Spontaneity of a reaction

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 $\Delta S^{\ominus} = \frac{-201}{2} = -101$ 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 $\Delta G^{\ominus}_f$ 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.

$$CH_4(g) + 2O_2 \xrightarrow{\Delta G^{\ominus}_x} CO_2(g) + 2H_2O(l)$$

$$C(s) + 2O_2(g) + 2H_2(g)$$

By Hess' law

$$\Delta G^{\ominus}_x = [\Delta G^{\ominus}_x(CO_2) + 2\Delta G^{\ominus}_f(H_2O)] - [\Delta G^{\ominus}_f(CH_4) + 2\Delta G^{\ominus}_f(O_2)]$$

Substituting the actual values

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

$\Delta G^{\ominus}$ 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 $\Delta G^{\ominus} = 178 - 298 \times \frac{165.3}{1000}$

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

which means that the reaction is not spontaneous.

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

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

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

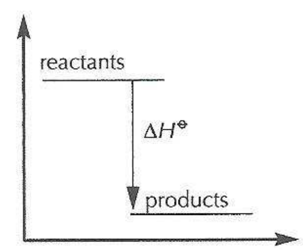
A. is endothermic with a positive $\Delta H^{\ominus}$.

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

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

D. is exothermic with a negative $\Delta H^{\ominus}$.

3.



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	+