \sum n \Delta G^\circ_f(\text{products}) - \sum n \Delta G^\circ_f(\text{reactants}) \text{ in } \text{J} \times \text{mol}^{-1}$$

where n = the stoichiometric coefficients in the chemical equation = 1.

For a series of reactions in equilibria, the above relationship needs to be calculated for each reaction step and the sum of the individual reactions needs to be determined. Note that you have already been given the ΔG° for each reaction step $A \rightarrow B$ and $B \rightarrow C$.

Thus:

$$\Delta G^\circ_r = (\sum n \Delta G^\circ_f(\text{Rxn 1 prod.}) - \sum n \Delta G^\circ_f(\text{Rxn 1 react.})) + (\sum n \Delta G^\circ_f(\text{Rxn 2 prod.}) - \sum n \Delta G^\circ_f(\text{Rxn 2 react.})).$$

This equation seems complicated, and it is used when you know the standard energies of formation of each the individual reactants and products and assumes you do not know any activation energies. For this question, we have a fully described energy flow diagram and so the standard free energy calculation is far easier. You simply have to visualize that the standard free energy for $A \rightarrow C$ is equal to the sum of the individual standard free energies for $A \rightarrow B$ and $B \rightarrow C$.

$$\Delta G^\circ_r = (16.5 \text{ kJ/mol}) + (-4.2 \text{ kJ/mol}) = \mathbf{+12.3 \text{ kJ/mol}}$$

- 4.b To calculate the **activation energy ΔG^\ddagger for $C \rightarrow A$** , you must again look for the highest point in the reaction series. In this case you use the activation energy for reaction $B \rightarrow C$ and add to it the ΔG° for reaction $C \rightarrow B$ to get the value of the high point in the energy flow diagram.

Thus:

$$\begin{aligned} \Delta G^\ddagger_r &= (+12.5 \text{ kJ/mol}) + (\Delta G^\circ_r \text{ for } C \text{ to } B) = \\ \Delta G^\ddagger_r &= (+12.5 \text{ kJ/mol}) + (+4.2 \text{ kJ/mol}) = \mathbf{16.7 \text{ kJ/mol}} \end{aligned}$$

- 4.b To calculate the **free energy ΔG°** (at 1 atm & 25° C) for the reverse reaction $C \rightarrow A$, simply reverse all the numbers signs, and sum up the individual ΔG° of both reactions (or simply reverse the answer given in 4a).

Thus:

$$\Delta G^\circ_r = -(-4.2 \text{ kJ/mol}) + (-16.5 \text{ kJ/mol}) = \mathbf{-12.3 \text{ kJ/mol}}$$

- 4.c To calculate the **activation energy** ΔG^\ddagger for $C \rightarrow B$, you must look for the highest point in the reaction. In this case you use the activation energy for reaction $B \rightarrow C$ and add to it the ΔG° for reaction $C \rightarrow B$ to get the value of the high point in the energy flow diagram for $C \rightarrow B$.

Thus:

$$\begin{aligned}\Delta G_r^\ddagger &= (+12.5 \text{ kJ/mol}) + (\Delta G_r^\circ \text{ for C to B}) = \\ \Delta G_r^\ddagger &= (+12.5 \text{ kJ/mol}) + (+4.2 \text{ kJ/mol}) = \mathbf{16.7 \text{ kJ/mol}}\end{aligned}$$

- 4.c To calculate **free energy** ΔG° (at 1 atm & 25° C) for the reaction $C \rightarrow B$, simply reverse the numbers sign for $B \rightarrow C$,

Thus:

$$\Delta G_r^\circ = -(-4.2 \text{ kJ/mol}) = \mathbf{+4.2 \text{ kJ/mol}}$$

-
- 4.d To calculate the **activation energy** ΔG^\ddagger for $B \rightarrow A$, you must look for the highest point in the reaction. In this case you can use the activation energy for reaction $A \rightarrow B$ and add the ΔG° for reaction $B \rightarrow A$ to get the value of the high point in the energy flow diagram for $B \rightarrow A$.

Thus:

$$\begin{aligned}\Delta G_r^\ddagger &= (+20.9 \text{ kJ/mol}) + (\Delta G_r^\circ \text{ for B to A}) = \\ \Delta G_r^\ddagger &= (+20.9 \text{ kJ/mol}) + (-16.5 \text{ kJ/mol}) = \mathbf{4.4 \text{ kJ/mol}}\end{aligned}$$

- 4.d To calculate **free energy** ΔG° (at 1 atm & 25° C) for the reaction $B \rightarrow A$, simply reverse the numbers sign for $A \rightarrow B$.

Thus:

$$\Delta G_r^\circ = -(+16.5 \text{ kJ/mol}) = \mathbf{-16.5 \text{ kJ/mol}}$$

EXTRA INFORMATION ON STANDARD FREE ENERGIES**First Law of thermodynamics states:**

The internal energy of an isolate system is constant.

Second Law of thermodynamics states:

A spontaneous change is accompanied by an increase in the total entropy of the system and its surroundings. i.e. Entropy tends to increase.

Third Law of thermodynamics states:

The entropy of a pure crystalline substance at absolute zero is zero. $S(0K)=0$.

The symbols used in Thermodynamics:

U= internal energy or total energy of a system

H = enthalpy or heat

$\Delta H_f^o = (J \times mol^{-1})$ = Standard enthalpy of formation at 1 atm

$\Delta H_c^o = (J \times mol^{-1})$ = Standard enthalpy of combustion at 1 atm

S = entropy or measure of disorder in a system

$S_m^o = J \times K^{-1} \times mol^{-1}$ = Standard molar entropy at 1 atm and a specific temperature

G = Gibbs free energy

The total amount of energy change during a reaction is called the standard Gibbs free-energy change,

$\Delta G_f^o = (J \times mol^{-1})$ = Standard free energy of formation at 1 atm and a specific temperature (25°C)

Standard free energy of reactions

$\Delta G_r^o = \Delta H_r^o - T\Delta S_r^o (J \times mol^{-1})$ = Standard free energy of reaction at 1 atm and a specific temperature (25°C)

Using free energies of formation to calculate the standard free energy for a reaction.

$\Delta G_r^o = \sum n\Delta G_f^o(\text{products}) - \sum n\Delta G_f^o(\text{reactants})$ in $(J \times mol^{-1})$ = Standard free energy of reaction at 1 atm & 25°C

where n = the stoichiometric coefficients in the chemical equation.

Because both the equilibrium constant, K_{eq} and the free energy change, G both measure whether a reaction is favorable or not, they can be related mathematically. With this equation you can use free energies of formation to determine the direction of spontaneity of a system not at standard conditions:

$\Delta G_r^o = \Delta G^o + RT\ln Q$ (in $J \times mol^{-1}$) where R = ideal gas constant (8.314 J/Kmol; T = absolute temperature; and Q is the reaction quotient (related to the K_{eq}).

Effect of Temperature on Reaction Spontaneity				
ΔH	ΔS	ΔG	Reaction Character	Example
		0	Reaction (Rxn) is at equilibrium $Q = K$	
-	+	Always -	Rxn is spontaneous at all temps Reverse Rxn is always non-spontan.	$2O_3(g) \rightarrow 3O_2(g)$
+	-	Always +	Rxn is non spontaneous at all temps Reverse Rxn is always spontaneous	$3O_2(g) \rightarrow 2O_3(g)$
-	-	-at low T + at high T	Rxn is spontaneous at low temps But becomes non-spont. at high temps	$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$
+	+	+ at low T - at high T	Rxn is non-spontaneous at low temps But becomes spontaneous as the temp. is raised	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Table from Brown Lemay and Bursten, Chemistry: the Central Science, 5th ed. page 686.

For further reading see pp.157-162 in McMurry's Organic Chemistry 4th ed. or pp.167-171 in 5th ed.