

## THERMODYNAMICS

### 1. Definitions

*system*: part of the universe under study.

*universe*: part of the universe outside of the system.

*heat* ( $q$ ): when given off is negative (**exothermic**) and when absorbed is positive (**endothermic**).

*work* ( $w$ ): work done by the system is negative and work done on the system is positive. PV work can be calculated using the formula:

$$w = -P_{\text{ex}}(\Delta V) = -P_{\text{ex}}(V_f - V_i)$$

### 2. Calorimetry: $q(\text{system}) = -q(\text{calorimeter})$

### 3. First Law of Thermodynamics

$$\Delta E = q + w \text{ and is independent of path}$$

or

The internal energy ( $E$ ) is a state function

or

$$\Delta E = 0 \text{ for a cyclic path}$$

or

It is impossible to create a machine which, operating cyclically, will yield net work without absorption of heat.

4. For a constant volume process,  $\Delta E = q_v$

5. Definition of enthalpy ( $H$ ):  $H = E + PV$  ( $H$  is a *state* function)

6. For a constant pressure process,  $\Delta H = q_p$

7. For a chemical reaction:  $\Delta H = \Delta E + \Delta n_{\text{gas}}RT$

8. Hess' Law:  $\Delta H$  for a change of state, for example a chemical reaction, is independent of the path. If the path consists of several steps, the value of  $\Delta H$  for the total process is equal to the sum of the values of  $\Delta H$  for the individual steps.

9.  $\Delta H^\circ = \Delta H$  for a chemical reaction when all reactants and products are in their standard states.

Standard state - normal state of substance at the temperature in question and a pressure of one atmosphere for gases.

10. For any reaction:  $\Delta H^\circ = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$

11. For any reaction when all species are in their gaseous forms:

$$\Delta H = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds formed})$$

12. Second Law of Thermodynamics

Entropy ( $S$ ) is a state function

or

For every spontaneous process occurring in an isolated system there is always an increase, or at best, no change, in the entropy.

or

$$\Delta S_{\text{isolated system}} \geq 0$$

or

$$\Delta S_{\text{universe}} > 0, \text{ for a spontaneous process}$$

13. Third Law of Thermodynamics

The entropy of a perfectly ordered pure crystalline substance at the absolute zero of temperature is equal to zero.

14. For any reaction:  $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$

15. Definition of Gibbs Free Energy ( $G$ ):  $G = H - TS$

16. For any reaction:  $\Delta G^\circ = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})$

17. For gases,  $\Delta G = \Delta G^\circ + RT \ln Q_p$  (at non-standard conditions)

At equilibrium  $\Delta G = 0$  and therefore  $Q_p = K_p$

hence at equilibrium  $\Delta G^\circ = -RT \ln K_p$

18. For solutions,  $\Delta G = \Delta G^\circ + RT \ln Q_c$  (at non-standard conditions)

At equilibrium  $\Delta G = 0$  and therefore  $Q_c = K_c$

hence at equilibrium  $\Delta G^\circ = -RT \ln K_c$

19.  $\ln K = (-\Delta H^\circ/RT) + (\Delta S^\circ/R)$  and therefore  $\ln(K_2/K_1) = (\Delta H^\circ/R)(T_2 - T_1/T_2T_1)$

20. For oxidation-reduction reactions,

$$\begin{aligned}\Delta G^\circ &= -n\mathcal{F}\mathcal{E}^\circ \text{ (at standard conditions)} \\ \Delta G &= -n\mathcal{F}\mathcal{E} \text{ (at non-standard conditions)}\end{aligned}$$