

Spontaneity

A process which has an urge or a natural tendency to occur under a given set of conditions is known as a spontaneous process.

Some of the spontaneous processes need no initiation, i.e., they take place by themselves.

Dissolution of common salt in water, evaporation of water in an open vessel, combination of NO and oxygen to form NO_2 , neutralisation reaction between NaOH and HCl, etc. are examples of such processes. But some other spontaneous processes need initiation. For example, hydrogen reacts with oxygen to form water only when initiated by passing an electric spark. Once initiated, it occurs by itself.

1. Is decrease in enthalpy a criterion for spontaneity?

By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. It becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

2. Entropy and spontaneity

Entropy (S) is the measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. The crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy. ΔS is independent of path.

ΔS is related with q and T for a reversible reaction as: $\Delta S = \frac{q_{\text{rev}}}{T}$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

3. Gibbs energy and spontaneity

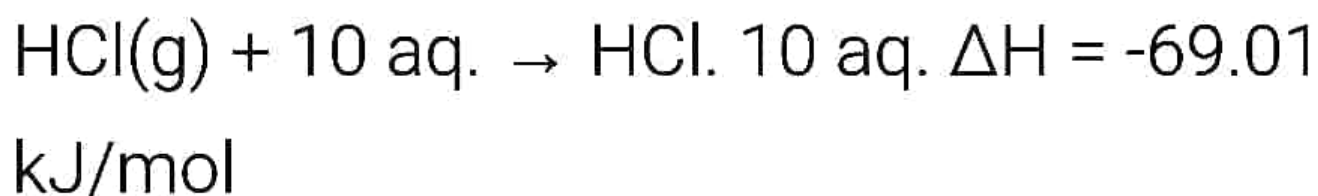
we define a new thermodynamic function the Gibbs energy or Gibbs function, G , as $G = H - TS$

Gibbs energy change is a better parameter to determine the spontaneity or feasibility of a process. It can be summarised as follows.

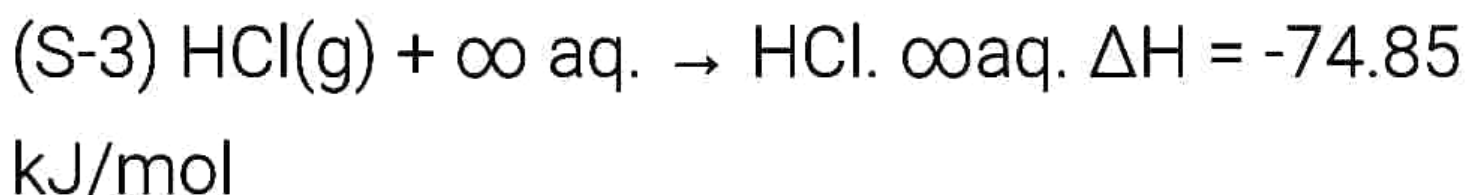
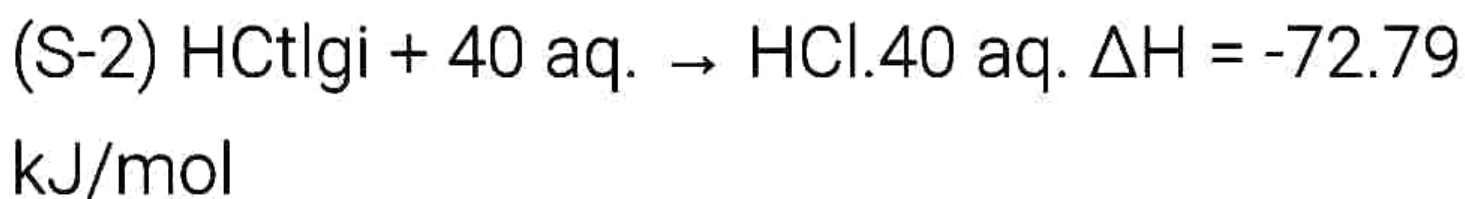
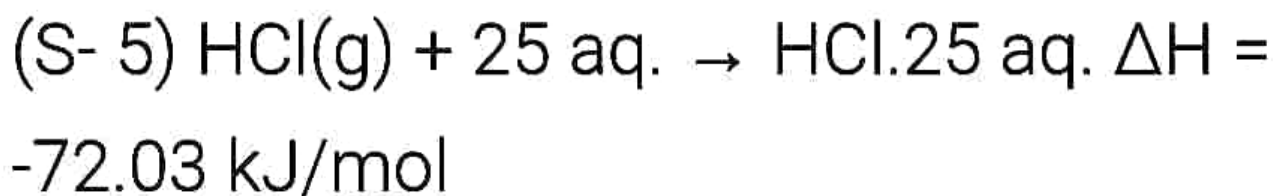
i) If ΔG is negative (i.e., <0) the process will be spontaneous. ii) If ΔG is zero, the process is in equilibrium state. iii) If ΔG is positive (i.e., >0), the process is non-spontaneous in the forward direction. The reverse process may be spontaneous.

Enthalpy of Dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation.



Let us consider the following set of enthalpy changes:



The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain

This value (-0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the
 $\text{HCl.25 aq.} + 15 \text{ aq.} \rightarrow \text{HCl.40 aq.}$

$$\Delta H = [-72.79 - (-72.03)] \text{ kJ/mol}$$
$$= -0.76 \text{ kJ/mol}$$

This value (-0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

Entropy and Second Law of Thermodynamics

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change.

This, in fact, is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Absolute Entropy and Third Law of Thermodynamics

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand, when temperature is lowered, the entropy decreases. The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero.

The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing $\frac{q_{\text{rev}}}{T}$ increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.