

You will need to use a Table of thermodynamic values to answer some of these questions. A Table of these like that given with the exams is included at the end of this document.

1. Physical processes, including chemical reactions, tend to go towards _____ energy and _____ entropy. [spr 02, ex 2]

The answers in order are

- (a) lower, higher (b) lower, lower (c) higher, higher (d) higher, lower

2. Fill in the blanks: [fall 01, ex 2]

The Three Laws of Thermodynamics, not necessarily in order, are:

The total _____ of the universe increases for a spontaneous process.

The total _____ of the universe is constant.

The _____ of a perfectly ordered crystal at 0 K is 0.

The answers in order (top to bottom) are

- (a) energy, entropy, entropy (b) entropy, energy, entropy
(c) energy, entropy, energy (d) entropy, entropy, energy
(e) energy, energy, energy

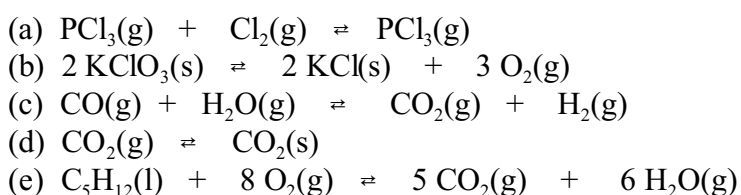
3. What factor ultimately determines whether any physical process, including a chemical reaction, is spontaneous or not? [spr 01, ex 2]

- (a) the change in entropy of the components involved in the process
(b) the change in enthalpy of the components involved in the process
(c) the change in enthalpy of the universe
(d) the change in entropy of the universe
(e) the change in entropy of the world outside the process
(ab) the change in enthalpy of the world outside the process

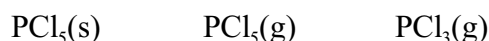
4. Which **one** of the following reactions is **most** likely to have a positive ΔS° ? [spr 02, ex 2]

- (a) $\text{Cu}^{2+}(\text{aq}) + 4 \text{Cl}^{-}(\text{aq}) \rightarrow \text{CuCl}_4^{2-}(\text{aq})$
(b) $\text{SiH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$
(c) $\text{SiF}_4(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 4 \text{HF}(\text{g})$
(d) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$
(e) $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

5. Which **one** of the following reactions is likely to have a ΔS° close to zero (in other words, neither positive nor negative)? [fall 01, ex 2]



- Place the following compounds in order of **increasing** S° : [spr 01, ex 2]



- (a) $\text{PCl}_5(\text{s}) < \text{PCl}_5(\text{g}) < \text{PCl}_3(\text{g})$ (b) $\text{PCl}_5(\text{s}) < \text{PCl}_3(\text{g}) < \text{PCl}_5(\text{g})$
 (c) $\text{PCl}_5(\text{g}) < \text{PCl}_5(\text{s}) < \text{PCl}_3(\text{g})$ (d) $\text{PCl}_5(\text{g}) < \text{PCl}_3(\text{g}) < \text{PCl}_5(\text{s})$
 (e) $\text{PCl}_3(\text{g}) < \text{PCl}_5(\text{g}) < \text{PCl}_5(\text{s})$ (ab) $\text{PCl}_3(\text{g}) < \text{PCl}_5(\text{s}) < \text{PCl}_5(\text{g})$

- Consider the following reaction for the next three questions: [spr 01, ex 2]



7. What is ΔS° for the reaction?
- (a) $-90.1 \text{ J}/(\text{mol}\cdot\text{K})$ (b) $-220.7 \text{ J}/(\text{mol}\cdot\text{K})$ (c) $301.7 \text{ J}/(\text{mol}\cdot\text{K})$
 (d) $220.7 \text{ J}/(\text{mol}\cdot\text{K})$ (e) $90.1 \text{ J}/(\text{mol}\cdot\text{K})$ (ab) $-301.7 \text{ J}/(\text{mol}\cdot\text{K})$
8. What is ΔH° for the reaction?
- (a) 285.5 kJ/mol (b) -90.7 kJ/mol (c) 90.7 kJ/mol
 (d) 311.7 kJ/mol (e) -285.6 kJ/mol (ab) -311.7 kJ/mol
9. What is ΔG° for the reaction at 25°C ?
- (a) 24.7 kJ/mol (b) 299.7 kJ/mol (c) 182.5 kJ/mol
 (d) -299.7 kJ/mol (e) -24.7 kJ/mol (ab) -182.5 kJ/mol

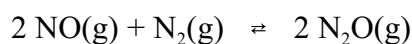
10. Using the thermodynamic information given, calculate ΔS° for the dissolution of barium nitrate in water at 25°C. (Hint: you need to first write out the reaction corresponding to barium nitrate dissolving in water. Also, read the thermodynamic information carefully – several similar species are listed – make sure you use values for the correct ones!)
[spr 02, ex 2]

(a) 88.6 J/K (b) -88.6 J/K (c) 57.8 J/K
(d) -57.8 J/K (e) 77 J/K

11. Using the thermodynamic information given, calculate K for the dissolution of barium nitrate in water at 25°C.
[spr 02, ex 2]

(a) 0.18 (b) 4.5×10^{-3} (c) 14 (d) 1.7×10^2 (e) 7.4×10^{-2}

12. What is K for the following reaction at 25°C?
[fall 01, ex 2]



(a) 3.2×10^4 (b) 0.27 (c) 7.1×10^{-9} (d) 6.8×10^{-7} (e) 1.5×10^6

13. For a certain reaction $\Delta H^\circ = 10.0 \text{ kJ}$ and $\Delta S^\circ = -20.0 \text{ J/K}$. What is K for this reaction at 25 °C?
[fall 00, ex 2]

(a) 1.8×10^7 (b) 5.2×10^{-5} (c) 9.3×10^{-4}
(d) 1.6×10^{-3} (e) 28

14. Which of the following statements is true regarding the reaction in the **previous question**?
[fall 00, ex 2]

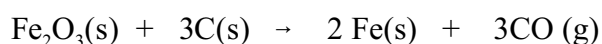
(a) At all T, K is >1.
(b) At all T, K is <1.
(c) At low T, K is >1, but at high T, K is <1.
(d) At low T, K is <1, but at high T, K is >1.
(e) Can not determine this from the information given.

15. Fill in the blanks:
[fall 00, ex 2]

If $\Delta G^\circ < 0$, then K is _____. If $\Delta G^\circ > 0$, then K is _____. If $\Delta G^\circ = 0$, then K is _____.

(a) >1, <1, =1 (b) <1, >1, =1 (c) <0, >0, =0
(d) >0, <0, =0 (e) <1, >1, =0

16. The combustion reactions of hydrocarbons are reactions where $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$. Based on this information, which one of the following statements is true regarding these reactions? [fall 01, ex 2]
- (a) At all T, K is < 1 .
 (b) At all T, K is > 1 .
 (c) At low T, K is < 1 , but at high T, K is > 1 .
 (d) At low T, K is > 1 , but at high T, K is < 1 .
 (e) Can't determine from the information given.
17. As discussed in lecture the following reaction has a very small K (10^{-58}) at room temperature. [spr 01, ex 2]

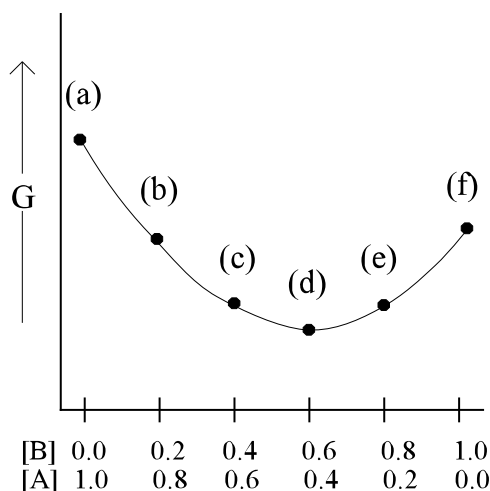


However, the reaction occurs readily at high temperature. (In fact it is the reaction used industrially to convert iron ore to iron metal and is done worldwide on the scale of $>100,000,000$ tons annually.) Based on this information, what can be said about the signs of ΔH° and ΔS° for this reaction?

- (a) $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$ (b) $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$ (c) $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$
 (d) $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ (e) $\Delta H^\circ = 0$ and $\Delta S^\circ > 0$

Consider the adjacent free energy diagram for the hypothetical reaction $A \rightleftharpoons B$ for the next three questions. Note that the x axis gives the concentrations of A and B at different points as the reaction goes from left to right (pure A to pure B). [spring 02, ex 2]

18. Which one of the following statements is **TRUE** at point b?
- (a) The reaction will spontaneously move in the direction $A \rightarrow B$.
 (b) The reaction will spontaneously move in the direction $B \rightarrow A$.
 (c) The reaction is at equilibrium.
19. What is the value of the equilibrium constant for this reaction?



- (a) 0.25 (b) 0.66 (c) 1.0 (d) 1.5 (e) 4.0

Thermodynamic Information:

Compound	ΔH°_f , kJ/mol	ΔG°_f , kJ/mol	S° , J/(mol K)
Ba(s)	0	0	62.48
Ba ²⁺ (aq)	-537.64	-560.74	9.6
Ba(NO ₂) ₂ (s)	-768.2		
Ba(NO ₃) ₂ (s)	-992.07	-796.72	213.8
CH ₃ OH(g)	-201.2	-161.9	238
CH ₃ OH(l)	-238.6	-166.2	127
CO(g)	-110.5	-137.2	197.5
CO ₂ (g)	-393.5	-394.4	213.7
H ₂ (g)	0	0	130.6
H ₂ O(l)	-285.8	-237.2	69.9
H ₂ O(g)	-241.8	-228.6	188.7
H ₂ S(g)	-20.6	-33.6	205.7
N(g)	472.7	455.6	153.2
N ₂ (g)	0	0	191.5
NO(g)	90.2	86.6	210.7
NO ₂ (g)	33.2	51.3	240.0
NO ₃ ⁻ (aq)	-207.4	-111.3	146.4
N ₂ O(g)	82.05	104.2	219.7
N ₂ O ₅ (g)	11	118	346
O ₂ (g)	0	0	205.0