ABSOLUTE ENTROPY VALUES

The standard entropy of a substance is the entropy change per mole that results from heating the substance from 0 K to the standard temperature of 298 K. Unlike enthalpy, absolute values of entropy can be measured. The standard entropy change for a reaction can then be determined by calculating the difference between the entropy of the products and the reactants.

$$\Delta S^\ominus = S^\ominus(\text{products}) - S^\ominus(\text{reactants})$$

e.g. for the formation of ammonia

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$
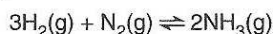
the standard entropies of hydrogen, nitrogen, and ammonia are respectively 131, 192, and 192 J K^{-1} mol^{-1}.
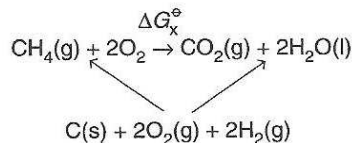
Therefore per mole of reaction

$$\Delta S^\ominus = 2 \times 192 - [(3 \times 131) + 192] = -201 \text{ J K}^{-1}\text{mol}^{-1}$$

(or per mole of ammonia $\Delta S^\ominus = \dfrac{-201}{2} = -101$ J K^{-1} mol^{-1})

DETERMINING THE VALUE OF $\Delta G^\ominus$

The precise value of $\Delta G^\ominus$ for a reaction can be determined from $\Delta G_f^\ominus$ values using an energy cycle, e.g. to find the standard free energy of combustion of methane given the standard free energies of formation of methane, carbon dioxide, water, and oxygen.

$$\begin{array}{c} \Delta G_x^\ominus \\ CH_4(g) + 2O_2 \rightarrow CO_2(g) + 2H_2O(l) \\ \searrow \qquad \swarrow \\ C(s) + 2O_2(g) + 2H_2(g) \end{array}$$

By Hess' law

$$\Delta G_x^\ominus = [\Delta G_x^\ominus(CO_2) + 2\Delta G_f^\ominus(H_2O)] - [\Delta G_f^\ominus(CH_4) + 2\Delta G_f^\ominus(O_2)]$$

Substituting the actual values

$$\Delta G_x^\ominus = [-394 + 2 \times (-237)] - [-50 + 2 \times 0] = -818 \text{ kJ mol}^{-1}$$

$\Delta G^\ominus$ values can also be calculated from using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$. For example, in Type 5 on the previous page the values for $\Delta H^\ominus$ and $\Delta S^\ominus$ for the thermal decomposition of calcium carbonate are +178 kJ mol^{-1} and +165.3 J K^{-1} mol^{-1} respectively. Note that the units of $\Delta S^\ominus$ are different to those of $\Delta H^\ominus$.

At 25 °C (298 K) the value for $\Delta G^\ominus = 178 - 298 \times \dfrac{165.3}{1000}$

$$= +129 \text{ kJ mol}^{-1}$$

which means that the reaction is not spontaneous.

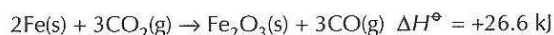The reaction will become spontaneous when $T\Delta S^\ominus > \Delta H^\ominus$.

$$T\Delta S^\ominus = \Delta H^\ominus \text{ when } T = \frac{\Delta H^\ominus}{\Delta S^\ominus} = \frac{178}{165.3/1000} = 1077 \text{ K } (804 \text{ °C})$$

Therefore above 804 °C the reaction will be spontaneous.

Note: this calculation assumes that the entropy value is independent of temperature, which is not strictly true.


IB QUESTIONS – ENERGETICS

1. Which statement about this reaction is correct?

 $$2Fe(s) + 3CO_2(g) \rightarrow Fe_2O_3(s) + 3CO(g) \quad \Delta H^\ominus = +26.6 \text{ kJ}$$

   A. 26.6 kJ of energy are released for every mole of Fe reacted

   B. 26.6 kJ of energy are absorbed for every mole of Fe reacted

   C. 53.2 kJ of energy are released for every mole of Fe reacted

   D. 13.3 kJ of energy are absorbed for every mole of Fe reacted

2. When solutions of HCl and NaOH are mixed the temperature increases. The reaction:

   $$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
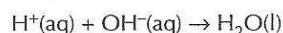
   A. is endothermic with a positive $\Delta H^\ominus$.

   B. is endothermic with a negative $\Delta H^\ominus$.

   C. is exothermic with a positive $\Delta H^\ominus$.

   D. is exothermic with a negative $\Delta H^\ominus$.
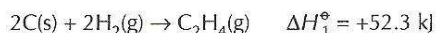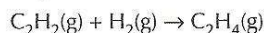
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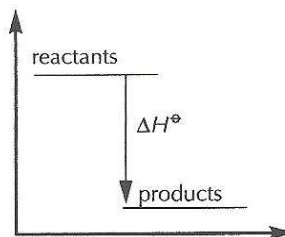
   What can be deduced about the relative stability of the reactants and products and the sign of $\Delta H^\ominus$, from the enthalpy level diagram above?

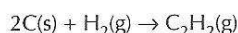 | | Relative stability | Sign of $\Delta H^\ominus$ |
   |---|---|---|
   | **A.** | Products more stable | – |
   | B. | Products more stable | + |
   | C. | Reactants more stable | – |
   | D. | Reactants more stable | + |

4. For the reaction:

$$2C(s) + 2H_2(g) \rightarrow C_2H_4(g) \qquad \Delta H_1^\ominus = +52.3 \text{ kJ}$$

If $\Delta H_2^\ominus = -174.4$ kJ for the reaction:

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

what can be said about the value of $\Delta H_3^\ominus$ for the reaction below?

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

A. $\Delta H_3^\ominus$ must be negative.

B. $\Delta H_3^\ominus$ must be a positive number smaller than 52.3 kJ.

C. $\Delta H_3^\ominus$ must be a positive number larger than 52.3 kJ.

D. No conclusion can be made about $\Delta H_3^\ominus$ without the value of H for $H_2(g)$.

5. The enthalpy changes for two different hydrogenation reactions of C_2H_2 are:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad \Delta H_1^\ominus$$
$$C_2H_2 + 2H_2 \rightarrow C_2H_6 \quad \Delta H_2^\ominus$$
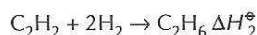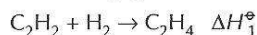
Which expression represents the enthalpy change for the reaction below?

$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad \Delta H^\ominus = \text{?}$$
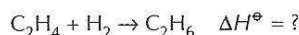
A. $\Delta H_1^\ominus + \Delta H_2^\ominus$

B. $\Delta H_1^\ominus - \Delta H_2^\ominus$

C. $\Delta H_2^\ominus - \Delta H_1^\ominus$

D. $-\Delta H_1^\ominus - \Delta H_2^\ominus$

6.
$$2KHCO_3(s) \xrightarrow{\Delta H^\ominus} K_2CO_3(s) + CO_2(g) + H_2O(l)$$

$+2HCl(aq) \qquad \Delta H_2^\ominus \quad +2HCl(aq)$

$\Delta H_1^\ominus$

$$2KCl(aq) + 2CO_2(g) + 2H_2O(l)$$

This cycle may be used to determine $\Delta H^\ominus$ for the decomposition of potassium hydrogencarbonate. Which expression can be used to calculate $\Delta H^\ominus$?

A. $\Delta H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus$ C. $\Delta H^\ominus = \frac{1}{2}\Delta H_1^\ominus - \Delta H_2^\ominus$

B. $\Delta H^\ominus = \Delta H_1^\ominus - \Delta H_2^\ominus$ D. $\Delta H^\ominus = \Delta H_2^\ominus - \Delta H_1^\ominus$

7. Use the bond energies for H–H (436 kJ mol^{-1}), Br–Br (193 kJ mol^{-1}) and H–Br (366 kJ mol^{-1}) to calculate $\Delta H^\ominus$ (in kJ mol^{-1}) for the reaction:

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$
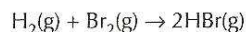
A. 263   C. –103

B. 103   D. –263

8. Which of the changes below occurs with the greatest increase in entropy?

A. $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

B. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

C. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

D. $C(s) + CO_2(g) \rightarrow 2CO(g)$

9. How would this reaction at 298 K be described in thermodynamic terms?

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

A. Endothermic with a significant increase in entropy

B. Endothermic with a significant decrease in entropy

C. Exothermic with a significant increase in entropy

D. Exothermic with a significant decrease in entropy

10. At 0 °C, the mixture formed when the following reaction reaches equilibrium consists mostly of $N_2O_4(g)$.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

What are the signs of ΔG, ΔH, ΔS at this temperature?

	ΔG	ΔH	ΔS
A.	+	+	+
B.	–	–	–
C.	–	+	+
D.	+	+	–

(HL)

11. Nitroglycerine decomposes violently when it is detonated according to the equation:

$$2C_3H_5(NO_3)_3(l) \rightarrow 3N_2(g) + \frac{1}{2}O_2(g) + 6CO_2(g) + 5H_2O(g)$$

$$\Delta H_f^\ominus \text{ (kJ mol}^{-1})$$

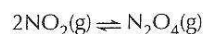|	
$C_3H_5(NO_3)_3(l)$	–364
$CO_2(g)$	–394
$H_2O(g)$	–242

What is the enthalpy change for the decomposition of 2 moles of nitroglycerine in terms of the $\Delta H_f^\ominus$ values above?

A. $5(242) + 6(394) - 2(364)$ kJ

B. $5(-242) - 6(-394) - 2(-364)$ kJ

C. $5(-242) + 6(-394) + 2(364)$ kJ

D. It cannot be determined because $\Delta H_f^\ominus$ of oxygen and nitrogen are not given.

12. Which substance has the largest lattice energy?

A. NaF   C. MgO

B. KCl   D. CaS

13. Which factor(s) will cause the lattice enthalpy of ionic compounds to increase in magnitude?

I. an increase in the charge on the ions

II. an increase in the size of ions

A. I only   C. Both I and II

B. II only   D. Neither I nor II

14. The Born–Haber cycle for the formation of potassium chloride includes the steps below:

I. $K(g) \rightarrow K^+(g) + e$ III. $Cl(g) + e \rightarrow Cl^-(g)$

II. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ IV. $K^+(g) + Cl^-(g) \rightarrow KCl(s)$

Which of these steps are exothermic?

A. I and II only   C. I, II and II only

B. III and IV only   D. I, III and IV only