

10. THERMODYNAMICS

These problems are intended to **supplement** the problems in the textbook, not **replace** them.

Data:

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K·mol)
$\text{Br}_2(g)$	+30.71	+3.14	+245.3
$\text{HBr}(g)$	-36.23	-53.22	+198.49
$\text{Ca}(s)$	0.0	0.0	+41.4
$\text{CaCl}_2(s)$	-795.8	-748.1	+104.6
$\text{CaO}(s)$	-635.5	-604.17	+39.75
$\text{CaSO}_4(s)$	-1434.0	-1321.8	+106.7
$\text{C}(s, \text{graphite})$	0.0	0.0	+5.69
$\text{CH}_4(g)$	-74.8	-50.8	+186.3
$\text{CH}_3\text{OH}(l)$	-238.6	-166.23	+126.8
$\text{C}_2\text{H}_2(g)$	+226.77	+209.2	+200.8
$\text{C}_6\text{H}_6(l)$	+49.0	+124.5	+172.8
$\text{CO}(g)$	-110.5	-137.2	+197.9
$\text{CO}_2(g)$	-393.5	-394.4	+213.6
$\text{Cl}_2(g)$	0.0	0.0	+222.96
$\text{HCl}(g)$	-92.30	-95.27	+186.69
$\text{F}_2(g)$	0.0	0.0	+202.7
$\text{HF}(g)$	-268.61	-270.70	+173.51
$\text{H}_2(g)$	0.0	0.0	+130.58
$\text{H}_2\text{O}(g)$	-241.82	-228.57	+188.83
$\text{H}_2\text{O}(l)$	-285.83	-237.13	+69.91

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K·mol)
$\text{Fe}(s)$	0.0	0.0	+27.15
$\text{FeCl}_2(s)$	-341.8	-302.3	+117.9
$\text{FeCl}_3(s)$	-400.0	-334	+142.3
$\text{Fe}_2\text{O}_3(s)$	-822.16	-740.98	+89.96
$\text{FeS}_2(s)$	-171.5	-160.1	+52.92
$\text{Pb}(s)$	0.0	0.0	+68.85
$\text{PbO}(s)$	-217.3	-187.9	+68.70
$\text{N}_2(g)$	0.0	0.0	+191.50
$\text{NH}_3(g)$	-46.19	-16.66	+192.5
$\text{NH}_3(aq)$	-80.29	-26.50	+111.3
$\text{NH}_4\text{Cl}(s)$	-314.4	-203.0	+94.6
$\text{NO}(g)$	+90.37	+86.71	+210.62
$\text{N}_2\text{O}(g)$	+81.6	+103.59	+220.0
$\text{O}_2(g)$	0.0	0.0	+205.0
$\text{O}_3(g)$	+142.3	+163.4	+237.6
$\text{KCl}(s)$	-435.9	-408.3	+82.7
$\text{KClO}_3(s)$	-391.2	-289.9	+143.0
$\text{SO}_2(g)$	-296.9	-300.4	+248.5
$\text{SO}_3(g)$	-395.2	-370.4	+256.2
$\text{H}_2\text{SO}_4(l)$	-814.0	-689.9	+156.1

Questions

Without using any calculations, predict whether the entropy change, ΔS , should be positive or negative for the following processes:

- $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$
- $\text{PCl}_3(g) + \text{Cl}_2(g) \rightarrow \text{PCl}_5(g)$
- $\text{SO}_2(g) + \text{CaO}(s) \rightarrow \text{CaSO}_3(s)$
- $\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq)$
- $\text{Ni}(s) + 2 \text{HCl}(aq) \rightarrow \text{H}_2(g) + \text{NiCl}_2(aq)$
- $\text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)$
- $\text{HC}_2\text{H}_3\text{O}_2(l) \rightarrow \text{HC}_2\text{H}_3\text{O}_2(s)$
- $\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s)$
- a gas is cooled from 40 °C to 25 °C at constant pressure
- a gas is compressed at a constant temperature from 4.0 L to 2.0 L

Calculate the standard entropy change, ΔS° , and the standard enthalpy change, ΔH° , for the following reactions at 25 °C:

- $\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$
- $\text{CO}(g) + 2 \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$
- $2 \text{C}_6\text{H}_6(l) + 7 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g)$

Calculate the standard free energy change, ΔG° , for the following reactions at 25 °C:

14. $2 \text{HCl}(g) + \text{CaO}(s) \rightarrow \text{CaCl}_2(s) + \text{H}_2\text{O}(g)$
15. $3 \text{CaO}(s) + 2 \text{Fe}(s) \rightarrow 2 \text{Ca}(s) + \text{Fe}_2\text{O}_3(s)$
16. $2 \text{C}_2\text{H}_2(g) + 5 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)$

Calculate the standard free energy change, ΔG° , for the following reactions at the temperature given:

17. 75.21 °C, $\text{Ca}(s) + 2 \text{H}_2\text{SO}_4(l) \rightarrow \text{CaSO}_4(s) + \text{SO}_2(g) + 2 \text{H}_2\text{O}(l)$
18. 982 K, $\text{C}_2\text{H}_2(g) + 5 \text{N}_2\text{O}(g) \rightarrow 2 \text{CO}_2(g) + \text{H}_2\text{O}(g) + 5 \text{N}_2(g)$
19. 18.4 °C, $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$

Find the temperature range over which the following reactions will be spontaneous, if all reactants and products are at standard state:

20. $\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$
21. $5 \text{SO}_3(g) + 2 \text{NH}_3(g) \rightarrow 2 \text{NO}(g) + 5 \text{SO}_2(g) + 3 \text{H}_2\text{O}(g)$
22. $\text{Ca}(s) + 2 \text{H}_2\text{SO}_4(l) \rightarrow \text{CaSO}_4(s) + \text{SO}_2(g) + 2 \text{H}_2\text{O}(l)$

Calculate the free energy change, ΔG , for the following reactions under the conditions stated:

23. $\text{H}_2(g) + \text{F}_2(g) \rightarrow 2 \text{HF}(g)$ for 47 °C, $P_{\text{H}_2} = 10.0 \text{ atm}$, $P_{\text{F}_2} = 3.0 \text{ atm}$, $P_{\text{HF}} = 0.15 \text{ atm}$
24. $2 \text{KClO}_3(s) \rightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$ for 875 °C, $P_{\text{O}_2} = 2.0 \text{ atm}$
25. $6 \text{Cl}_2(g) + 2 \text{Fe}_2\text{O}_3(s) \rightarrow 4 \text{FeCl}_3(s) + 3 \text{O}_2(g)$ for 582 K, $P_{\text{Cl}_2} = 864 \text{ torr}$, $P_{\text{O}_2} = 475 \text{ torr}$

Calculate K at 25.00 °C for the following reactions:

26. $\text{C}(s, \text{graphite}) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_4(g)$
27. $3 \text{PbO}(s) + 2 \text{NH}_3(g) \rightleftharpoons 3 \text{Pb}(s) + \text{N}_2(g) + 3 \text{H}_2\text{O}(g)$
28. $2 \text{HCl}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{HBr}(g) + \text{Cl}_2(g)$

Answers

If you cannot figure out how to get the correct answer, go to your instructor, Science Tutoring Center, etc.

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|-------------|------------------------------|--|---------------------------|
| 1. positive | 9. negative | 17. -723.9 kJ | 25. +227 kJ |
| 2. negative | 10. negative | 18. -1932 kJ | 26. 8×10^8 |
| 3. negative | 11. -0.1982 kJ/K, -92.38 kJ | 19. -92.9 kJ | 27. 4×10^{15} |
| 4. negative | 12. -0.3323 kJ/K, -128.1 kJ | 20. for $T < 466.1 \text{ K}$ (193.0 °C) | 28. 6.5×10^{-15} |
| 5. positive | 13. +0.2068 kJ/K, -3122.9 kJ | 21. for $T > 69.5 \text{ K}$ (-203.7 °C) | |
| 6. positive | 14. -182.0 kJ | 22. for all temperatures | |
| 7. negative | 15. +1071.53 kJ | 23. -560.8 kJ | |
| 8. negative | 16. -2573.1 kJ | 24. -637.1 kJ | |