

THERMODYNAMICS Exercise 1 6CO_2 gas photosynthesis to 6O_2 aqua and $\text{C}_6\text{H}_{12}\text{O}_6$

<http://aris.gusc.lv/BioThermodynamics/Aprekini.xls>

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? CO_2 gas assimilation reaction in green plants with blue and red photons $E=h\nu$ absorption in photosynthetic reaction center PRC+h ν for production 6O_2 aqua and $\text{C}_6\text{H}_{12}\text{O}_6$ using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{C}_6\text{H}_{12}\text{O}_6$ (aq)	-1263.78	269.45
O_2 aqua	-11.715	110.876
H_2O	-285.85	69.9565
CO_2 ↑ gas	-393.509	213.74

Initial compounds => products glucose + oxygen



<= biooxidation (Krebs cycle, Glycolyse)

$$1. \Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$1. \Delta H_r = \Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta H^\circ_{\text{O}_2} - 6\Delta H^\circ_{\text{H}_2\text{O}} - 6\Delta H^\circ_{\text{CO}_2} = \dots \text{kJ/mol} \dots$$

$$\dots = -1263.78 - 6 \cdot 11.715 - (6 \cdot -285.85 + 6 \cdot -393.509) = -1334.07 + 4076.154 = +2742.084 \text{ kJ/mol endothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -2742.084 / 298.15 = -9196.995 \dots \text{J/mol/K} \dots$$

$$\Delta S_r = \Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta S^\circ_{\text{O}_2} - 6\Delta S^\circ_{\text{H}_2\text{O}} - 6\Delta S^\circ_{\text{CO}_2} = \dots \text{J/mol/K} \dots$$

$$\dots = 269.45 + 6 \cdot 110.876 - (6 \cdot 69.9565 + 6 \cdot 213.74) = 934.706 - 1702.179 = -767.473 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -767.473 - 9196.9948 = -9964.4678 \dots \text{J/mol/K} \dots$$

$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +2742.084 - 298.15 \cdot -767.473 = +3942.084 + 228.822 = +2970.906 \text{ endoergic} \dots$$

$$\dots \text{kJ/mol} \dots$$

$$T \cdot \Delta S_{\text{total}} = -9964.4678 \cdot 298.15 = -2970.9 \dots \text{kJ/mol} \dots$$

$$\text{bound } T\Delta S_{\text{total}} \leftarrow \text{accumulate energy } \Delta G_{\text{reversereaction}} \leftarrow \text{Q} = -2742.084 \text{ kJ/mol not spontaneous } \Delta G_{\text{reaction}} = +2970.906 \text{ kJ/mol} \dots$$

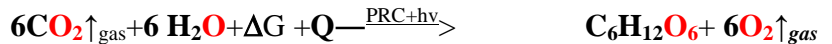
THERMODYNAMICS Exercise 1a 6CO_2 ↑ gas photosynthesis to 6O_2 ↑ gas and $\text{C}_6\text{H}_{12}\text{O}_6$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? CO_2 gas assimilation reaction in green plants with blue and red photons $E=h\nu$ absorption in photosynthetic reaction center PRC+h ν for production 6O_2 ↑ gas and $\text{C}_6\text{H}_{12}\text{O}_6$ using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
O_2 ↑ gas	0	205,04

Initial compounds

=> products glucose + oxygen



$$1. \Delta H_r = \Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta H^\circ_{\text{O}_2} - 6\Delta H^\circ_{\text{H}_2\text{O}} - 6\Delta H^\circ_{\text{CO}_2} = \dots \text{kJ/mol} \dots$$

$$\dots = -1263.78 - 6 \cdot 0 - (6 \cdot -285.85 + 6 \cdot -393.509) = -1263.78 + 4076.154 = +2812.37 \text{ kJ/mol endothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -2812.37 / 298.15 = -9432.59 \dots \text{J/mol/K} \dots$$

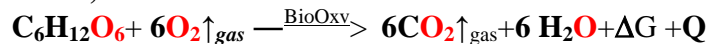
$$\Delta S_r = \Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta S^\circ_{\text{O}_2} - 6\Delta S^\circ_{\text{H}_2\text{O}} - 6\Delta S^\circ_{\text{CO}_2} = \dots \text{J/mol/K} \dots$$

$$\dots = 269.45 + 6 \cdot 205.04 - (6 \cdot 69.9565 + 6 \cdot 213.74) = 1499.69 - 1702.179 = -202.489 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -202.489 - 9432.59 = -9635.079 \dots \text{J/mol/K} \dots$$

$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +2812.37 - 298.15 \cdot -0.202489 = 2812.37 + 60.3721 = +2872.74 \dots \text{kJ/mol endoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = -9635.079 \cdot 298.15 = -2872.7 \dots \text{kJ/mol bound } T\Delta S_{\text{total}} \leftarrow \text{accumulate energy}$$



$$1. \Delta H_r = 6\Delta H^\circ_{\text{H}_2\text{O}} + 6\Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta H^\circ_{\text{O}_2} = \dots \text{kJ/mol} \dots$$

$$\dots = 6 \cdot -285.85 + 6 \cdot -393.509 - (-1263.78 - 6 \cdot 0) = -4076.154 + 1263.78 = -2812.37 \text{ kJ/mol exothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -2812.37 / 298.15 = +9432.59 \dots \text{J/mol/K} \dots$$

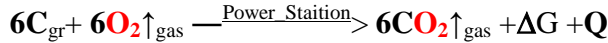
$$\Delta S_r = 6\Delta S^\circ_{\text{H}_2\text{O}} + 6\Delta S^\circ_{\text{CO}_2} - \Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta S^\circ_{\text{O}_2} = \dots \text{J/mol/K} \dots$$

$$\dots = 6 \cdot 69.9565 + 6 \cdot 213.74 - (269.45 + 6 \cdot 205.04) = 1702.179 - 1499.69 = +202.489 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 202.489 + 9432.59 = 9635.079 \dots \text{J/mol/K} \dots$$

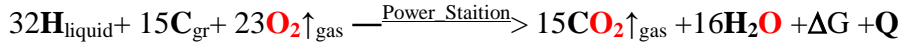
$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -2812.37 - 298.15 \cdot 0.202489 = -2812.37 - 60.3721 = -2872.74 \dots \text{kJ/mol exoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = 9635.079 \cdot 298.15 = +2872.7 \dots \text{kJ/mol bound } T\Delta S_{\text{total}} \leftarrow \text{lost free energy}$$



Substance	$\Delta H^\circ_{\text{r}}$, kJ/mol	$\Delta S^\circ_{\text{r}}$, J/mol/K
C_{gr}	0	5.74

- $\Delta H_{\text{r}} = 6\Delta H^\circ_{\text{CO}_2} - 6\Delta H^\circ_{\text{C}_{\text{gr}}} + 6\Delta H^\circ_{\text{O}_2} = \dots \text{exothermic } \text{kJ/mol}$
 $= 6 \cdot -393,509 - (6 \cdot 0 - 6 \cdot 0) = -2361,05 - 0 = -2361,05 \dots \text{kJ/mol}$
- $\Delta S_{\text{dispersed}} = -\Delta H_{\text{r}} / T = -2361,05 / 298,15 = 7919 \dots \text{J/mol/K}$
- $\Delta S_{\text{r}} = 6\Delta S^\circ_{\text{CO}_2} - 6\Delta S^\circ_{\text{C}_{\text{gr}}} - 6\Delta S^\circ_{\text{O}_2} = 6 \cdot 213,74 - (6 \cdot 5,74 + 6 \cdot 205,04) = 1282,44 - 1264,68 = 17,76 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{r}} + \Delta S_{\text{dispersed}} = 17,76 + 7919 = 7936,76 \dots \text{J/mol/K}$
- $\Delta G_{\text{r}} = \Delta H_{\text{r}} - T \cdot \Delta S_{\text{r}} = -2361,05 - 298,15 \cdot 0,01776 = +2361,05 - 5,295 = -2366,35 \dots \text{kJ/mol exoergic}$
- $T \cdot \Delta S_{\text{total}} = 7936,76 \cdot 298,15 = +2366,35 \dots \text{kJ/mol bound T}\Delta\text{Sn} \leftarrow \text{lost free energy}$



Substance	$\Delta H^\circ_{\text{r}}$, kJ/mol	$\Delta S^\circ_{\text{r}}$, J/mol/K
H_{atomic}	218.0	114.7

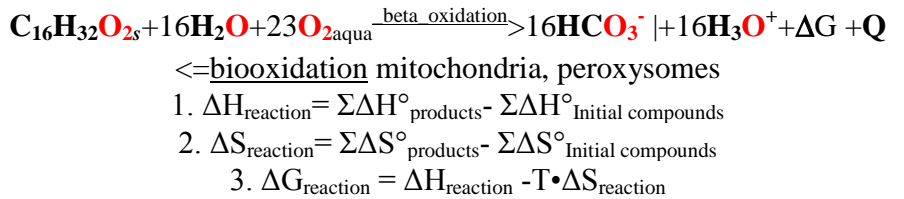
- $\Delta H_{\text{r}} = 15\Delta H^\circ_{\text{CO}_2} + 16\Delta H^\circ_{\text{H}_2\text{O}} - 32\Delta H^\circ_{\text{H}} - 15\Delta H^\circ_{\text{C}_{\text{gr}}} - 23\Delta H^\circ_{\text{O}_2} = -17452,2$
 $= 15 \cdot -393,509 + 16 \cdot -285,85 - (32 \cdot 218 + 15 \cdot 0 + 23 \cdot 0) = -10476 - 6976 = \dots \text{kJ/mol}$
- $\Delta S_{\text{dispersed}} = -\Delta H_{\text{r}} / T = -17452,2 / 298,15 = 58535 \dots \text{J/mol/K}$
- $\Delta S_{\text{r}} = 15\Delta S^\circ_{\text{CO}_2} + 16\Delta S^\circ_{\text{H}_2\text{O}} - 32\Delta S^\circ_{\text{H}} - 15\Delta S^\circ_{\text{C}_{\text{gr}}} - 23\Delta S^\circ_{\text{O}_2} = \dots \text{J/mol/K}$
 $= 15 \cdot 213,74 + 16 \cdot 69,9565 - (32 \cdot 114,7 + 15 \cdot 5,74 + 23 \cdot 205,04) = 4325,4 - 8472,42 = -4147 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{r}} + \Delta S_{\text{dispersed}} = 58535 - 4147 = 54388 \dots \text{J/mol/K}$
- $\Delta G_{\text{r}} = \Delta H_{\text{r}} - T \cdot \Delta S_{\text{r}} = -17452,2 - 298,15 \cdot -4,147 = -17452,2 + 1236,43 = -16215,8 \dots \text{kJ/mol exoergic}$
- $T \cdot \Delta S_{\text{total}} = 54388 \cdot 298,15 = +16215,8 \dots \text{kJ/mol bound T}\Delta\text{Sn} \leftarrow \text{lost free energy}$

Calculate ΔH_{r} , ΔS_{r} , ΔG_{r} at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**?

Beta oxidation in mitochondria, peroxysomes of palmitic acid with $\text{O}_{2\text{aqua}}$ standard conditions (25°C) 298.15 K, using data on table! Will reaction **exoergic** or **endoergic**!

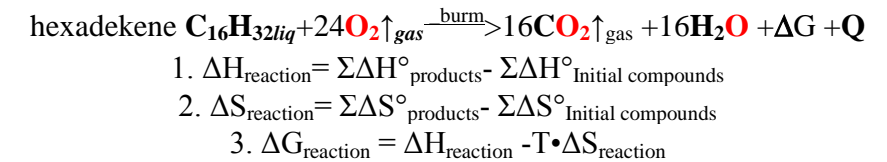
Initial compounds => products bicarbonate + hydronium ions

Substance	$\Delta H^\circ_{\text{r}}$, kJ/mol	$\Delta S^\circ_{\text{r}}$, J/mol/K
$\text{C}_{16}\text{H}_{32}\text{O}_{2\text{s}}$	-891.5	452.4
$\text{C}_{16}\text{H}_{32}\text{O}_{2\text{liquid}}$	-838.1	-
$\text{O}_{2\text{aqua}}$	-11.715	110.876
H_2O	-285.85	69.9565
H_3O^+	-285,81	-3,854
HCO_3^-	-689,93	98,324



- $\Delta H_{\text{r}} = 16\Delta H^\circ_{\text{HCO}_3^-} + 16\Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{C}_{16}\text{H}_{32}\text{O}_2} - 16\Delta H^\circ_{\text{H}_2\text{O}} - 23\Delta H^\circ_{\text{O}_2} = \dots \text{kJ/mol}$
- $\Delta S_{\text{dispersed}} = -\Delta H_{\text{r}} / T = -9853,87 / 298,15 = 33050 \dots \text{J/mol/K}$
- $\Delta S_{\text{r}} = 16\Delta S^\circ_{\text{HCO}_3^-} + 16\Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{C}_{16}\text{H}_{32}\text{O}_2} - 16\Delta S^\circ_{\text{H}_2\text{O}} - 23\Delta S^\circ_{\text{O}_2} = \dots \text{J/mol/K}$
 $= 16 \cdot 98,324 + 16 \cdot -3,854 - (16 \cdot 69,9565 + 23 \cdot 110,876 + 452,4) = 1511,52 - 4121,85 = -2610,33 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{r}} + \Delta S_{\text{dispersed}} = 33050 - 2610,33 = 30439,7 \dots \text{J/mol/K}$
- $\Delta G_{\text{r}} = \Delta H_{\text{r}} - T \cdot \Delta S_{\text{r}} = -9853,87 - 298,15 \cdot -2,61033 = -9853,87 + 778,27 = -9075,6 \dots \text{kJ/mol exoergic}$
- $T \cdot \Delta S_{\text{total}} = 30439,7 \cdot 298,15 = 9075,6 \dots \text{kJ/mol bound T}\Delta\text{Sn} \leftarrow \text{lost free energy}$

Substance	$\Delta H^\circ_{\text{r}}$, kJ/mol	$\Delta S^\circ_{\text{r}}$, J/mol/K
$\text{C}_{16}\text{H}_{32\text{Liq}}$	-328.7	587.9
$\text{O}_2\uparrow_{\text{gas}}$	0	205,04
H_2O	-285.85	69.9565
$\text{CO}_2\uparrow_{\text{gas}}$	-393.509	213.74



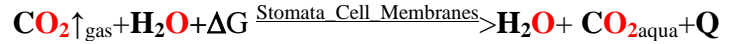
- $\Delta H_{\text{r}} = 16\Delta H^\circ_{\text{CO}_2} + 16\Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{C}_{16}\text{H}_{32}} - 24\Delta H^\circ_{\text{O}_2} = \dots \text{kJ/mol}$
 $= 16 \cdot -393,509 + 16 \cdot -285,85 - (24 \cdot 0 - 328,7) = -10869,7 + 328,7 = -10541 \text{ kJ/mol exothermic}$
- $\Delta S_{\text{dispersed}} = -\Delta H_{\text{r}} / T = -10541 / 298,15 = 33050 \dots \text{J/mol/K}$
- $\Delta S_{\text{r}} = 16\Delta S^\circ_{\text{CO}_2} + 16\Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{C}_{16}\text{H}_{32}} - 24\Delta S^\circ_{\text{O}_2} = \dots \text{J/mol/K}$
 $= 16 \cdot 213,74 + 16 \cdot 69,9565 - (24 \cdot 205,04 + 587,9) = 4539,14 - 5508,86 = -969,716 \text{ J/mol/K}$
- $\Delta S_{\text{total}} = \Delta S_{\text{r}} + \Delta S_{\text{dispersed}} = 33050 - 969,716 = 32080,7 \dots \text{J/mol/K}$
- $\Delta G_{\text{r}} = \Delta H_{\text{r}} - T \cdot \Delta S_{\text{r}} = -10541 - 298,15 \cdot -0,969716 = -10541 + 289,121 = -10251,9 \dots \text{kJ/mol exoergic}$
- $T \cdot \Delta S_{\text{total}} = 32080,7 \cdot 298,15 = 10251,9 \dots \text{kJ/mol bound T}\Delta\text{Sn} \leftarrow \text{lost free energy}$

THERMODYNAMICS Exercise II CO_2 gas assimilation in water $\text{CO}_{2\text{aqua}}$ reaction

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? From CO_2 gas assimilation in water $\text{CO}_{2\text{aqua}}$ reaction for green plants +stomata enclosed surface of cell membranes on photosynthetic reaction center PRC+h ν using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds => products

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K	ΔG_r° , kJ/mol
$\text{CO}_{2\text{aqua}}$	-413,7076	117,57	-385,98
H_2O	-285,85	69,9565	-237,191
$\text{CO}_2\uparrow_{\text{gas}}$	-393,509	213,74	-394,359



- $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
- $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
- $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{CO}_{2\text{aqua}}} - \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{CO}_{2\text{gas}}} = \dots \text{kJ/mol} \dots$
 $\dots = -413,7076 - 285,85 - (-393,509 - 285,85) = -413,7076 - (-393,509) = -20,1986 \text{ kJ/mol exothermic} \dots$

$\Delta S_{\text{dispersed}} = -\Delta H_r / T = 20,1986 / 298.15 = 67,746436 \dots \text{J/K/mol} \dots$

2. $\Delta S_r = \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{CO}_{2\text{aqua}}} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{CO}_{2\text{gas}}} = \dots \text{J/mol/K} \dots$
 $\dots = 117,57 + 69,9565 - (213,74 + 69,9565) = 117,57 - (213,74) = -96,17 \dots \text{J/mol/K} \dots$

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -96,17 + 67,746436 = -28,424 \dots \text{J/K/mol} \dots$

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -20,1986 - 298.15 \cdot (-96,17) = -20,1986 + 28.673 = +8,474 \dots \text{kJ/mol} \dots$
**endoergic**.....

$T \cdot \Delta S_{\text{total}} = -28,424 \cdot 298,15 \text{K} = -8,47 \dots \text{kJ/mol} \dots$

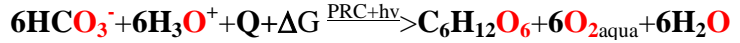
bound $T\Delta S_n \leftarrow$ accumulate energy $\Delta G_{\text{reversereaction}} \leftarrow \cdot Q = -3942.084 \text{ kJ/mol} \dots$ **not spontaneous** $\Delta G_{\text{reaction}} = +8,474 \text{kJ/mol} \dots$

THERMODYNAMICS Exercise III Bicarbonate 6HCO_3^- photosynthesis to 6O_2 and $\text{C}_6\text{H}_{12}\text{O}_6$

Calculate ΔH_r , ΔS_r , ΔG_r . Reaction is **exothermic**, **athermic**, **endothermic**? From water, Bicarbonate assimilation reaction in green plants with blue and red photon $E=h\nu$ absorption photosynthesis in photosynthetic reaction center PRC+h ν for $6\text{O}_{2\text{aqua}}$ and $\text{C}_6\text{H}_{12}\text{O}_6$ at standard conditions 298.15 K using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$	-1263,78	269,45
$\text{O}_{2\text{aqua}}$	-11,715	110,876
H_2O	-285,85	69,9565
H_3O^+	-285,81	-3,854
HCO_3^-	-689,93	98,324

Initial compounds => products glucose + oxygen + water



<biooxidation (Krebs cycle, Glycolyse)

- $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
- $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
- $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

$$1. \Delta H_r = \Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta H^\circ_{\text{O}_2} + 6\Delta H^\circ_{\text{H}_2\text{O}} - 6\Delta H^\circ_{\text{H}_3\text{O}^+} - 6\Delta H^\circ_{\text{HCO}_3^-} = +2805,27 \text{ kJ/mol}$$

$$\dots = -1263,78 - 6 \cdot 11,715 - 6 \cdot 285,85 - (6 \cdot -689,93 + 6 \cdot -285,81) = 5854,44 - 3049,17 = +2805,27 \text{ kJ/mol } \textbf{endothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -2805,27 \cdot 1000 / 298,15 = -9408,9217 \dots \text{ J/mol/K} \dots$$

$$\Delta S_r = \Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta S^\circ_{\text{O}_2} + 6\Delta S^\circ_{\text{H}_2\text{O}} - 6\Delta S^\circ_{\text{H}_3\text{O}^+} - 6\Delta S^\circ_{\text{HCO}_3^-} = \dots \text{ J/mol/K} \dots$$

$$\dots = 269,45 + 6 \cdot 110,876 + 6 \cdot 69,9565 - (6 \cdot 98,324 + 6 \cdot -3,854) = 566,82 - 1354,45 = -787,625 \text{ J/mol/K} \dots$$

$$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -787,625 - 9408,9217 = -10196,5467 \text{ J/mol/K} \dots$$

$$3. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = +2805,27 - 298,15 \cdot (-10196,5467) = +2805,27 + 3049,17 = +5854,44 \text{ kJ/mol } \textbf{endoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = -10196,5467 \text{ J/mol} \cdot 298,15 \text{ K} = -3049,17 \text{ kJ/mol} \dots$$

bound $T\Delta S_{\text{total}} \leftarrow$ accumulate energy $\Delta G_{\text{reverse reaction}} \leftarrow \dots Q = -2805,27 \text{ kJ/mol}$ not spontaneous $\Delta G^\circ_{\text{reaction}} = +2805,27 \text{ kJ/mol} \dots$

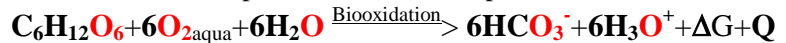
page 3: <http://aris.gusc.lv/BioThermodynamics/BioChemicalProcesE.pdf>.

Accumulate energy $T\Delta S_{\text{total}} = -2570,4 \text{ kJ/mol}$ is bound in products: $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O} \dots$

BioFuel $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 6\text{O}_{2\text{aqua}}$!

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$	-1263,78	269,45
$\text{O}_{2\text{aqua}}$	-11,715	110,876
H_2O	-285,85	69,9565
H_3O^+	-285,81	-3,854
HCO_3^-	-689,93	98,324

Initial compounds \leftrightarrow products



$$1. \Delta H_r = 6\Delta H^\circ_{\text{H}_3\text{O}^+} + 6\Delta H^\circ_{\text{HCO}_3^-} - \Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta H^\circ_{\text{O}_2} - 6\Delta H^\circ_{\text{H}_2\text{O}} = -2805,27 \dots \text{ kJ/mol}$$

$$= -1263,78 + 6 \cdot -11,715 + 6 \cdot -285,85 - (-1263,78 - 6 \cdot -11,715 - 6 \cdot -285,85) = -2805,27 \text{ kJ/mol } \textbf{endothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = 9408,9217 \dots \text{ J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta S^\circ_{\text{O}_2} + 6\Delta S^\circ_{\text{H}_2\text{O}} - 6\Delta S^\circ_{\text{H}_3\text{O}^+} - 6\Delta S^\circ_{\text{HCO}_3^-} = \dots \text{ J/mol/K} \dots$$

$$= -787,625 + 6 \cdot 110,876 + 6 \cdot 69,9565 - (6 \cdot 98,324 + 6 \cdot -3,854) = -787,625 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -787,625 + 9408,9217 = +8621,2967 \text{ J/mol/K} \dots$$

$$3. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -2805,27 - 298,15 \cdot (+8621,2967) = -2805,27 - 2570,4 = -5375,67 \text{ kJ/mol } \textbf{exoergic} \dots$$

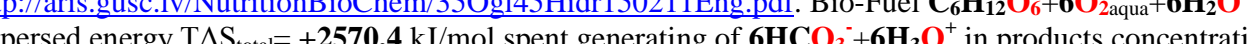
$$3. T \cdot \Delta S_{\text{total}} = 8621,2967 \text{ J/mol} \cdot 298,15 \text{ K} = +2570,4 \text{ kJ/mol} \dots$$

bound $T\Delta S_{\text{total}} \leftarrow$ dispersed free energy $\Delta G_{\text{reverse reaction}} \leftarrow \dots Q = 2805,27 \text{ kJ/mol} \dots$ spontaneous $\Delta G_{\text{reaction}} = -2570,4 \text{ kJ/mol} \dots$

page 3: <http://aris.gusc.lv/NutritionBioChem/35Ogl45Hidr150211Eng.pdf>. Bio-Fuel $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O}$

bound, dispersed energy $T\Delta S_{\text{total}} = +2570,4 \text{ kJ/mol}$ spent generating of $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ in products concentration.

Generator gas $6\text{CO} \uparrow + 6\text{H}_{2\text{gas}}$ is home heating, street lightning fuel of 19th as 20th century beginning in Riga city.



Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{CO} \uparrow_{\text{gas}}$	-110,525	197,674
$\text{H}_{2\text{gas}}$	0	130,68
$\text{O}_2 \uparrow_{\text{gas}}$	0	205,04
$\text{H}_2\text{O} \uparrow_{\text{gas}}$	-241,8352	188,74024

$$1. \Delta H_r = 6\Delta H^\circ_{\text{CO}_2} + 6\Delta H^\circ_{\text{H}_2\text{O}} - 6\Delta H^\circ_{\text{H}_2\text{gas}} - 6\Delta H^\circ_{\text{COgas}} - 6\Delta H^\circ_{\text{O}_2\text{gas}} = \dots \text{ kJ/mol}$$

$$= 6 \cdot -393,509 + 6 \cdot -241,8352 - (6 \cdot 0 + 6 \cdot -110,525) = -3812,074 + 663,18 = -3148,894 \text{ kJ/mol } \textbf{exothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -3148,894 / 298,15 = -10561,4 \text{ J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{\text{CO}_2} + 6\Delta S^\circ_{\text{H}_2\text{O}} - 6\Delta S^\circ_{\text{H}_2\text{gas}} - 6\Delta S^\circ_{\text{COgas}} - 6\Delta S^\circ_{\text{O}_2\text{gas}} = \dots \text{ J/mol/K} \dots$$

$$= 6 \cdot 213,74 + 6 \cdot 188,74024 - (6 \cdot 130,68 + 6 \cdot 197,66 + 6 \cdot 205,04) = 2414,88 - 3200,28 = -785,399 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -785,399 + 10561,4 = 9776,001 \text{ J/mol/K} \dots$$

$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -3148,894 - 298,15 \cdot (-9776,001) = -3148,894 + 2914,72 = -234,174 \text{ kJ/mol } \textbf{exoergic} \dots$$

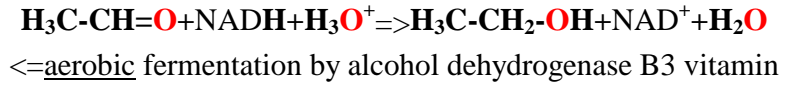
$$T \cdot \Delta S_{\text{total}} = 9776,001 \text{ J/mol} \cdot 298,15 \text{ K} = +2914,7 \text{ kJ/mol} \dots$$

bound $T\Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reverse reaction}} \leftarrow \dots Q = 2805,27 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise IV Vitamin B3 etanal $\text{H}_3\text{C}-\text{CH}=\text{O}$ reducing to ethanol $\text{H}_3\text{C}-\text{CH}_2-\text{OH}$ product

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**?
 Vitamin B3 for anaerobic ethanal reduction to ethanol product with alcohol dehydrogenase using the data table!
 Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	ΔH_f° , kJ/mol	ΔS_f° , J/mol/K
$\text{H}_3\text{C}-\text{CH}=\text{O}_{aq}$	-212,23	-281,84
$\text{NADH}_{(aq)}$	-1036,66	-140,50
$\text{H}_3\text{O}^+_{(aq)}$	-285,81	-3,854
$\text{H}_3\text{C}-\text{CH}_2-\text{OH}_{aq}$	-288,3	-357,74
$\text{NAD}^+_{(aq)}$	-1007,48	-183
$\text{H}_2\text{O}_{(aq)}$	-285,85	69,96



- $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
- $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
- $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{CH}_3\text{CH}_2\text{OH}} + \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{NAD}^+} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{CH}_3\text{CHO}} - \Delta H^\circ_{\text{NADH}} = \dots \text{kJ/mol} \dots$
 $\dots = -288,3 - 1007,48 - 285,85 - (-212,23 - 1036,66 - 285,81) = -1581,63 + 1534,7 = -46,93 \text{ kJ/mol}$ **exothermic**...

2. $\Delta S_{\text{dispersed}} = -\Delta H_r / T = -(-46,93) / 298,15 = +157,4 \dots \text{J/K/mol} \dots$

$\Delta S_r = \Delta S^\circ_{\text{CH}_3\text{CH}_2\text{OH}} + \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{NAD}^+} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{CH}_3\text{CHO}} - \Delta S^\circ_{\text{NADH}} = \dots \text{J/K/mol} \dots$
 $\dots = -357,7394 - 183 + 69,956 - (-281,838 - 140,50 - 3,854) = -470,78 + 426,192 = -44,588 \text{ J/mol/K} \dots$

3. $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 157,4 - 44,588 = +112,812 \dots \text{J/K/mol} \dots$

$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -46,93 - 298,15 \cdot (-44,588) / 1000 = -33,636 \dots \text{kJ/mol} \dots$
 ... **exoergic**...

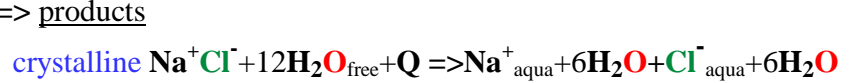
$T \cdot \Delta S_{\text{total}} = +112,812 \text{ J/K/mol} \cdot 298,15 \text{ K} = +33,635 \dots \text{kJ/mol} \dots$

bound $T \Delta S_{\text{total}} \leftarrow \text{dispersed-lost energy } \Delta G_{\text{reversereaction}} \leftarrow \dots Q = +46,93 \text{ kJ/mol}$ **spontaneous** $\Delta G_{\text{reaction}} = -33,636 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise V For **crystalline** salt **Na⁺Cl⁻** hydration reaction

Calculate ΔH_r , ΔS_r , ΔG at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? For **crystalline** salt **Na⁺Cl⁻** hydration reaction with water using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
crystalline Na⁺Cl⁻	-411.12	72.00
Na⁺_{aqua}	-240.10	59.00
Cl⁻_{aqua}	-167.2	56.50



1. $\Delta H_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{initial compounds}}$

2. $\Delta S_{\text{reaction}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{initial compounds}}$

3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{Na}^+} + \Delta H^\circ_{\text{Cl}^-} - \Delta H^\circ_{\text{Na}^+\text{Cl}^-} = \dots \text{kJ/mol} \dots$
 $\dots = -240.1 - 167.2 - (-411.12) = -407.3 + 411.12 = +3.82 \text{ kJ/mol}$ **endothermic**.....

2. $\Delta S_{\text{dispersed}} = -\Delta H_r / T = -3.82 / 298.15 = -12.812 \dots \text{J/mol/K} \dots$

2. $\Delta S_r = \Delta S^\circ_{\text{Na}^+} + \Delta S^\circ_{\text{Cl}^-} - \Delta S^\circ_{\text{Na}^+\text{Cl}^-} = 59.00 + 56.50 - (72.00) = 115.5 - 72.00 = +43.5 \dots \text{J/mol/K} \dots$

3. $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -12.812 + 43.5 = +30.688 \dots \text{J/mol/K} \dots$

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +3.82 - 298.15 \cdot 0.0435 = -9.15 \dots \text{kJ/mol} \dots$
exoergic.....

3. $T \cdot \Delta S_{\text{total}} = +30.688 \text{ J/mol} \cdot 298.15 \text{ K} = +9.15 \dots \text{kJ/mol} \dots$

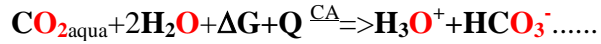
bound TΔSn ← dispersed-lost energy ΔG_{reversereaction} ← Q = -3.82..... **spontaneous** ΔG_r = -9.15 kJ/mol.....

THERMODYNAMICS Exercise VI Carbonic Anhydrase made acid/base equilibrium $\text{H}_2\text{O}^{\text{CA}}/\text{CO}_2/\text{H}_3\text{O}^++\text{HCO}_3^-$

Calculate ΔH_r , ΔS_r , ΔG at standard conditions (298.15 K). Reaction is **exothermic**, **athermic**, **endothermic**? For the Enzyme Carbonic anhydrase (CA) made acid/base equilibrium $\text{H}_2\text{O}^{\text{CA}}/\text{CO}_2/\text{H}_3\text{O}^++\text{HCO}_3^-$ using CA driven reaction of aqua CO_2 with water molecules $2\text{H}_2\text{O}$ using data table! Will be **exoergic** or **endoergic**!

Initial compounds => products

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
H_3O^+	-285.81	-3.854
HCO_3^-	-689.93	98.324
H_2O	-285.85	69.9565
$\text{CO}_{2\text{aqua}}$	-413.7976	117.5704



1. $\Delta H_{\text{reaction}} = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{initial compounds}}$

2. $\Delta S_{\text{reaction}} = \Delta S^\circ_{\text{products}} - \Delta S^\circ_{\text{initial compounds}}$

3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{HCO}_3^-} - 2\Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{CO}_2} = \dots\dots\dots$

$= -285.81 - 689.93 - (2 \cdot -285.85 - 413.7976) = -975.74 + 985.3276 = +9.7576$ **endothermic**.....

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$\Delta S_{\text{dispersed}} = -\Delta H_r / T = -9.7576 / 298.15 = -32.727$ J/mol.....

.....
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2. $\Delta S_r = \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{HCO}_3^-} - 2\Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{CO}_2} = \dots\dots\dots$ J/mol/K.....
 $= -3.854 + 98.324 - (2 \cdot 69.9565 + 117.5704) = 94.47 - 257.482 = -163.0134$ J/mol/K.....

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$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -32.727 - 163.0134 = -195.169$ J/mol.....

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3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +9.7576 + 298.15 \cdot 0.1630134 = +58.19$ **endoergic**..... kJ/mol.....

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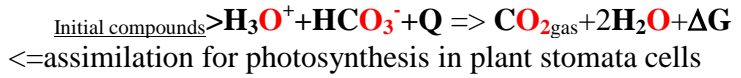
$T \cdot \Delta S_{\text{total}} = -195.7404 \cdot 298,15 \text{ K} = -58.19$ kJ/mol.....

bound TΔSn ← accumulated free energy ΔGreverse_{reaction} ← .Q = -9.7576 kJ/mol **endoergic** ΔG°_{reaction} = +58.19 kJ/mol.....

THERMODYNAMICS Exercise VII $\text{H}_2\text{O} + \text{CO}_2$ using ionic channels drive reaction $\text{H}_3\text{O}^+ + \text{HCO}_3^-$ to gas CO_2

Calculate ΔH_r , ΔS_r , ΔG at standard conditions (298.15 K). Acid/base equilibrium $\text{H}_2\text{O} + \text{CO}_2$ using proton and ionic channels drive reaction in lungs $\text{H}^+ + \text{HCO}_3^-$ to breath out gas CO_2 with water $2\text{H}_2\text{O}$ (**exothermic, athermic or endothermic?**). To use data table! Will be **exoergic** or **endoergic**! products

Substance	$\Delta H_r^\circ, \text{kJ/mol}$	$\Delta S_r^\circ, \text{J/mol/K}$
H_3O^+	-285.81	-3.854
HCO_3^-	-689.93	98.324
H_2O	-285.85	69.9565
$\text{CO}_2 \uparrow_{\text{gas}}$	-393,509	213,74



1. $\Delta H_{\text{reaction}} = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{initial compounds}}$
2. $\Delta S_{\text{reaction}} = \Delta S^\circ_{\text{products}} - \Delta S^\circ_{\text{initial compounds}}$
3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{HCO}_3^-} = \dots \text{kJ/mol} \dots$

.....

$\dots = 2 \cdot (-285,85) - 393,509 - (-285,81 - 689,93) = -965,209 + 975,74 = +10,531 \text{ kJ/mol}$ **endothermic**.....

$\Delta S_{\text{dispersed}} = -\Delta H_r / T = -10,531 / 298,15 = -35,3211 \dots \text{J/K/mol} \dots$

.....

2. $\Delta S_r = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{CO}_2} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{HCO}_3^-} = \dots \text{J/mol/K} \dots$

$\dots = 2 \cdot 69,9565 + 213,74 - (-3,854 + 98,324) = 353,653 - 94,47 = 259,183 \dots$

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 259,183 - 35,3211 = +223,8619 \dots \text{J/K/mol} \dots$

.....

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = 10,531 - 298,15 \cdot 0,259183 = -66,74441$ **exoergic**.....

..... **exoergic**.....

$T \cdot \Delta S_{\text{total}} = 223,8619 \cdot 298,15 \text{ K} = +66,7444 \dots \text{kJ/mol} \dots$

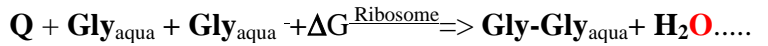
bound $T\Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow \cdot Q = -10,531 \text{ kJ/mol}$ **exoergic spontaneous** $\Delta G_{\text{reaction}} = -66,7444 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise VIII glycine + glycine → glycylglycine dipeptide synthesis

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions (298.15 K). Reaction is **exothermic**, **athermic**, **endothermic**? For peptide synthesis polycondensation Enzyme ribosome governed reaction with amino acids glycine Gly (G) using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

..... J.Phys.Chem.Ref.Data, Vol. 19, No. 4, 1990; Chem. Phys. CRC, 2010-2005, p.876,882,1220,1223

glycine+ glycine → glycylglycine dipeptide synthesis



1. $\Delta H_{reaction} = \sum \Delta H^\circ_{products} - \sum \Delta H^\circ_{initial\ compounds}$

2. $\Delta S_{reaction} = \sum \Delta S^\circ_{products} - \sum \Delta S^\circ_{initial\ compounds}$

3. $\Delta G_{reaction, kJ/mol} = \Delta H_{reaction} - T \cdot \Delta S_{reaction}$

$\Delta G^\circ_{formation\ kJ/mol\ H_2O} = -237.19\ kJ/mol$

$Gly_{aqua}\ \Delta G_r = \sum \Delta G^\circ_{product} - \sum \Delta G^\circ_{initial_compounds}$

$Gly-Gly_{aqua}; \Delta G_r = -200,5 - 213,275 - (2 \cdot -180,13) = -53.515 \dots$

$H_2O; \dots$

Substance	$\Delta H^\circ_r, kJ/mol$	$\Delta S^\circ_r, J/mol/K$
Gly _{aqua}	-554.56	76.45
Gly-Gly _{aqua}	-790.99	-1
H ₂ O	-285.83	69.9565
I=0 M	I=0,1 M	I=0.2 M
-180.13	-177.07.	-176.08
-200.55	-195.65	-194.07
-213.275	-213.275	213.275

$\Delta G_r = -195.65 - 213,275 - (2 \cdot -177.07) = -54,785\ kJ/mol$ **endoergic**.....

$\Delta G_r = -194,07 - 213,275 (2 \cdot -176,08) = -55,185\ kJ/mol$ **endoergic**.....

1. $\Delta H_r = \Delta H^\circ_{Gly-Gly} + \Delta H^\circ_{H_2O} - 2 \Delta H^\circ_{Gly} = -790.99 - 285.83 - (2 \cdot -554.56) = -1076.82 + 1109.12 = +32.3\ kJ/mol$ **endothermic**.....

2. $\Delta S_{dispersed} = -\Delta H_r / T = -32.3 / 298.15 = -108.335 \dots J/K/mol$

$\Delta S_r = \Delta S^\circ_{Gly-Gly} + \Delta S^\circ_{H_2O} - 2 \Delta S^\circ_{Gly} = \dots J/mol/K$
 $\dots = -1 + 69.9565 - (2 \cdot 76.45) = 68,957 - 152.9 = -83,944\ J/mol/K$

3. $\Delta S_{total} = \Delta S_r + \Delta S_{dispersed} = -83,944 - 108,335 = -192,279 \dots J/K/mol$

Page 3: <http://aris.gusc.lv/BioThermodynamics/08ThGlyGlyH2OCRC10sol.pdf>

$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = 32,3 - 298,15 \cdot -0,083944 = 32,3 + 25,0279 = 57,328$ **endoergic**.....kJ/mol

ionic force is total ions summary concentration

$I = 1\ mol/L (1\ M)$

for standart enthalpy $\Delta H^\circ_r, kJ/mol$

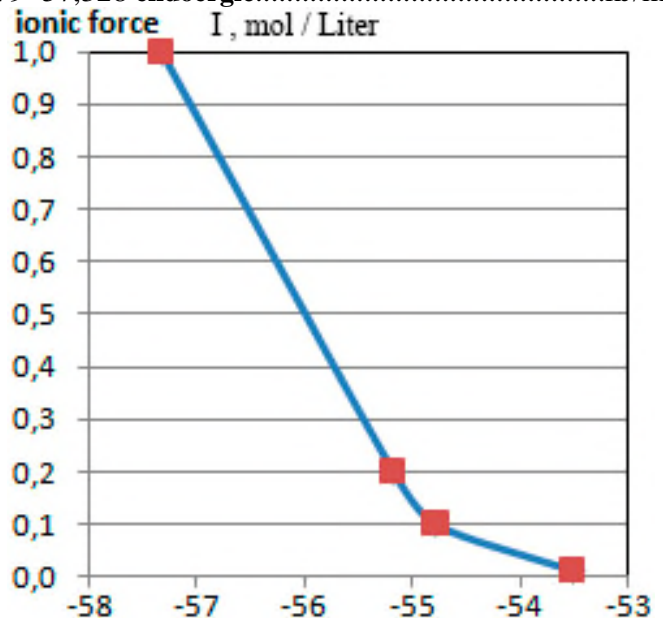
and

for standart entropy $\Delta S^\circ_r, J/mol/K$

measured values calculated

$\Delta G_r = 57\ kJ/mol$

Chem. Phys. CRC, 2010-2005,
p.876,882,1220,1223



$T \cdot \Delta S_{total} = -192,279\ J/mol \cdot 298,15\ K = -57,328 \dots kJ/mol$

bound $T \Delta S_n \leftarrow$ lost free energy $\Delta G_{reversereaction} \leftarrow Q = -32.3 \dots kJ/mol$ non spontaneous $\Delta G^\circ_{reaction} = 57,328 \dots kJ/mol$

THERMODYNAMICS Exercise IX From water bicarbonate solution for CO₂ gas evaporation

Calculate ΔH_r, ΔS_r, ΔG_r at standard conditions 298.15 K. Is **exothermic**, **athermic** or **endothermic**? Along concentration gradients through proton H⁺ channels [H₃O]_{right}/[H₃O]_{left} and through bicarbonate HCO₃⁻ channels [HCO₃]_{right}/[HCO₃]_{left} evaporation in lungs of water and CO₂ gas. To use the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds => products

Substance	ΔH _r ^o , kJ/mol	ΔS _r ^o , J/mol/K
H ₃ O ⁺	-285,81	-3,854
HCO ₃ ⁻	-689,93	98,324
H ₂ O	-285,85	69,9565
H ₂ O↑ _{gas}	-241,8352	188,7402
CO ₂ ↑ _{gas}	-393,509	213,74



1. ΔH_{reaction} = ΣΔH_{products}^o - ΣΔH_{initial compounds}^o

2. ΔS_{reaction} = ΣΔS_{products}^o - ΣΔS_{initial compounds}^o

3. ΔG_{reaction} = ΔH_{reaction} - T•ΔS_{reaction}

channels H⁺ :

ΔG_H=RTln([H₃O]_{right}/[H₃O]_{left})

channels HCO₃⁻:

ΔG_{HCO3}=RTln([HCO₃]_{right}/[HCO₃]_{left})

1. ΔH_r==ΔH^o_{H2O}+ΔH^o_{H2O↑_{gas}}+ΔΔH^o_{CO2}-ΔH^o_{H3O}-ΔH^o_{HCO3}=..... kJ/mol.....
 ... = -285,85-241,8352-393,509-(-285,81-689,93) = -921.19+975.74= +54.546 kJ/mol **endothermic**..... kJ/mol....

2. ΔS_{dispersed}= -ΔH_r/T=-54,546/298,15= -182,9475.....J/K/mol....

ΔS_r==ΔS^o_{H2O}+ ΔS^o_{H2O↑_{gas}}+ ΔS^o_{CO2}-ΔS^o_{H3O}-ΔS^o_{HCO3}=.....J/K/mol....

.....= 69,956+188,74+213,74-(-3,854+98,324)= 353,652-94.47= +377,966 J/mol/K.....

ΔS_H=-Rln(10^{-5.5}/0,02754)=75,42909 J/mol/K.....ΔS_{HCO3}=-Rln(0,0154/0,0338919)=6,55847 J/mol/K.....

ΔS_{rH}=377,966+75,42909+6,55847 = 459,954 J/mol/K.....

3. ΔS_{total}= ΔS_r+ ΔS_{dispersed}= -182,95+377,966 =195,016 J/K/mol.....

ΔS_{Htotal}= ΔS_{rH}+ ΔS_{dispersed} = -182,95+459,954=277,004 J/K/mol.....

ΔG_r = ΔH_r - T•ΔS_r = +54,546-298,15*0,377966 = -58,144..... kJ/mol....

ΔG_H=RTln(10^{-5.5}/0,02754)=-22,48918 kJ/mol.....ΔG_{HCO3}=RTln(0,0154/0,0338919)=-1,9554 kJ/mol.....

ΔG_{rH} = ΔH_r - T•ΔS_{rH} = +54,546-298,15*0,459954 = -82,589..... kJ/mol....

.....**exoergic**.....

T•ΔS_{total}=195,016 J/K/mol•298,15 K=+58.144.....kJ/mol....

T•ΔS_{Htotal}=277,004 J/K/mol•298,15 K=-58,144-22,48918-1,9554 = +82.589 kJ/mol.....

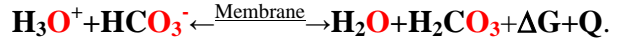
bound TΔSn← dispersed-lost energy ΔG_{reverse_{reaction}}←.Q= -54.546 kJ/mol.spontaneous ΔG_{reaction} =-58,14 kJ/mol...

bound TΔSn← dispersed-lost energy ΔG_{reverse_{reaction}}←.Q= -54.546 kJ/mol.spontaneous ΔG_{reaction} =-82,589 kJ/mol...

THERMODYNAMICS Exercise X. bicarbonate and proton on membrane *lung* epithelial cell surface H_2CO_3
 Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? For transfer bicarbonate and proton through channels on membrane from cell solution of *lung* to epithelial cell surface forming H_2CO_3 using the data table! Mention whether the reaction will be **exoergic** or **anergic** or **endoergic**!

..... Initial compounds \rightarrow products

Substance	$\Delta H_r^\circ, \text{kJ/mol}$	$\Delta S_r^\circ, \text{J/mol/K}$
H_3O^+	-285.81	-3.854
HCO_3^-	-689.93	98.324
H_2O	-285.85	69.9565
H_2CO_3	-699,65	187.00



1. $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
2. $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{H}_2\text{CO}_3} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{HCO}_3^-} = \dots \text{kJ/mol} \dots$
 $= -285,85 - 699,65 - (-285,81 - 689,93) = -985,5 + 975,74 = -9.76 \text{ kJ/mol}$ **exothermic**....

$\Delta S_{\text{dispersed}} = - \Delta H_r / T = +9.76 / 298.15 = +32.735 \dots \text{J/K/mol} \dots$

2. $\Delta S_r = \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{H}_2\text{CO}_3} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{HCO}_3^-} = \dots \text{J/mol/K} \dots$
 $= 69,956 + 187 - (-3,854 + 98,324) = 256,956 - 94,47 = +162,486 \text{ J/mol/K} \dots$

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = +32.735 + 162,486 = 195,221 \dots \text{J/K/mol} \dots$

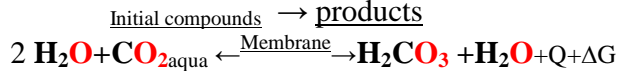
3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -9,76 - 298,15 \cdot 0,162486 = -58.2052 \dots \text{kJ/mol} \dots$
**exoergic**.....

$T \cdot \Delta S_{\text{total}} = 195,221 \text{ J/K/mol} \cdot 298,15 \text{ K} = +58,2052 \dots \text{kJ/mol} \dots$
 bound $T \Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow Q = -9.76 \text{ kJ/mol} \dots$ **spontaneous** $\Delta G_{\text{reaction}} = -58.2 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XI. $\text{CO}_{2\text{aqua}}$ two water molecules $2\text{H}_2\text{O}$ at *lung* epithelial cell surface H_2CO_3

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? For carbon dioxide water solution driven reaction of aqua CO_2 with water molecules $2\text{H}_2\text{O}$ at *lung* epithelial cell surface forming H_2CO_3 ! Mention reaction will be **exoergic** or **anenergetic** or **endoergic**!

Substance	$\Delta H_r^\circ, \text{kJ/mol}$	$\Delta S_r^\circ, \text{J/mol/K}$
$\text{CO}_{2\text{aqua}}$	-413.7976	117.5704
H_2O	-285.85	69.9565
H_2CO_3	-699,65	187.00



1. $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
2. $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{H}_2\text{CO}_3} - 2\Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{CO}_{2\text{aqua}}} = \dots\dots\dots \text{kJ/mol} \dots\dots$
 $= -285.85 - 699,65 - (2 \cdot -285.81 - 413,7976) = -985.5 + 985.418 = -0,0824 \text{ kJ/mol}$ **athermic**.....

.....Proofing membrane channel penetrating athermic-neutral process $\Delta H_r = 0.0 \text{ kJ/mol}$ in friction less manner.
No heat dispersion through membrane channel

$\Delta S_{\text{dispersed}} = -\Delta H_r / T = +0,0824 / 298.15 = +0,27637 \dots\dots\dots \text{J/K/mol} \dots\dots$
Proofing membrane channel penetrating athermic-neutral process $\Delta H_r = 0.0 \text{ kJ/mol}$ in friction less manner.
No heat dispersion through membrane channel

2. $\Delta S_r = \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{H}_2\text{CO}_3} - 2\Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{CO}_{2\text{aqua}}} = \dots\dots\dots \text{J/K/mol} \dots\dots$
 $= 69.956 + 187 - (117,5704 + 2 \cdot 69.956) = 256,956 - 257,4824 = -0,5264 \text{ J/mol/K} \dots\dots$

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -0,5264 + 0,27637 = -0,25 \dots\dots\dots \text{J/K/mol} \dots\dots$

$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -0,0824 - 298.15 \cdot -0,0005264 = 0,07455 \dots\dots\dots \text{kJ/mol} \dots\dots$
**anenergetic** weak **endoergic**.....

$T \cdot \Delta S_{\text{total}} = -0,25 \text{ J/K/mol} \cdot 298,15 \text{ K} = -0,0745 \dots\dots\dots \text{kJ/mol} \dots\dots$
 bound $T \Delta S_{\text{total}} \leftarrow$ accumulate free energy $\Delta G_{\text{reversereaction}} \leftarrow Q = +0,0824 \text{ kJ/mol} \dots$ weak **endoergic** $\Delta G_{\text{reaction}} = 0,0745 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XII. H_2CO_3 decomposition CO_2 gas H_2O at *lung* epithelial cell surface

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? From water carbonic acid H_2CO_3 decomposition reaction to carbon dioxide CO_2 gas and water H_2O at *lung* epithelial cell surface from H_2CO_3 using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

.....Initial compounds => products

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{CO}_2 \uparrow_{\text{gas}}$	-393,509	213,74
H_2O	-285,85	69,9565
H_2CO_3	-699,65	187,00



1. $\Delta H_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{initial compounds}}$
2. $\Delta S_{\text{reaction}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{initial compounds}}$
3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

1. $\Delta H_r = \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{CO}_2} - \Delta H^\circ_{\text{H}_2\text{CO}_3} = \dots \dots \dots \text{kJ/mol} \dots$
 $\dots = -285,85 - 393,509 - (-699,65) = -679,359 + 699,65 = +20,291 \text{ kJ/mol}$ **endothermic**.....

$\Delta S_{\text{dispersed}} = -\Delta H_r / T = -20,291 / 298,15 = -68,056 \dots \dots \dots \text{J/K/mol} \dots$

2. $\Delta S_r = \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{CO}_2} - \Delta S^\circ_{\text{H}_2\text{CO}_3} = \dots \dots \dots \text{J/K/mol} \dots$
 $\dots = 69,956 + 213,74 - (187) = 257,482 - 94,47 = +96,696 \text{ J/mol/K} \dots$

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -68,056 + 96,696 = 28,64 \dots \dots \dots \text{J/K/mol} \dots$

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +20,291 - 298,15 \cdot 0,096696 = -8,538912 \dots \dots \dots \text{kJ/mol} \dots$
exoergic.....

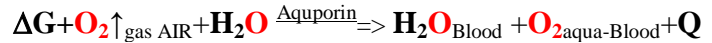
$T \cdot \Delta S_{\text{total}} = 28,64 \text{ J/K/mol} \cdot 298,15 \text{ K} = +8,539 \dots \dots \dots \text{kJ/mol} \dots$
 bound $T \Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow Q = -20,291 \text{ kJ/mol}$ **spontaneous** $\Delta G_{\text{reaction}} = -8,539 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XIII. $O_2 \uparrow$ gas respiration through membrane aquaporins to form $O_{2\text{aqua-Blood}}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K using the data table! Reaction is **exothermic**, **athermic**, **endothermic**? AIR $O_2 \uparrow$ gas assimilation reaction for human body respiration through membrane aquaporins to form $O_{2\text{aqua-Blood}}$! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds => products

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$O_{2\text{aqua}}$	-11,715	110,876
H_2O	-285,85	69,9565
$O_2 \uparrow_{\text{gas}}$	0,0	205,04



$$1. \Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$\Delta H_r = \Delta H^\circ_{H_2O} + \Delta H^\circ_{O_{2\text{aqua-Blood}}} - \Delta H^\circ_{H_2O} - \Delta H^\circ_{O_2\text{gas-AIR}} = \dots \text{kJ/mol} \dots$$

$$\dots = (-285,85 + -11,715) - (-285,85 + 0,0) = -285,85 - 11,715 + 285,85 = -11,715 \text{ kJ/mol } \mathbf{exothermic} \dots$$

$$\Delta S_{\text{dispersed}} = -\Delta H_r / T = 11,715 / 298,15 = +39,292 \dots \text{J/K/mol} \dots$$

$$\dots = 110,876 + 69,9565 - (69,9565 + 205,04) = 110,876 - 205,04 = -94,164 \text{ J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{H_2O} + \Delta S^\circ_{O_{2\text{aqua-Blood}}} - \Delta S^\circ_{H_2O} - \Delta S^\circ_{O_2\text{gas-AIR}} = \dots \text{J/K/mol} \dots$$

$$\dots = 69,9565 + 110,876 - (205,04 + 69,9565) = 180,83 - 274,997 = -94,164 \text{ J/mol/K} \dots$$

$$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -94,164 + 39,292 = -54,872 \dots \text{J/K/mol} \dots$$

$$3. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -11,715 + (298,15 \cdot 0,094164) = -11,715 - 19,1305 = -30,8455 \dots \text{kJ/mol} \dots$$

endoergic.....

$$T \cdot \Delta S_{\text{total}} = -0,054872 \text{ kJ/mol} \cdot 298,15 \text{ K} = -16,36 \dots \text{kJ/mol} \dots$$

bound $T \Delta S_n \leftarrow$ accumulate energy $\Delta G_{\text{reversereaction}} \leftarrow$. $Q = 11,715 \text{ kJ/mol}$ non-spontaneous **endoergic** $\Delta G_{\text{reaction}} = +16,36 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XIV. $O_{2,aqu}$ through green plants membrane aquaporins to form AIR $O_{2,gas}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K using the data table. Reaction is **exothermic**, **athermic**, **endothermic**? From water $O_{2,aqu}$ evaporation reaction through green plants membrane aquaporins to form AIR $O_{2,gas}$ for life bodies breathing out to AIR! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds => products

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$O_{2,aqua}$	-11,715	110,876
H_2O	-285,85	69,9565
$O_{2,gas}$	0,0	205,04
$H_2O_{gas\ AIR}$	-241,835	188,74



- $\Delta H_{reaction} = \sum \Delta H^\circ_{products} - \sum \Delta H^\circ_{initial\ compounds}$
- $\Delta S_{reaction} = \sum \Delta S^\circ_{products} - \sum \Delta S^\circ_{initial\ compounds}$
- $\Delta G_{reaction} = \Delta H_{reaction} - T \cdot \Delta S_{reaction}$

1. $\Delta H_r = \Delta H^\circ_{H_2O_{gas-AIR}} + \Delta H^\circ_{O_{2,gas-AIR}} - \Delta H^\circ_{H_2O} - \Delta H^\circ_{O_{2,aqua}} = \dots \text{kJ/mol} \dots$
 $\dots = -241,835 + 0,0 - (-285,85 - 11,715) = -241,835 + 297,565 = +55,73 \text{ kJ/mol} \text{ endothermic} \dots$
 $\dots, \dots, \dots, \dots, \text{kJ/mol} \dots$

$\Delta S_{dispersed} = - \Delta H_r / T = -55,73 / 298,15 = -186,9193 \dots \text{J/K/mol} \dots$
 $\dots \text{J/K/mol} \dots$

2. $\Delta S_r = \Delta S^\circ_{H_2O_{gas-AIR}} + \Delta S^\circ_{O_{2,gas-AIR}} - \Delta S^\circ_{H_2O} - \Delta S^\circ_{O_{2,aqua}} = \dots \text{J/K/mol} \dots$
 $\dots = 205,04 + 188,74 - (69,9565 + 110,876) = 393,78 - 180,8325 = +212,9475 \text{ J/mol/K} \dots$
 $\dots, \dots, \dots, \dots, \text{J/K/mol} \dots$

$\Delta S_{total} = \Delta S_r + \Delta S_{dispersed} = 212,9475 - 186,9193 = +26,0282 \dots \text{J/K/mol} \dots$

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = +55,73 - (298,15 \cdot 0,2129475) = +55,73 - 63,4903 = -7,76 \dots \text{kJ/mol} \dots$
 $\dots \text{exoergic} \dots$

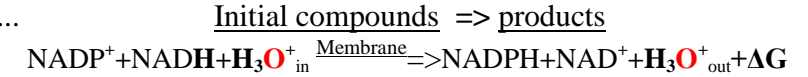
$T \cdot \Delta S_{total} = +0,0260282 \text{ kJ/K/mol} \cdot 298,15 \text{ K} = +7,76 \dots \text{kJ/mol} \dots$

bound $T \Delta S_{total} \leftarrow$ accumulate energy $\Delta G_{reversereaction} \leftarrow Q = -55,73 \text{ kJ/mol}$. non-spontaneous **exoergic** $\Delta G_{reaction} = -7,76 \text{ kJ/mol}$

THERMODYNAMICS Exercise XV. vitamin B3 $\text{H}_3\text{O}^+_{\text{in}}$ to $\text{H}_3\text{O}^+_{\text{out}}$ inter membrane space

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K using the data table! Reaction is **exothermic**, **athermic**, **endothermic**? For vitamin B3 reduced form NADH and oxidized form NADP^+ translocate hydrogen ions as protons through membrane from inner $\text{H}_3\text{O}^+_{\text{in}}$ to out side mitochondria $\text{H}_3\text{O}^+_{\text{out}}$ inter membrane space Reaction will be **exoergic**, **endoergic** or **anenergetic**!.....

Substance	$\Delta H^\circ_r, \text{kJ/mol}$	$\Delta S^\circ_r, \text{J/mol/K}$
NADP^+	-1007,48	577,897
$\text{NADH}_{(aq)}$	-1036,66	-140,50
$\text{H}_3\text{O}^+_{\text{out}}$	-285,81	-3,854
NADPH	-1036,66	763,005
$\text{NAD}^+_{(aq)}$	-1007,48	-183
$\text{H}_3\text{O}^+_{\text{in}}$	-285,81	-3,854



1. $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$

2. $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$

3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

Proton translocating transhydrogenase (EC1.6.1.1) ENZYME found in bacteria and animal mitochondria

that couples the transfer of reducing equivalents between

NAD(H) and NADP(H) to the translocation of protons across the membrane

1. $\Delta H_r = \Delta H^\circ_{\text{H}_3\text{O}^+_{\text{out}}} + \Delta H^\circ_{\text{NADPH}} + \Delta H^\circ_{\text{NAD}^+} - \Delta H^\circ_{\text{NADP}^+} - \Delta H^\circ_{\text{H}_3\text{O}^+_{\text{in}}} - \Delta H^\circ_{\text{NADH}} = \dots \text{kJ/mol} \dots$
 $\dots = -1036,66 - 1007,48 - 285,81 - (-1007,48 - 1036,66 - 285,81) = -2329,95 + 2329,95 = 0,0 \text{ kJ/mol}$ **athermic neutral**....

.....Proofing membrane channel penetrating athermic-neutral process $\Delta H_r = 0,0 \text{ kJ/mol}$ in friction less manner.

.....No heat dispersion through membrane channel

.....

..... $\Delta S_{\text{dispersed}} = -\Delta H_r / T = -0 / 298,15 = +0,0 \dots \text{J/K/mol} \dots$

.....Proofing membrane channel penetrating athermic-neutral process $\Delta H_r = 0,0 \text{ kJ/mol}$ in friction less manner.

.....No heat dispersion through membrane channel

.....

2. $\Delta S_r = \Delta S^\circ_{\text{H}_3\text{O}^+_{\text{out}}} + \Delta S^\circ_{\text{NADPH}} + \Delta S^\circ_{\text{NAD}^+} - \Delta S^\circ_{\text{NADP}^+} - \Delta S^\circ_{\text{H}_3\text{O}^+_{\text{in}}} - \Delta S^\circ_{\text{NADH}} = \dots \text{J/mol/K} \dots$
 $\dots = 763,005 - 183 - 3,854 - (577,897 - 140,50 - 3,854) = 576,2 - 433,543 = +142,6 \text{ J/mol/K} \dots$

.....

$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 0,0 + 142,6 = +142,6 \dots \text{J/mol/K} \dots$

.....

3. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = 0,0 - 298,15 \cdot (+142,6) / 1000 = -42,516 \dots \text{kJ/mol} \dots$
exoergic.....

.....

$T \cdot \Delta S_{\text{total}} = -142,6 \text{ J/K/mol} \cdot 298,15 \text{ K} = +42.516 \dots \text{kJ/mol} \dots$

bound $T \Delta S_n \leftarrow$ lost energy for proton gradient $\leftarrow \text{H}^+_{\text{out}}$ $Q = +0,0 \text{ kJ/mol} \dots$ **spontaneous exoergic** $\Delta G_{\text{reaction}} = -42,516 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XVI. $\text{NADH} + \text{H}_3\text{O}^+ + \text{O}_{2\text{aqua}} \xleftarrow{\text{FMN(B2vitamin)}} \text{NAD}^+ + \text{H}_2\text{O} + \text{H}_2\text{O}_{2\text{aqua}} + \text{Q}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K Reaction is **exothermic**, **athermic**, **endothermic** is **endoergic** or **exoergic**? For vitamin B3 reduced form NADH or NADPH flavin B2 vitamin FMN enzyme using oxygen $\text{O}_{2\text{aqua}}$ as electron acceptor for the oxidation of NADH with the production of hydrogen peroxide using the data table!

Substance	$\Delta H_r^\circ, \text{kJ/mol}$	$\Delta S_r^\circ, \text{J/mol/K}$
$\text{O}_{2\text{aqua}}$	-11,715	110,876
$\text{NADH}_{(\text{aq})}$	-1036,66	-140,50
H_3O^+	-285,81	-3,854
H_2O	-285,85	69,9565
$\text{NAD}^+_{(\text{aq})}$	-1007,48	-183
$\text{H}_2\text{O}_{2\text{aqua}}$	-191,17	143,9

Initial compounds => products
 $\text{NADH} + \text{H}_3\text{O}^+ + \text{O}_{2\text{aqua}} \xrightarrow{\text{FMN(B2vitamin)}} \text{NAD}^+ + \text{H}_2\text{O} + \text{H}_2\text{O}_{2\text{aqua}} + \text{Q}$

- $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
- $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$
- $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$

NADH and NADPH oxidase (EC 1.6.99.1) ENZYME

$1 \Delta H_r = \Delta H^\circ_{\text{H}_2\text{O}_{2\text{aqua}}} + \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{NAD}^+} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{O}_{2\text{aqua}}} - \Delta H^\circ_{\text{NADH}} = \dots$
 $\dots \Delta H_r = -1007,48 - 191,17 - 285,85 - (-1036,66 - 11,715 - 285,81) = -1484,5 + 1334,185 = -150,315 \text{ kJ/mol}$ **exothermic**.....
kJ/mol....

$\Delta S_{\text{dispersed}} = -\Delta H_r / T = +150,315 / 298.15 = +504,0416 \dots \text{J/K/mol} \dots$

$2. \Delta S_r = \Delta S^\circ_{\text{H}_2\text{O}_{2\text{aqua}}} + \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{NAD}^+} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{O}_{2\text{aqua}}} - \Delta S^\circ_{\text{NADH}} = \dots \text{J/mol/K} \dots$
 $\dots = -183 + 143,9 + 69,9565 - (110,876 - 140,50 - 3,854) = -39,1 - 29,624 = +64,335 \text{ J/mol/K} \dots$

$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = +64,335 + 504,0416 = +568,3766 \dots \text{J/mol/K} \dots$

$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -150,315 - 298,15 \cdot (+64,335 / 1000) = -150,315 - 19,1815 = -169,5 \dots \text{kJ/mol} \dots$
**exoergic**.....

$T \cdot \Delta S_{\text{total}} = +568,3766 \text{ J/mol} \cdot 298,15 \text{ K} = +169,5 \dots \text{kJ/mol} \dots$

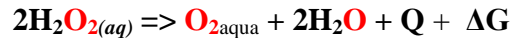
bound TΔSn ← dispersed-lost energy ← $\text{NADH} + \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ \cdot \text{Q} = 150,315 \text{ kJ/mol}$ **spontaneous** $\Delta G_{\text{reaction}} = -169,5 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XVII Peroxide $2\text{H}_2\text{O}_2(aq)$ conversion to $\text{O}_2(aq) + 2\text{H}_2\text{O} + \text{Q}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Peroxide $2\text{H}:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:\text{H}$ conversion to $\text{O}_2(aq) + 2\text{H}_2\text{O} + \text{Q}$ at human temperature (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds peroxide => products oxygen+water

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_2\text{O}_2(aq)$	-191,17	143,9
$\text{O}_2(aq)$	-11,715	110,876
H_2O	-285,85	69,9565



$$1. \Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$1. \Delta H_r = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = \dots \text{kJ/mol}$$

$$\dots = -11,715 - 2 \cdot 285,85 - (2 \cdot -191,17) = -133407583,4 + 383,415 = -201,08 \text{ kJ/mol } \mathbf{exothermic} \dots$$

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$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -(-201,08) / 310,15 = 648,33 \dots \text{J/K/mol} \dots$$

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$$\Delta S_r = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{O}_2} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = \dots \text{J/mol/K}$$

$$\dots = 110,876 + 2 \cdot 69,9565 - (2 \cdot 143,9) = 250,789 - 287,8 = -37,011 \text{ J/mol/K} \dots$$

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$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -37,011 + 648,33 = +611,319 \dots \text{J/mol/K}$$

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$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -201,08 - 310,15 \cdot (-0,037011) = -201,08 + 11,478962 = -189,601 \dots \text{kJ/mol}$$

$$\dots \text{kJ/mol} \dots$$

.....**exoergic**.....

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$$T \cdot \Delta S_{\text{total}} = 0,611319 \cdot 310,15 = +189,6 \dots \text{kJ/mol}$$

$$\text{bound } T\Delta S_{\text{total}} \leftarrow \text{dispersed-lost energy } \Delta G_{\text{reversereaction}} \leq \text{Q} = -201,08 \text{ kJ/mol } \mathbf{spontaneous} \Delta G_{\text{reaction}} = -189,6 \text{ kJ/mol} \dots$$

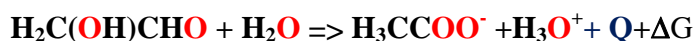
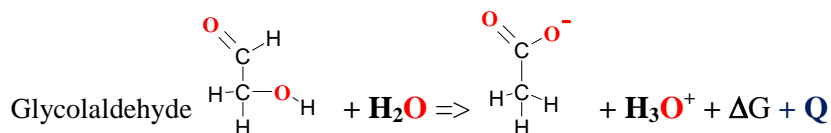
THERMODYNAMICS Exercise XVIII Glycolaldehyde $\text{H}_2\text{C}(\text{OH})\text{CHO}$ conversion to $\text{H}_3\text{CCOO}^- + \text{H}_3\text{O}^+ + \text{Q}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**?

Glycolaldehyde $\text{H}_2\text{C}(\text{OH})\text{CHO}$ conversion to acetate $\text{H}_3\text{CCOO}^- + \text{H}_3\text{O}^+ + \text{Q}$ (25 C) 298.15 K, using the data table!

Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds Glyoxal => products acetate + $\text{H}_3\text{O}^+ + \text{Q}$

Substance	ΔH_f° , kJ/mol	ΔS_f° , J/mol/K
$\text{H}_2\text{C}(\text{OH})\text{CHO}$	-212	272,5
H_3CCOO^-	-486	85.3
$\text{H}_2\text{O}_{(aq)}$	-285.85	69,96
$\text{H}_3\text{O}^+_{(aq)}$	-285.81	-3,854



- $\Delta H_r = \Delta H_f^\circ \text{H}_3\text{CCOO}^- + \Delta H_f^\circ \text{H}_3\text{O}^+ - \Delta H_f^\circ \text{H}_2\text{O} + \Delta H_f^\circ \text{H}_2\text{C}(\text{OH})\text{CHO} = \text{kJ/mol} \dots \dots \dots \text{kJ/mol} \dots \dots$
 $\dots \dots \dots = -486 - 285,81 - (-212 - 285,85) = -770,11 + 497,85 = -273,96 \text{ kJ/mol}$ **exothermic**....
- $\Delta S_{\text{dispersed}} = -\Delta H_r / T = 273,96 / 298,15 = +918,966 \dots \dots \dots \text{J/K/mol} \dots \dots$
 $\Delta S_r = \Delta S_f^\circ \text{H}_3\text{CCOO}^- + \Delta S_f^\circ \text{H}_3\text{O}^+ - \Delta S_f^\circ \text{H}_2\text{O} - \Delta S_f^\circ \text{H}_2\text{C}(\text{OH})\text{CHO} = \dots \dots \dots \text{J/mol/K} \dots \dots$
 $\dots \dots \dots = 85,3 - 3,854 - (69,96 + 272,5) = 81,446 - 342,46 = -261,014 \text{ J/mol/K} \dots \dots \dots$
- $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 918,966 - 261,014 = 657,952 \text{ J/mol/K} \dots \dots \dots \text{J/mol/K} \dots \dots$
- $4\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -273,96 + 298,15 \cdot 0,261014 = -196,139 \dots \dots \dots \text{kJ/mol}$ **exoergic**.....
 $T \cdot \Delta S_{\text{total}} = +657,952 \text{ J/mol} \cdot 298,15 \text{ K} = +196,168 \dots \dots \dots \text{kJ/mol} \dots \dots$

bound $T \Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow Q = 273,96 \text{ kJ/mol} \dots \dots$ **spontaneous** $\Delta G_{\text{reaction}} = -196,14 \text{ kJ/mol} \dots$

Formation in space. UV-irradiation of methanol ices containing CO yielded organic compounds such as glycolaldehyde and **methyl formate**, the more abundant isomer of glycolaldehyde.

Ethylene Glycol and glycolaldehyde require temperatures above 30 K.^{[12][13]} The most consistent formation reactions seems to be on the surface of ice in **cosmic dust**. Glycolaldehyde has been identified in gas and dust near the center of the **Milky Way** galaxy,^[16] in a star-forming region 26000 light-years from Earth,^[17] and around a **protostellar** binary star, **IRAS 16293-2422**, 400 light years from Earth.^{[18][19]} Observation of in-falling glycolaldehyde spectra 60 AU from **IRAS 16293-2422** suggests that complex organic molecules may form in stellar systems prior to the formation of planets, eventually arriving on young planets early in their formation.^[13]

Detection in space. The interior region of a **dust cloud** is known to be relatively cold. With temperatures as cold as 4 Kelvin the gases within the cloud will freeze and fasten themselves to the dust, which provides the reaction conditions conducive for the formation of complex molecules such as glycolaldehyde. When a star has formed from the dust cloud, the temperature within the core will increase. This will cause the molecules on the dust to evaporate and be released. The molecule will emit radio waves that can be detected and analyzed. The **Atacama Large Millimeter/submillimeter Array** (ALMA) first detected glycolaldehyde. ALMA consists of 66 antennas that can detect the radio waves emitted from **cosmic dust**.^[20]

On October 23, 2015, researchers at the **Paris Observatory** announced the discovery of glycolaldehyde and **ethyl alcohol** on **Comet Lovejoy**, the first such identification of these substances in a comet.^{[21][22]}

Glycolaldehyde is formed from many sources, including the amino acid **glycine** and from purone catabolism. It can form by action of ketolase on **fructose 1, 6-bisphosphate** in an alternate glycolysis pathway. This compound is transferred by **thiamin** pyrophosphate during the pentose phosphate shunt. In Tissue neurons; Mitochondria;

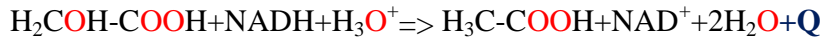
Solar-type protostar with ALMA. Glycolaldehyde (HCOCH_2OH) is the simplest sugar and an important intermediate in the path toward forming more complex biologically relevant molecules. First detection of 13 transitions of glycolaldehyde around a solar-type young star, through Atacama Large Millimeter Array (ALMA) observations of the Class 0 protostellar binary IRAS 16293-2422 at 220 GHz (6 transitions) and 690 GHz (7 transitions). Glycolaldehyde co-exists with its isomer, methyl formate (HCOOCH_3), which is a factor 10-15 more abundant toward the two sources. The data also show a tentative detection of ethylene glycol, the reduced alcohol of glycolaldehyde. In the 690 GHz data, the seven transitions predicted to have the highest optical depths based on modeling of the 220 GHz lines all show red-shifted absorption profiles toward one of the components in the binary (IRAS16293B) indicative of infall and emission at the systemic velocity offset from this by about 0.2" (25 AU). We discuss the constraints on the chemical formation of glycolaldehyde and other organic species - in particular, in the context of laboratory experiments of photochemistry of methanol-containing ices. The relative abundances appear to be consistent with UV photochemistry of a $\text{CH}_3\text{OH-CO}$ mixed ice that has undergone mild heating. The order of magnitude increase in line density in these early ALMA data illustrate its huge potential to reveal the full chemical complexity associated with the formation of solar system analogs.

THERMODYNAMICS Exercise XIX Glycolic acid $\text{H}_2\text{COH-COOH}$ conversion to $\text{H}_3\text{C-COOH} + \text{Q}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Glycolic acid $\text{H}_2\text{COH-COOH}$ conversion to acetate $\text{H}_3\text{C-COOH} + \text{Q}$ (25 C) 298.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds Glycolic acid => products acetate + $\text{H}_3\text{O}^+ + \text{Q}$

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_2\text{COH-COOH}$	- 651	318,6
$\text{NADH}_{(aq)}$	-1036,66	-140,5
$\text{H}_3\text{O}^+_{(aq)}$	-285.81	-3,854
$\text{H}_3\text{C-COOH}$	-480.6	85.3
$\text{NAD}^+_{(aq)}$	-1007,48	-183
$\text{H}_2\text{O}_{(aq)}$	-285.85	69,96

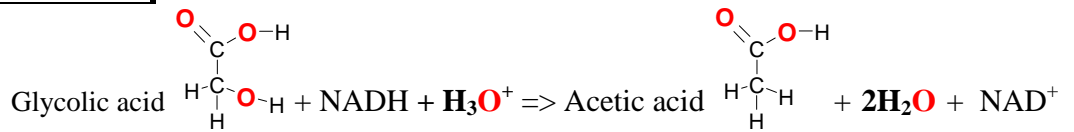


B3 vitamin => reduction

$$1. \Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$



$$1. \Delta H_r = \Delta H^\circ_{\text{CH}_3\text{COOH}} + 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{NAD}^+} - \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{COH-COOH}} - \Delta H^\circ_{\text{NADH}} = \text{kJ/mol} \dots \text{kJ/mol} \dots$$

$$\dots = -480,6 - 1007,48 - 2 \cdot 285,85 - (-651 - 1036,66 - 285,81) = -2059,78 + 1973,47 = -86,31 \text{ kJ/mol} \text{ exothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -86,31 / 298,15 = +289,485 \dots \text{J/K/mol} \dots$$

$$\Delta S_r = \Delta S^\circ_{\text{CH}_3\text{COOH}} + 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{NAD}^+} - \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{H}_2\text{COH-COOH}} - \Delta S^\circ_{\text{NADH}} = \dots \text{J/K/mol} \dots$$

$$\dots = 85,3 - 183 + 2 \cdot 69,956 - (318,6 - 140,50 - 3,854) = 42,212 + (-174,246) = -132 \text{ J/mol} \cdot \text{K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 289,485 - 132 = +157,485 \text{ J/mol} \cdot \text{K} \dots \text{J/K/mol} \dots$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -86,31 + 298,15 \cdot 0,132 = -46,9542 \dots \text{kJ/mol} \dots$$

exoergic.....

$$T \cdot \Delta S_{\text{total}} = +157,485 \text{ J/K/mol} \cdot 298,15 \text{ K} = +46,9542 \dots \text{kJ/mol} \dots$$

bound $T\Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow Q = +86,31 \text{ kJ/mol} \dots$ **spontaneous** $\Delta G_{\text{reaction}} = -46,9542 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XX Pyruvate $\text{H}_3\text{CC}=\text{O}\text{COO}^-$ decarboxylation $\text{H}_3\text{CCHO} + \text{HCO}_3^-$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Pyruvate $\text{H}_3\text{CC}=\text{O}\text{COO}^-$ conversion to acetaldehyde $\text{H}_3\text{CCHO} + \text{HCO}_3^-$ (25 C) 298.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Substance	$\Delta H_r^\circ, \text{kJ/mol}$	$\Delta S_r^\circ, \text{J/mol/K}$
$\text{H}_3\text{CC}=\text{O}\text{COOH}_{(\text{aq})}$	-607,82	179,91
$\text{H}_3\text{CC}=\text{O}\text{COO}^-_{(\text{aq})}$	-603,7	-433,54
$\text{H}_3\text{CCHO}_{(\text{aq})}$	-212,23	160,2
H_3CCHO_l	-192,2	160,2
$\text{H}_2\text{O}_{(\text{aq})}$	-285,85	69,96
$\text{H}_3\text{O}^+_{(\text{aq})}$	-285,81	-3,854
HCO_3^-	-689,93	98,324

Initial compounds Pyruvic acid+Q => products bicarbonate + H_3O^+



$$1. \Delta H_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{initial compounds}}$$

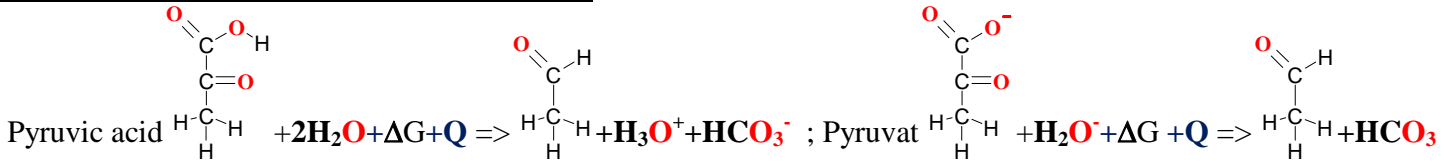
MassachusettsTinstutute

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$$2. \Delta S_{\text{reaction}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$



$$1. \Delta H_r = \Delta H^\circ_{\text{H}_3\text{CCHO}} + \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{HCO}_3^-} - 2 \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{CC}=\text{O}\text{COOH}} = -8,45 \text{ kJ/mol} \dots \text{MassachusettsTinstutute}$$

$$\dots = -212,23 - 285,81 - 689,93 - (-2 \cdot 285,85 - 607,82) = -1187,97 + 1179,52 = -8,45 \text{ kJ/mol} \text{ exothermic} \dots$$

$$1. \Delta H_r = \Delta H^\circ_{\text{H}_3\text{CCHO}} + \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{HCO}_3^-} - 2 \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} = +11,58 \text{ kJ/mol} \dots$$

$$\dots = -192,2 - 285,81 - 689,93 - (-2 \cdot 285,85 - 607,82) = -1187,97 + 1179,52 = 11,58 \text{ kJ/mol} \text{ endothermic} \dots$$

$$1. \Delta H_r = \Delta H^\circ_{\text{H}_3\text{CCHO}} + \Delta H^\circ_{\text{HCO}_3^-} - \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} = +7,42 \text{ kJ/mol} \dots$$

$$\dots = -192,2 - 689,93 - (-285,85 - 603,7) = -882,13 + 889,55 = +7,42 \text{ kJ/mol} \text{ endothermic} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = 8,45 / 298,15 = +28,35 \dots \text{J/mol/K} \dots \text{MassachusettsTinstutute}$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -11,58 / 298,15 = -38,8395 \dots \text{J/mol/K} \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -7,42 / 298,15 = -24,8868 \dots \text{J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{\text{H}_3\text{CCHO}} + \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{HCO}_3^-} - 2 \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CC}=\text{O}\text{COOH}} = \dots \text{J/mol/K} \dots \text{MassachusettsTinstutute}$$

$$\dots = 160,2 - 3,854 + 98,324 - (2 \cdot 69,96 + 179,91) = -187,368 - 319,83 = -65,16 \text{ J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{\text{H}_3\text{CCHO}} + \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{HCO}_3^-} - 2 \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} = \dots \text{J/mol/K} \dots$$

$$\dots = 160,2 + 98,324 - (69,96 + 179,91) = 254,67 - 319,83 = -65,16 \text{ J/mol/K} \dots$$

$$2. \Delta S_r = \Delta S^\circ_{\text{H}_3\text{CCHO}} + \Delta S^\circ_{\text{HCO}_3^-} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} = \dots \text{J/mol/K} \dots$$

$$\dots = 160,2 - 3,854 + 98,324 - (69,96 - 433,54) = 258,524 - 249,87 = 8,654 \text{ J/mol/K} \dots$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -65,16 - 28,35 = -36,81 \text{ J/mol/K} \dots \text{MassachusettsTinstutute} \text{ J/mol/K}$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -65,16 - 38,8395 = -104 \text{ J/mol/K} \dots \text{J/mol/K}$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 8,654 - 24,8868 = -16,233 \text{ J/mol/K} \dots \text{J/mol/K}$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -8,45 - 298,15 \cdot (-0,06516) = +10,98 \dots \text{kJ/mol} \text{ endoergic} \dots \text{MassachusettsTinstutute}$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = 11,58 - 298,15 \cdot (-0,06516) = +31,01 \dots \text{kJ/mol} \text{ endoergic} \dots$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = 7,42 - 298,15 \cdot (-0,008654) = +4,84 \dots \text{kJ/mol} \text{ endoergic} \dots$$

$$T \cdot \Delta S_{\text{total}} = -36,81 \text{ J/mol} \cdot 298,15 \text{ K} = -10,97 \dots \text{kJ/mol} \dots \text{MassachusettsTinstutute}$$

$$\text{bound } T \Delta S_n \leftarrow \text{accumulate energy } \Delta G_{\text{reversereaction}} \leftarrow Q = -8,45 \text{ kJ/mol} \text{ not spontaneous } \Delta G_{\text{reaction}} = 10,98 \text{ kJ/mol} \dots$$

$$T \cdot \Delta S_{\text{total}} = -104 \text{ J/mol} \cdot 298,15 \text{ K} = -31,01 \dots \text{kJ/mol} \dots$$

$$\text{bound } T \Delta S_n \leftarrow \text{accumulate energy } \Delta G_{\text{reversereaction}} \leftarrow Q = 11,58 \text{ kJ/mol} \text{ not spontaneous } \Delta G_{\text{reaction}} = 31,01 \text{ kJ/mol} \dots$$

$$T \cdot \Delta S_{\text{total}} = -16,233 \text{ J/mol} \cdot 298,15 \text{ K} = -4,84 \dots \text{kJ/mol} \dots$$

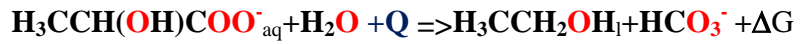
$$\text{bound } T \Delta S_n \leftarrow \text{accumulate energy } \Delta G_{\text{reversereaction}} \leftarrow Q = 7,42 \text{ kJ/mol} \text{ not spontaneous } \Delta G_{\text{reaction}} = 4,84 \text{ kJ/mol} \dots$$

THERMODYNAMICS Exercise XXI Lactate $\text{H}_3\text{CCH}(\text{OH})\text{COO}^-_{\text{aq}}$ decarboxylation $\text{H}_3\text{CCH}_2\text{OH} + \text{HCO}_3^-$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Lactate $\text{H}_3\text{CC}=\text{OCOO}^-$ conversion to ethanol $\text{H}_3\text{CCHO} + \text{HCO}_3^-$ (25 C) 298.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds Lactate+Q => products ethanol bicarbonate

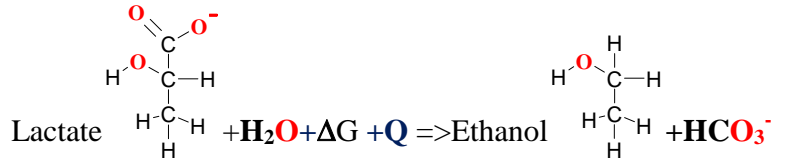
Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_3\text{CCH}(\text{OH})\text{COO}^-_{\text{aq}}$	-686,2	-557,71
$\text{H}_3\text{CCH}_2\text{OH}_l$	-277,6	160,7
$\text{H}_2\text{O}_{(\text{aq})}$	-285,85	69,96
HCO_3^-	-689,93	98,324



1. $\Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$
CRC

2. $\Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$

3. $\Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$



1. $\Delta H_r = \Delta H^\circ_{\text{H}_3\text{CCH}_2\text{OH}} + \Delta H^\circ_{\text{HCO}_3^-} - \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{CCH}_2\text{OHCOO}^-} = 4,52 \text{ kJ/mol} \dots \dots \dots$
 $\dots \dots \dots = -277,6 - 689,93 - (-285,85 - 686,2) = -967,53 + 972,06 = +4,52 \text{ kJ/mol}$ **endothermic**...

2. $\Delta S_{\text{dispersed}} = -\Delta H_r / T = -4,52 / 298,15 = -15,16 \dots \dots \dots \text{ J/K/mol} \dots$

2. $\Delta S_r = \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OH}} + \Delta S^\circ_{\text{HCO}_3^-} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OHCOO}^-} = \dots \dots \dots \text{ J/mol/K} \dots$
 $\dots \dots \dots = 160,7 + 98,324 - (69,96 - 557,71) = 259,02 + 487,75 = 746,77 \text{ J/mol/K} \dots$

3. $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -15,16 + 746,77 = 731,61 \text{ J/mol/K} \dots \dots \dots \text{ J/mol/K}$

4. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = 4,52 - 298,15 \cdot 0,74677 = -218,13 \dots \dots \dots \text{ kJ/mol}$ **exoergic**.....

$T \cdot \Delta S_{\text{total}} = 731,61 \text{ J/K/mol} \cdot 298,15 \text{ K} = \mathbf{218,13} \dots \dots \dots \text{ kJ/mol} \dots$

bound $T \Delta S_{\text{total}} \leftarrow$ dispersed-lost energy $\Delta G_{\text{reversereaction}} \leftarrow Q = -4,52 \text{ kJ/mol}$ **spontaneous** $\Delta G_{\text{reaction}} = -218,13 \text{ kJ/mol} \dots$

THERMODYNAMICS Exercise XXII alanine $\text{H}_3\text{CCHNH}_3^+\text{COO}^-$ deamination pyruvate $\text{H}_3\text{CC}=\text{OCOO}^-$
 Physiologic conditions pH=7,36 T=310,15 K (37° C)

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 310.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Alanine deamination to pyruvic acid and pyruvate $\text{H}_3\text{CC}=\text{OCOO}^-$ (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds Alanine + $\text{O}_{2\text{aqua}}$ => products pyruvate + NH_3 + H_3O^+ + Q

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_3\text{CC}=\text{OCOOH}_{(\text{aq})}$	-607,82	179,91
$\text{H}_3\text{CC}=\text{OCOO}^-_{(\text{aq})}$	-603,7	-433,54
$\text{H}_3\text{CCHNH}_3^+\text{COO}^-_{(\text{aq})}$	-554,80	-616,47
$\text{NH}_4^+_{(\text{aq})}$	-132,5	113,4
$\text{NH}_3_{(\text{aq})}$	-76,44	-90,65
$\text{H}_2\text{O}_{(\text{aq})}$	-285,85	69,96
$\text{H}_3\text{O}^+_{(\text{aq})}$	-285,81	-3,854
$\text{O}_{2\text{aqua}}$	-11,715	110,876

$$1. \Delta H_{\text{reaction}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}} ; \text{CRC}$$

$$\text{NH}_4^+_{(\text{aq})} + \text{H}_2\text{O} + \Delta G + \text{Q} \Rightarrow \text{H}_3\text{O}^+ + \text{NH}_3_{(\text{aq})}$$

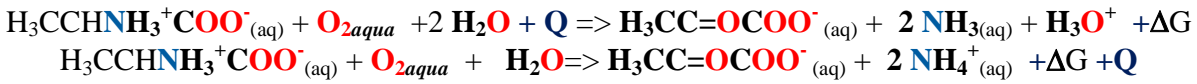
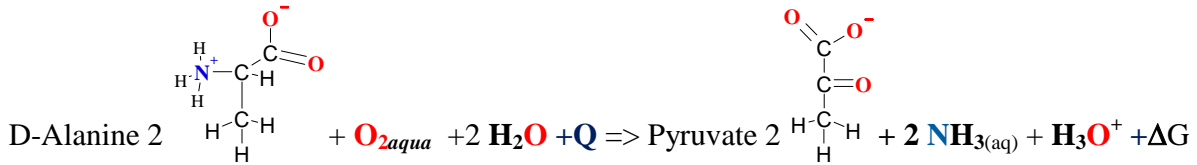
$$\Delta G^\circ_{\text{NH}_4} = -79,3; \Delta G^\circ_{\text{H}_3\text{O}} = -213,27; \Delta G^\circ_{\text{H}_2\text{O}} = -237,19; \Delta G^\circ_{\text{NH}_4} = -79,3$$

$$\Delta G^\circ_{\text{NH}_3} = \Delta G_r - \Delta G^\circ_{\text{H}_3\text{O}} + \Delta G^\circ_{\text{NH}_4} + \Delta G^\circ_{\text{H}_2\text{O}} = -48,326$$

$$\text{pKa} = 9,245 ; \Delta G_r = -RT \ln(10^{-\text{pKa}}) = 54,894$$

$$\Delta G_r = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}} - \Delta G^\circ_{\text{NH}_4} - \Delta G^\circ_{\text{H}_2\text{O}} = 54,894$$

$$= 54,894 - (-213,27) + (-79,3) + (-237,19) = -48,326$$



- $\Delta H_r = 2\Delta H^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta H^\circ_{\text{NH}_3} + \Delta H^\circ_{\text{H}_3\text{O}} - 2\Delta H^\circ_{\text{alanine}} - \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}} = 46,925$ **endothermic**..... kJ/mol
 ... = $2 \cdot -603,7 + 2 \cdot -76,44 - 285,81 - (2 \cdot -554,8 - 11,715 + 2 \cdot -285,85) = -1646,09 + 1693,015 = 46,925$ endothermic..... kJ/mol
- $\Delta H_r = 2\Delta H^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta H^\circ_{\text{NH}_4} - 2\Delta H^\circ_{\text{alanine}} - \Delta H^\circ_{\text{O}_2} - \Delta H^\circ_{\text{H}_2\text{O}} = -65,235$ **exothermic**..... kJ/mol
 ... = $2 \cdot -603,7 + 2 \cdot -132,5 - (2 \cdot -554,8 - 11,715 - 285,85) = -1472,4 + 1407,165 = -65,235$ exothermic..... kJ/mol
- $\Delta S_{\text{dispersed}} = -\Delta H_r/T = -46,925/310,15 = -151,298$ J/K/mol...
- $\Delta S_{\text{dispersed}} = -\Delta H_r/T = 65,235/310,15 = 210,334$ J/K/mol...
- $\Delta S_r = 2\Delta S^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta S^\circ_{\text{NH}_3} + \Delta S^\circ_{\text{H}_3\text{O}} - 2\Delta S^\circ_{\text{alanine}} - \Delta S^\circ_{\text{O}_2} - 2\Delta S^\circ_{\text{H}_2\text{O}} = 209,75$ J/mol/K...
 = $2 \cdot -433,54 + 2 \cdot -90,65 - 3,854 - (2 \cdot -616,47 + 110,876 - 2 \cdot 69,96) = -1052,234 + 1261,984 = 209,75$ J/mol
- $\Delta S_r = 2\Delta S^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta S^\circ_{\text{NH}_4} - 2\Delta S^\circ_{\text{alanine}} - \Delta S^\circ_{\text{O}_2} - \Delta S^\circ_{\text{H}_2\text{O}} = 143,644$ J/mol/K...
 = $2 \cdot -433,54 + 2 \cdot 113,4 - (2 \cdot -616,47 + 110,876 - 69,96) = -640,28 + 1192,024 = 551,744$ J/mol
- $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 209,75 - 151,298 = 58,452$ J/mol/K..... J/mol/K
- $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 551,744 + 210,334 = 762,078$ J/mol/K..... J/mol/K
- $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = 46,925 - 310,15 \cdot 0,20975 = 46,925 - 65,05 = -18,13$ **exoergic**..... kJ/mol
- $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -65,235 - 310,15 \cdot 0,551744 = -65,235 - 171,12 = -236,3584$ **exoergic**..... kJ/mol
- $T \cdot \Delta S_{\text{total}} = 58,452 \text{ J/K/mol} \cdot 310,15 \text{ K} = 18,13$ kJ/mol.....
- $T \cdot \Delta S_{\text{total}} = 762,078 \text{ J/K/mol} \cdot 310,15 \text{ K} = 236,36$ kJ/mol.....
- bound $T \Delta S_n \leftarrow$ **dispersed energy** $\Delta G_{\text{reversereaction}} \text{Q} = 65,2 \text{ kJ/mol}$ **spontaneous** $\Delta G_{\text{reaction}} = -236,36$ kJ/mol
- $\text{pK}_{\text{eq}} = -\log(\text{K}_{\text{eq}}) = -\ln(10) \cdot (-\Delta G_r / R/T) = -\ln(10) \cdot (18,13 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 7,03064 = -1,95028$
- $\text{pK}_{\text{eq}} = -\log(\text{K}_{\text{eq}}) = -\ln(10) \cdot (-\Delta G_r / R/T) = -\ln(10) \cdot (236,36 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 91,6576 = -4,51806$
- $\text{K}_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-\text{pK}_{\text{eq}}} = 10^{1,95028} = 8,92 \cdot 10^1$ temperature 310,15 K (37° C)
- $\text{K}_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-\text{pK}_{\text{eq}}} = 10^{4,51806} = 3,3 \cdot 10^4$ temperature 310,15 K (37° C)
- $\text{NH}_4^+_{(\text{aq})} + \text{H}_2\text{O} + \Delta G + \text{Q} \Rightarrow \text{H}_3\text{O}^+ + \text{NH}_3_{(\text{aq})}$ $\text{pKa} = 9,245 ; \Delta G_r = -RT \ln(10^{-\text{pKa}}) = 54,894$
- $\Delta G_r = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}} - \Delta G^\circ_{\text{NH}_4} - \Delta G^\circ_{\text{H}_2\text{O}} = 54,894$ kJ/mol
- $\Delta G_r = -RT \ln(10^{-9,245}) = -8,3144 \cdot 310,15 \cdot -21,2874 = 8,3144 \cdot 6602,29 = 54894,05$ J/mol = 54,894..... kJ/mol
- $\Delta G^\circ_{\text{NH}_3} = \Delta G_r - \Delta G^\circ_{\text{H}_3\text{O}} + \Delta G^\circ_{\text{NH}_4} + \Delta G^\circ_{\text{H}_2\text{O}} = 54,894 - (-213,27) + (-79,3) + (-237,19) = -48,326$ kJ/mol
- $\Delta S^\circ_{\text{NH}_3} = (\Delta H^\circ_{\text{NH}_3} - \Delta G^\circ_{\text{NH}_3}) / T = (-76,44 - (-48,326)) / 310,15 = 90,65$ J/mol/K

THERMODYNAMICS Exercise XXII(a) alanine $\text{H}_3\text{CCHNH}_3^+\text{COO}^-$ deamination pyruvate $\text{H}_3\text{CC}=\text{OCOO}^-$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 310.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Alanine deamination to pyruvic acid and pyruvate $\text{H}_3\text{CC}=\text{OCOO}^-$ (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds Alanine + $\text{O}_{2\text{aqua}}$ => products pyruvate + $\text{NH}_4\text{OH} + \text{H}_3\text{O}^+ + \text{Q}$

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_3\text{CC}=\text{OCOOH}_{(\text{aq})}$	-607,82	179,91
$\text{H}_3\text{CC}=\text{OCOO}^-_{(\text{aq})}$	-603,7	-433,54
$\text{H}_3\text{CCHNH}_3^+\text{COO}^-_{(\text{aq})}$	-554,80	-616,47
$\text{HO}^-\text{NH}_4^+_{(\text{l})}$	-361,2	165,6
$\text{H}_2\text{O}_{(\text{aq})}$	-285,85	69,96
$\text{H}_3\text{O}^+_{(\text{aq})}$	-285,81	-3,854
$\text{O}_{2\text{aqua}}$	-11,715	110,876

$$1. \Delta H_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{initial compounds}}$$

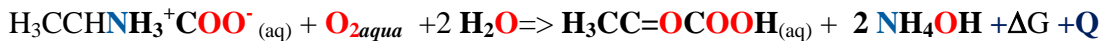
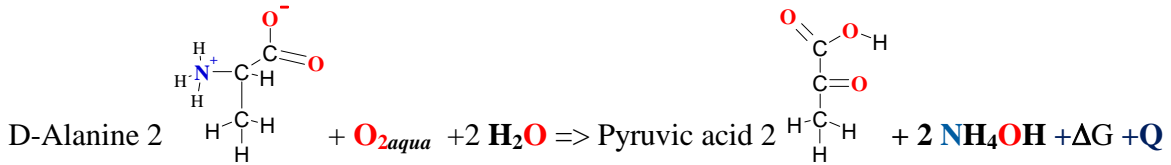
CRC

$$2. \Delta S_{\text{reaction}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$1. \Delta H_r = 2\Delta H^\circ_{\text{H}_3\text{CC}=\text{OCOOH}} + 2\Delta H^\circ_{\text{NH}_4\text{OH}} - 2\Delta H^\circ_{\text{alanine}} - \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}} = 2 \cdot (-607,82) + 2 \cdot (-361,2) - 689,93 - (2 \cdot (-554,8) - 11,715 + 2 \cdot (-285,85)) = -2627,97 + 1693,015 = -934,955 \text{ kJ/mol exothermic} \dots \dots \dots$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = 934,955 / 298,15 = 3135,85 \dots \dots \dots \text{ J/K/mol}$$



$$2. \Delta S_r = 2\Delta S^\circ_{\text{H}_3\text{CC}=\text{OCOOH}} + 2\Delta S^\circ_{\text{NH}_4\text{OH}} - 2\Delta S^\circ_{\text{alanine}} - \Delta S^\circ_{\text{O}_2} - 2 \Delta S^\circ_{\text{H}_2\text{O}} = \dots \dots \dots \text{ J/mol/K} \dots \dots \dots$$

$$\dots \dots \dots = 2 \cdot 179,91 + 2 \cdot 165,6 - (2 \cdot (-616,47) + 110,876 + 2 \cdot 69,96) = 691,02 - 982,4 = 1673,164 \text{ J/mol/K} \dots \dots \dots$$

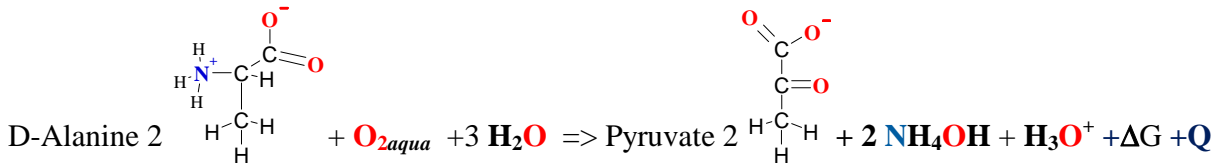
$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 1673,164 + 3135,85 = 4809,01 \dots \dots \dots \text{ J/mol/K}$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -934,955 - 298,15 \cdot 1,673164 = -1433,809 \dots \dots \dots \text{ kJ/mol exoergic} \dots \dots \dots$$

$$T \cdot \Delta S_{\text{total}} = 4809,01 \text{ J/K/mol} \cdot 298,15 \text{ K} = 1433,81 \dots \dots \dots \text{ kJ/mol} \dots \dots \dots$$

$$\text{bound } T\Delta S_{\text{total}} \leftarrow \text{dispersed energy } \Delta G_{\text{reversereaction}} \text{ Q} = 935 \text{ kJ/mol spontaneous } \Delta G_{\text{reaction}} = -1433 \text{ kJ/mol} \dots$$

Physiologic conditions pH=7,36 T=310,15 K (25° C)



$$1. \Delta H_r = 2\Delta H^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta H^\circ_{\text{NH}_4\text{OH}} + \Delta H^\circ_{\text{H}_3\text{O}^+} - 2\Delta H^\circ_{\text{alanine}} - \Delta H^\circ_{\text{O}_2} - 3 \Delta H^\circ_{\text{H}_2\text{O}} = -926,675 \dots \dots \dots \text{ kJ/mol}$$

$$\dots \dots \dots = 2 \cdot (-603,7) + 2 \cdot (-361,2) - 689,93 - 285,81 - (2 \cdot (-554,8) - 11,715 + 3 \cdot (-285,85)) \dots \dots \dots$$

$$\dots \dots \dots = -2905,54 - 1978,865 = -926,675 \text{ kJ/mol exothermic} \dots \dots \dots \text{ kJ/mol}$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = 926,675 / 310,15 = 2987,828 \dots \dots \dots \text{ J/K/mol} \dots \dots \dots$$

$$2. \Delta S_r = 2\Delta S^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + 2\Delta S^\circ_{\text{NH}_4\text{OH}} + \Delta S^\circ_{\text{H}_3\text{O}^+} - 2\Delta S^\circ_{\text{alanine}} - \Delta S^\circ_{\text{O}_2} - 3 \Delta S^\circ_{\text{H}_2\text{O}} = 792,21 \dots \dots \dots \text{ J/mol/K} \dots \dots \dots$$

$$\dots \dots \dots = 2 \cdot (-433,54) + 2 \cdot 165,6 - 3,854 - (2 \cdot (-616,47) + 110,876 - 3 \cdot 69,96) = -539,734 + 1331,944 = 792,21 \dots \dots \dots \text{ J/mol/K}$$

$$3. \Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 792,21 + 2987,828 = 3780,04 \text{ J/mol/K} \dots \dots \dots \text{ J/mol/K}$$

$$4. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -926,675 - 310,15 \cdot 0,79221 = -1172,38 \dots \dots \dots \text{ kJ/mol exoergic} \dots \dots \dots$$

$$T \cdot \Delta S_{\text{total}} = 3780,04 \text{ J/K/mol} \cdot 310,15 \text{ K} = 1172,38 \dots \dots \dots \text{ kJ/mol} \dots \dots \dots$$

$$\text{bound } T\Delta S_{\text{total}} \leftarrow \text{dispersed energy } \Delta G_{\text{reversereaction}} \text{ Q} = 927 \text{ kJ/mol spontaneous } \Delta G_{\text{reaction}} = -1172 \dots \dots \dots \text{ kJ/mol}$$

$$pK_{\text{eq}} = -\log(K_{\text{eq}}) = -\ln(10) \cdot (-\Delta G_r / R/T) = -\ln(10) \cdot (1172,38 \cdot 1000 / (8,3144 / 310,15)) = -\ln(10) \cdot 450,95 = -6,111136 \dots \dots \dots$$

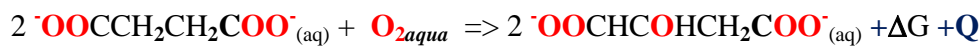
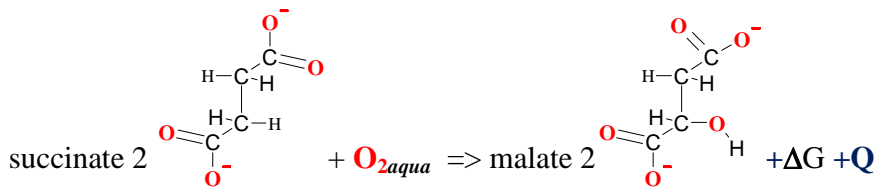
$$K_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-pK_{\text{eq}}} = 10^{6,111136} = 1,29 \cdot 10^6 \text{ temperature } 310,15 \text{ K } (37^\circ \text{ C})$$

THERMODYNAMICS Exercise XXIII succinate $\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ malate $\text{H}^+\text{OOCCH}(\text{OH})\text{CH}_2\text{COO}^-$
 Physiologic conditions pH=7,36 T=310,15 K (37° C)

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 310.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? succinate $\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ to malate $\text{H}^+\text{OOCCH}(\text{OH})\text{CH}_2\text{COO}^-$ (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds succinate + $\text{O}_{2\text{aqua}}$ => products malate ionic force I=0 .

Substance	ΔH° , kJ/mol	ΔS° , J/mol/K	ΔG_r , kJ/mol	ΔH_r , kJ/mol	ΔS_r , J/mol/K	pK
$\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ (aq)	-	-	24.02	3.36	-69.29	pK2=
$\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ (aq)	-908,7	-1,268	32.18	0.16	-107.40	pK1=
$\text{H}^+\text{OOCCH}(\text{OH})\text{CH}_2\text{COO}^-$ (aq)	-1079,8	-1,3314	30.02	0.16	-100.15	pK1=
$\text{O}_{2\text{aqua}}$	-11,715	110,876	-	-	-	-

1. $\Delta H_r = 2\Delta H^\circ_{\text{malate}} - 2\Delta H^\circ_{\text{succinate}} - \Delta H^\circ_{\text{O}_2} = \dots$ kJ/mol
 $= 2 \cdot (-1079,8) - 2 \cdot (-908,7) - (-11,715) = -2159,6 + 1817,4 + 11,715 = -330,485$ **exothermic**kJ/mol
 2. $\Delta S_{\text{dispersed}} = -\Delta H_r / T = 330,485 / 310,15 = 1065,565$ J/K/mol



2. $\Delta S_r = 2\Delta S^\circ_{\text{malate}} - 2\Delta S^\circ_{\text{succinate}} - \Delta S^\circ_{\text{O}_2} = \dots$ J/mol/K
 $= 2 \cdot (-1,3314) - 2 \cdot (-1,268) - 110,876 = -2,6628 - 108,34 = -111,0$ J/mol/K
 3. $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = 1065,565 - 111 = 954,565$ J/mol/K
 4. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -330,485 - 310,15 \cdot 0,111 = -296,06$ **exoergic** kJ/mol
 $T \cdot \Delta S_{\text{total}} = 954,565 \text{ J/K/mol} \cdot 310,15 \text{ K} = 296,06$ kJ/mol
 bound $T \Delta S_{\text{total}} \leftarrow$ dispersed energy $\Delta G_{\text{reversereaction}} Q = 330,485$ kJ/mol **spontaneous** $\Delta G_{\text{reaction}} = -296$ kJ/mol...

$\text{pK}_{\text{eq}} = -\log(K_{\text{eq}}) = -\ln(10) \cdot (-\Delta G_r / R/T) = -\ln(10) \cdot (296,06 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 79,9081 = -4,38088$

$K_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-\text{pK}_{\text{eq}}} = 10^{4,38088} = 2,4 \cdot 10^4$ temperature 310,15 K (37° C)

CRC Substance	ΔH° , kJ/mol	ΔS° , J/mol/K	ΔG_r , kJ/mol	ΔH_r , kJ/mol	ΔC_r , J/mol/K	pK	pK
$\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ (aq)	-	-	-	3.0	-121	4,207	pK1=
$\text{H}^+\text{OOCCH}_2\text{CH}_2\text{COO}^-$ (aq)	-	-	-	-0,5	-217	5,636	pK2=
$\text{H}^+\text{OOCCH}(\text{OH})\text{CH}_2\text{COO}^-$ (aq)	-	-	-	-3,6	-31	6,27	pK2=
$\text{H}^+\text{OOCCH}(\text{OH})\text{CH}_2\text{COO}^-$ (aq)	-	-	-	1,1	-21	1,92	pK1=

THERMODYNAMICS Exercise XXIV xanthine $C_5H_4N_4O_2$ ureate $C_5H_4N_4O_3^-$ (s)

Physiologic conditions pH=7,36 T=310,15 K (37° C)

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 310.15 K. Reaction is **exothermic**, **athermic**, **endothermic**?
 Xanthine $C_5H_4N_4O_2$ (s) to ureate $C_5H_4N_4O_3^-$ (s) (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Initial compounds xanthine + $O_{2,aqua} \Rightarrow$ products ureate ionic force $I=0,25$.

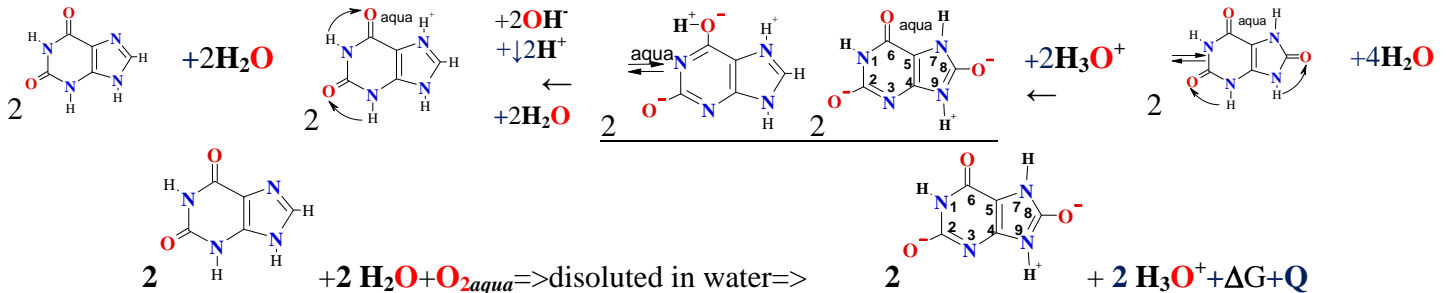
pK_a Alberty, Robert A.Q 2006.

CRC 2010 Substance	ΔH° , kJ/mol	ΔS° , J/mol/K	ΔG_r , kJ/mol	ΔH_r , kJ/mol	ΔC_r , J/mol/K	pK	pK
Uric acid $C_5H_5N_4O_3^+$ (aq)	-	-	-193,84	3,0	-121	pK2=	4,207
ureate $C_5H_4N_4O_3$ (aq)	-	-	-	-0,5	-217	pK1=	5,636
ureate $C_5H_3N_4O_3^-$ (s)	-618,80	173,20	-204,41	-	-	pK0=	11,3
xanthine $C_5H_5N_4O_2^+$ (aq)	-	-	-	1,1	-21	pK2=	1,92
xanthine $C_5H_4N_4O_2$ (s)	-379,60	161,10	-429,565	-3,6	-31	pK1=	6,27
xanthine $C_5H_3N_4O_2^-$ (aq)	-	-	-	-	-	pK0=	11,1
$O_{2,aqua}$	-11,715	110,876	16,4	-	-	-	-
H_2O (aq)	-285,85	69,96	-237,191	-	-	-	-
H_3O^+ (aq)	-285,81	-3,854	-213,275	-	-	-	-

1. $\Delta H_r = 2\Delta H^\circ_{C_5H_3N_4O_3^-} + 2\Delta H^\circ_{H_3O^+} - 2\Delta H^\circ_{H_2O} - 2\Delta H^\circ_{C_5H_4N_4O_2} - \Delta H^\circ_{O_2} = -466,605$ **exothermic**..... kJ/mol.....
 = $2 \cdot -618,80 + 2 \cdot -285,81 - (-11,715 + 2 \cdot -285,85 - 2 \cdot 379,6) = -1809,22 + 1342,615 = -466,605$ kJ/mol.....

2. $\Delta S_{dispersed} = -\Delta H_r / T = 466,605 / 310,15 = 1504,449$ J/K/mol.....

Xanthine protonation and ionisation (dissociation)



Initial compounds $2 C_5H_4N_4O_2(aqua) + 2 H_2O + O_{2,aqua} \Rightarrow 2 C_5H_3N_4O_3^-(s) + 2 H_3O^+ + \Delta G + Q$ produkti
 Xanthine_{aqua} Ureate_{aqua}

2. $\Delta S_r = 2\Delta S^\circ_{C_5H_3N_4O_3^-} + 2\Delta S^\circ_{H_3O^+} - 2\Delta S^\circ_{H_2O} - 2\Delta S^\circ_{C_5H_4N_4O_2} - \Delta S^\circ_{O_2} = \dots$ J/mol/K...
 = $2 \cdot 173,2 + 2 \cdot -3,854 - 110,876 - 2 \cdot 69,96 - 2 \cdot 161,1 = 338,692 - 572,996 = -234,304$ J/mol/K.....

3. $\Delta S_{total} = \Delta S_r + \Delta S_{dispersed} = 1504,449 - 234,304 = 1270,145$ J/mol/K.....

4. $\Delta G_r = \Delta H_r - T \cdot \Delta S_r = -466,605 - 310,15 \cdot -0,234304 = -393,936$ **exoergic**. kJ/mol.....

$T \cdot \Delta S_{total} = 1270,145 \text{ J/K/mol} \cdot 310,15 \text{ K} = 393,94$ kJ/mol.....

bound $T\Delta S_n \leftarrow$ dispersed energy $Q = 466,605 \text{ kJ/mol}$ **spontaneous** $\Delta G_{reaction} = -393,936 \text{ kJ/mol}$

$pK_{eq} = -\log(K_{eq}) = -\ln(10) \cdot (-\Delta G_r / R/T) = -\ln(10) \cdot (466,605 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 180,945 = -5,19819$

$K_{eq} = \text{EXP}(-\Delta G_r / R/T) = 10^{-pK_{eq}} = 10^{5,19819} = 1,58 \cdot 10^5$ temperature 310,15 K (37° C)

5. $\Delta G_r = 2\Delta G^\circ_{C_5H_3N_4O_3^-} + 2\Delta G^\circ_{H_3O^+} - 2\Delta G^\circ_{H_2O} - 2\Delta G^\circ_{C_5H_4N_4O_2} - \Delta G^\circ_{O_2} = -1215,38$ **exothermic**..... kJ/mol.....
 = $2 \cdot -204,41 + 2 \cdot -213,275 - (16,4 + 2 \cdot -237,191 - 2 \cdot -429,565) = -835,37 - 401,148 = -1236,52$ kJ/mol.....

1. Alberty, Robert A.Q 2006, p463, John Wiley & Sons, Biochemical Thermodynamics Applications of Mathematica

2. David R. Lide, CRC Handbook of Chemistry and Physics, 2010, ©, p.2760

