Thermodynamics1Key

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Thermodynamics

1. Consider the following reaction at equilibrium.

   $Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$ $\Delta H^0_{rxn} = -100\ kJ\ mol^{-1}$ $K_p = 600$

   a. Is heat a product or a reactant for this reaction? How do you know?

   $\Delta H < 0$, exothermic. Heat is product

   b. What will the sign of ΔG° be? ΔG° > 0   ΔG° < 0

   when K > 1, ΔG° < 0 (products favored)

   c. Under standard conditions, is this reaction spontaneous?

   Yes. ΔG° < 0

   d. What is the sign of ΔS°   ΔS° > 0   ΔS° < 0   Cannot determine

   ΔG = ΔH − TΔS   ΔG & ΔH are both (−). ΔS could be (+) or (−)

   e. For each of the following, determine if the equilibrium will shift toward products or reactants or if there will be no change.

   i. The temperature is increased in a flask that was at equilibrium. React ⇌ Prod + heat

   ↑T, shift to reactants

   ii. ZnO (s) is added to the reaction chamber. No change

   iii. Carbon monoxide is added to the chamber.

   react. CO is a product

2. For each change listed in Problem 1e, determine if:

   a. Q < K,   Q > K,   Q = K

   b. $\Delta G_{rxn} > 0$, $\Delta G_{rxn} < 0$ $\Delta G_{rxn} = 0$.

   i. Q > K, ΔG > 0

   ii. Q = K, ΔG = 0

   iii. Q > K, ΔG > 0

For problems 3-9, refer to this reaction:

$$H_2O_2(l) \rightleftharpoons H_2O(l) + O_2(g)$$

$2H_2O_2(l) \rightleftharpoons 2H_2O(l) + O_2(g)$

3. Use the table of bond enthalpies below to determine ΔH°. Is the reaction is enthalpically favorable (a favorable reaction contributes to a spontaneous reaction). Note that the reaction is not necessarily balanced.

   2 H−O−O−H ⟶ 2 H−O−H + O=O

   break
   4 × O−H 4(464)
   2 × O−O 2(142)

   make
   4 × O−H 4(−464)
   1 × O=O −502

   4(464) + 2(142) + 4(−464) + −502

   ΔH = −218 kJ/mol

4. Is the equilibrium constant is larger at 100 K or 250 K? Clearly justify your answer.

   ΔH < 0, so heat is a prod. Increasing T will shift the equilibrium to make more react. ↑T, ↓K

5. From your answer to problem 3, determine ΔH° for each of these reactions:

   a. 3 $H_2O_2(l) \rightleftharpoons$ 3 $H_2O(l)$ + 3 $O_2(g)$ 3(−218) = −654 kJ/mol

   b. $H_2O(l) + O_2(g) \rightleftharpoons H_2O_2(l)$ reversed ΔH = 218 kJ/mol

   c. $4H_2O(l) + 4O_2(g) \rightleftharpoons 4H_2O_2(l)$ rev × 4   ΔH = 4(218) = 872 kJ/mol

   Yep, I made an error here! Ignore!

6. Use the following information to calculate ΔG° for the decomposition of H_2O_2:

$H_2 (g) + O_2 (g) \rightleftharpoons H_2O_2 (l)$	ΔG° = -120.4 kJ mol^{-1}	ΔH° = -187.8 kJ mol^{-1}	S° = 109.6 J mol^{-1} K^{-1}
$H_2 (g) + ½ O_2 (g) \rightleftharpoons H_2O (l)$	ΔG° = -237.1 kJ mol^{-1}	ΔH° = -285.8 kJ mol^{-1}	S° = 70.0 J mol^{-1} K^{-1}
$H_2 (g) + ½ O_2 (g) \rightleftharpoons H_2O (g)$	ΔG° = -228.6 kJ mol^{-1}	ΔH° = -241.8 kJ mol^{-1}	S° = 188.8 J mol^{-1} K^{-1}

rev ×2

×2

$2H_2O_2 (l) \rightleftharpoons 2H_2(g) + 2O_2(g)$ ΔG° = 240.8 kJ/mol

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O (l)$ ΔG° = -474.2 kJ/mol

$2H_2O_2 (l) \rightleftharpoons 2H_2O (l) + O_2(g)$ **ΔG° = -233.4 kJ/mol**

7. The values listed in problem 6 are known as formation energies – the ΔG, ΔH, and S required to create a compound from its most stable elemental components. They are incredibly useful because they have been measured and tabulated so they are very easy to find. Consequently, you are able to calculate ΔH, ΔG, and ΔS for absolutely any reaction!

   a. The most stable form of most elements is an elemental solid; however, the common diatomic molecules are in their most stable form as diatomic molecules. Determine the most stable form of the following elements:

Carbon	sulfur	oxygen	lead	nitrogen	hydrogen	iodine
C(s)	S(s)	$O_2(g)$	Pb(s)	$N_2(g)$	$H_2(g)$	$I_2(s)$

   b. As you saw in problem 6, you can use these reactions in Hess' Law to calculate ΔG, ΔH, or ΔS for a reaction…but there is an easier way! Add up the formation energy of products. Add up to formation energy of reactants. Now products minus reactants. And done.

   Using the information in problem 6, calculate ΔG°, ΔH°, and ΔS°. Does ΔG° match what you found in problem 6?

ΔG° = 2(-237.1) - (2(-120.4)) = -233.4 kJ/mol

ΔH° = 2(-285.8) - (2(-187.8)) = -196 kJ/mol

ΔS° = [2(70) + 205.2] - (2(109.6)) = 126 J/mol·K

O_2 is included in ΔS calculation because it is NOT ∅!

8. If 50 g of H_2O_2 is allowed to decompose, determine how much heat is released. Assume 100% yield. (Hint: ΔH° has the units of kJ/mol, so use it as a conversion factor!)

$\frac{50 g H_2O_2}{} \cdot \frac{mol}{34.02 g} \cdot \frac{-196 kJ}{2 mol H_2O_2}$ = -144 kJ of heat

↳ 2 mol of H_2O_2 in balanced reaction

9. Calculate K at 25 °C.

ΔG° = -RTlnK

$-233.4 \frac{kJ}{mol} \left(\frac{10^3 J}{1 kJ}\right) = -8.314 \frac{J}{mol \cdot K} (298.15 K)$

lnK = 94.16

$K = 7.8 \times 10^{40}$

10. Consider the reaction below. For the reaction below, calculate ΔG when the indicated concentrations are mixed together at 75 °C. Report you answer in kJ mol^{-1}.

$PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$ $[Cl_2] = 0.5\ M$ $[PCl_3] = 0.1\ M$ $[PCl_5] = 0.1\ M$

K = 1.1 x 10^5 at 75°C

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

$\Delta G^\circ = -8.314\,(273.15+75) \ln 1.1\times10^5$

$\Delta G^\circ = -33{,}600\ \frac{kJ}{mol}$

$Q = \frac{[PCl_5]}{[Cl_2][PCl_3]}$

K > Q, so ΔG < 0

$\Delta G = -33600 + (8.314)(273.15+75) \ln 2$

$Q = \frac{0.1}{(0.1)(0.5)} = 2$

$\Delta G \approx -31593.7\ kJ/mol$

11. Consider the reaction in problem 10. The same reaction has a K = 1.25 x 10^2 at 175 °C.

a. Is the reaction endothermic or exothermic?

b. Calculate ΔH.

↑T = ↓K, so this means that it is exothermic

react ⇌ prod + heat

$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln \frac{1.25\times10^2}{1.1\times10^5} = \frac{\Delta H}{8.314}\left(\frac{1}{348.15} - \frac{1}{448.15}\right)$

$-6.78 = \Delta H\,(7.71\times10^{-5})$

$\Delta H = -87948\ J/mol$

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

$$\Delta G^0 = -RT\ln K$$

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

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$R = 8.314\ \frac{J}{mol\ K}$$

TABLE 14.5 Average molar bond enthalpies

Bond	Molar bond enthalpy, H_{bond}/kJ·mol^{-1}	Bond	Molar bond enthalpy, H_{bond}/kJ·mol^{-1}
O–H	464	C≡N	890
O–O	142	N–H	390
C–O	351	N–N	159
O=O	502	N=N	418
C=O	730	N≡N	945
C–C	347	F–F	155
C=C	615	Cl–Cl	243
C≡C	811	Br–Br	192
C–H	414	H–H	435
C–F	439	H–F	565
C–Cl	331	H–Cl	431
C–Br	276	H–Br	368
C–N	293	H–S	364
C=N	615		

TABLE 23.1 Standard molar entropies ($S°$), enthalpies of formation ($\Delta H_f°$), and Gibbs energies of formation ($\Delta G_f°$) of various substances at 25°C and one bar (see also Appendix D)*

Substance	$S°$/ J·K⁻¹·mol⁻¹	$\Delta H_f°$/ kJ·mol⁻¹	$\Delta G_f°$/ kJ·mol⁻¹	Substance	$S°$/ J·K⁻¹·mol⁻¹	$\Delta H_f°$/ kJ·mol⁻¹	$\Delta G_f°$/ kJ·mol⁻¹
Ag(*s*)	42.6	0	0	$H_2O_2(l)$	109.6	−187.8	−120.4
AgCl(*s*)	96.3	−127.0	−109.8	$H_2S(g)$	205.8	−20.6	−33.4
C(*s*, diamond)	2.4	1.9	2.9	N(*g*)	153.3	472.7	455.5
C(*s*, graphite)	5.7	0	0	$N_2(g)$	191.6	0	0
$CH_4(g)$	186.3	−74.6	−50.5	$NH_3(g)$	192.8	−45.9	−16.4
$C_2H_2(g)$	200.9	227.4	209.9	$N_2H_4(l)$	121.2	50.6	149.3
$C_2H_4(g)$	219.3	52.4	68.4	NO(*g*)	210.8	91.3	87.6
$C_6H_6(l)$	173.4	49.1	124.5	$NO_2(g)$	240.1	33.2	51.3
$CH_3OH(l)$	126.8	−239.2	−166.6	$N_2O(g)$	220.0	81.6	103.7
$CH_3Cl(g)$	234.6	−81.9	−58.4	$N_2O_4(g)$	304.4	11.1	99.8
$CH_3Cl(l)$	145.3	−102	−51.5	$N_2O_5(s)$	178.2	−43.1	113.9
$CH_2Cl_2(g)$	270.2	−95.4	−68.8	Na(*g*)	153.7	107.5	77.0
$CH_2Cl_2(l)$	177.8	−124.2	−70.0	Na(*s*)	51.3	0	0
$CHCl_3(g)$	295.7	−102.7	6.0	O(*g*)	161.1	249.2	231.7
$CHCl_3(l)$	201.7	−134.1	−73.7	$O_2(g)$	205.2	0	0
CO(*g*)	197.7	−110.5	−137.2	P(*s*, white)	41.1	0	0
$CO_2(g)$	213.8	−393.5	−394.4	P(*s*, red)	22.8	−17.6	−12.1
Cl(*g*)	165.2	121.3	105.3	$PCl_3(g)$	311.8	−287.0	−267.8
$Cl_2(g)$	223.1	0	0	$PCl_5(g)$	364.6	−374.9	−305.0
H(*g*)	114.7	218.0	203.3	S(*s*, rhombic)	28.5	0	0
$H_2(g)$	130.7	0	0	S(*s*, monoclinic)	32.6	0.3	0.1
$H_2O(g)$	188.8	−241.8	−228.6	$SO_2(g)$	248.2	−296.8	−300.1
$H_2O(l)$	70.0	−285.8	−237.1	$SO_3(g)$	256.8	−395.7	−371.1

*Most data from *CRC Handbook of Chemistry and Physics*, 87th Online Edition, 2006–2007.