Entropy changes for some simple processes

Phase changes at constant T and P

$$\Delta S_{trans} = \Delta H_{trans}/T_{trans}$$

Solid → Liquid, Solid → Vapour, Liquid → Vapour and Solid I → Solid II.

Reversible Isothermal volume change

Isothermal (i.e. T constant) $\Delta u = 0$, from first law $q = W = \int P_{ext}\, dV = \int PdV = \int (nRT/V)dV = nRT\ln(V_2/V_1) = q_{rev}$.

But $\Delta S = q_{rev}/T = (nRT/T)\ln(V_2/V_1) = nR\ln(V_2/V_1)$.

Note that for expansion $V_2 > V_1$ and ΔS is positive. Thus the expansion of a gas to fill all available space is spontaneous.

Irreversible Isothermal volume change

ΔS is a state function independent of path, hence ΔS is the same as for reversible path between the two states, $\Delta S = nR\ln(V_2/V_1)$.

Mixing of two gaseous samples (even if both are at constant T & P).

$$\Delta S = n_1R\ln[(V_1 + V_2)/V_1] + n_2R\ln[(V_1 + V_2)/V_2]$$

Therefore, even if $V_1 = V_2$, ΔS must increase i.e. mixing is a spontaneous process.

Reversible Adiabatic & Irreversible Adiabatic change $dq_{rev} = 0$, therefore $\Delta S = 0$.

Entropy change on heating or cooling a substance at constant volume process

$\Delta S = \int_{(T_1 < x < T_2)} C_v dT/T$. Also at constant pressure $\Delta S = \int_{(T_1 < x < T_2)} C_p dT/T$. The investigation of this expression depends on whether C_v & C_p are temperature dependent or are completely constant and independent of temperature in the range considered.

Entropy change for an Ideal gas

Simultaneous heating and expansion of a gas initial T_1V_1 and final T_2V_2, this can be seen as 2 reversible steps, $q_{rev} = \Delta u + W$ and $q_{rev} = C_v dT + PdV$.

Step 1: Heat at constant volume V_1 from T_1 to T_2, $\Delta S_1 = \int_{(T_1 < x < T_2)} C_v dT/T$.

Step 2: Expand gas Isothermally at T_2 from V_1 to V_2,

$\Delta S_2 = \int_{(V_1 < x < V_2)} RdV/V = \int_{(V_1 < x < V_2)} (1/T)\, (RT/V)dV$
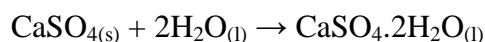
Therefore, $\Delta S_{total} = \Delta S_1 + \Delta S_2 = (T_1 < x < T_2)\square\ (C_v/T)\ dT + (V_1 < x < V_2)\square\ (R/V)\ dV$

$$= (T_1 < x < T_2)\square\ (C_v/T)\ dT + Rln(V_2/V_1).$$

Similarly, $\Delta S_{total} = (T_1 < x < T_2)\square\ (C_v/T)\ dT - Rln(P_2/P_1)$

For a process occurring at constant volume $\Delta S = C_v ln(T_2/T_1)$

Application of 2_{nd} law to some simple types of chemical reaction

$A \rightarrow B$, Ice $\rightarrow$ Liquid water

$CaSO_{4(s)} + 2H_2O_{(l)} \rightarrow CaSO_4.2H_2O_{(l)}$

In this way we deliberately avoid complications due to gaseous expansion. If we assume reactions occur in calorimeter at pressure P immersed in a heavily lagged thermo flask maintained at temperature T. Then let the entropy change accompanying 1 mole of $A \rightarrow 1$ mole of B be ΔS. If x mole of A has reacted, then entropy change of reaction is $x\Delta S$. Entropy change of both is $-x\Delta H/T$, where ΔH is the enthalpy change accompanying the transformation of 1 mole of $A \rightarrow 1$ mole of B. Therefore, $\Delta S_{(total\ for\ isolated\ system\ or\ universe)} = x\Delta S - x\Delta H/T = x(\Delta S - \Delta H/T) = -x/T(\Delta H - T\Delta S)$.

$\Delta S_{total} = -x/T[(H_2 - H_1) - T(S_2 - S_1)] = -x/T[(H_2 - TS_2) - (H_1 - TS_1)]$

Since H, S and T are properties of the state of system, the quantity $H - T\Delta S$ is also a state property which is denoted by ΔG that is the Gibbs free energy.

Therefore, $\Delta S_{total} = -x/T(\Delta H - T\Delta S) = -x/T(G_2 - G_1) = -x/T(\Delta G)$. For the process to be spontaneous in this isolated the system $\Delta S > 0$ i.e. +ve since x is the number, than ΔG must be negative.

Thus for spontaneous process $\Delta G = \Delta H - T\Delta S$ must be –ve. If ΔG is zero, $\Delta S_{total} = 0$ then the system must be in thermodynamic equilibrium. If ΔG is +ve, then ΔS_{total} is –ve, then the change under consideration cannot be spontaneous i.e. it will not occur naturally.

Molecular Interpretation of Entropy

Entropy is a measure of the disorder or change in a system. High orderliness means low entropy, e.g. as in crystal and solids. Whereas low orderliness indicates high entropy e.g. as in a gas. Hence entropy increases with volume increases or with temperature increases. For example melting i.e. change from solid to liquid usually involves little entropy increase, whereas evaporation i.e. change from liquid to gas involves high entropy change.

Example:- 14g of Nitrogen gas at 10^oC and a pressure of 1 atm are heated to 14^oC. Calculate the entropy change when the process takes place at constant pressure. Take the heat capacity of Nitrogen in the relevant temperature range to be given by

$C_p = 26.98 + 5.90 \times 10^{-3}T - 3.40 \times 10^{-7}T^2$ $Jmol^{-1}k^{-1}$. Answer = $5.473Jk^{-1}$.
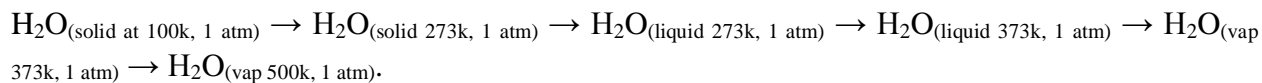
Calculate the heat of formation (ΔH) for 1 mole of ammonia gas at 120^oC. You are given that the std heat of formation for ammonia $\Delta H^o_f(NH_3) = 46.18kJmol^{-1}$.

The following data are provided for the reaction, $CO_{(s)} + 1/2O_{2(g)} \rightarrow CO_{2(g)}$. Std enthalpies of formation $CO_2 = -393.4kJmol^{-1}$, $CO = -110.5kJmol^{-1}$, $O_2 = -121.5Jmol$-$1k^{-1}$. Std entropy of formation $CO_2 = 213.6Jmol^{-1}k^{-1}$, $CO = 197.9Jmol^{-1}k^{-1}$ and $O_2 = 205.0Jmol^{-1}k^{-1}$. Calculate the free energy change for this reaction at 25^oC and 1 atm.

Calculate the change in entropy ΔS when one mole of water at 100k is heated at constant, pressure of 1 atm to 500k. You may assume the normal freezing point and boiling point of water to be 273k and 373k. Latent heat of vaporization is $40.28kJmol^{-1}$, latent heat fusion is $6.00kJmol^{-1}$, molar heat capacities in units of $Jmol^{-1}k^{-1}$

Solid, $C_p = 2.092 + 0.125T$, liquid, $C_p = 75.29$ and Vapour, $C_p = 30.315 + 9.621 \times 10^{-3}T + 1.184 \times 10^{-6}T^2$.

First identify the various steps,

$H_2O_{(solid\ at\ 100k,\ 1\ atm)} \rightarrow H_2O_{(solid\ 273k,\ 1\ atm)} \rightarrow H_2O_{(liquid\ 273k,\ 1\ atm)} \rightarrow H_2O_{(liquid\ 373k,\ 1\ atm)} \rightarrow H_2O_{(vap\ 373k,\ 1\ atm)} \rightarrow H_2O_{(vap\ 500k,\ 1\ atm)}$.

$\Delta S = (100 < x < 273)\square\ C_p\ (dT/T) = (100 < x < 273)\square\ [(2.092 + 0.125T)/T]dT = \square\ (2.092/T + 0.125)dT = 2.092\ln(273/100) + 0.125(273 - 100) = 23.726$.

$\Delta S = \Delta H_{fussion}/T_{fussion} = (6.003 \times 10^3)/273 = 21.989$.

$\Delta S = (100 < x < 273)\square\ C_p\ (dT/T) = (273 < x < 373)\square\ (75.3/T)dT = 75.3\ln(373/273) = 23.486$

$\Delta S = \Delta H_{vap}/T_{vap} = (40.282 \times 10^3)/373 = 107.99$

$\Delta S = (373 < x < 500)\square\ C_p\ (dT/T) = (373 < x < 500)\square\ [(30.315 + 9.621 \times 10^{-3}T + 1.184 \times 10^{-6}T^2)/T]dT$

$\Delta S = (373 < x < 500)\square\ [(30.35/T) + 9.621 \times 10^{-3} + 1.184 \times 10^{-6}T]dT$

$= 30.35\ln(T_2/T_1) + 9.621 \times 10^{-3}(T_2 - T_1) + (1.184 \times 10^{-6}/2)[T_2^2 - T_1^2]$

$= 8.893 + 1.222 + 0.0654 = 10.192$

$\Delta S_{total} = 23.726 + 21.989 + 23.486 + 107.995 + 10.192 = 187.388Jmol^{-1}$.

Gibbs free energy and Total Energy

$\Delta G = \Delta H - T\Delta S$

ΔH can be regarded as total energy absorbed or evolved. ΔS has to do with ordering of the system. Therefore $T\Delta S$ can be regarded as energy involved in organizing or ordering the system. The balance $\Delta H - T\Delta S$ denoted by ΔG is called the free energy which is the energy available to do work by the system. The implication of this is that the total energy of the system is partially tied down with organizing the component of the system, while the rest is energy freely available to do useful work.

Relationship between ΔG and the Equilibrium constant k.

From $H = u + PV$, $G = H - TS$, then $G = u - TS + PV$.

$dG = dH - TdS - SdT$. ($G = H - TS$), but $dH = du + PdV + VdP$ (from $H = u + PdV$)

$TdS = du + PdV$ at equilibrium, therefore $dG = du + PdV + VdP - du - PdV - SdT$

$\qquad = -SdT + VdP$

At constant temperature $dT = 0$, $(dG/dP)_T = V$ or $dG = VdP$. For 1 mole of a perfect gas,

$PV = RT$, $V = RT/P$ and $dG = (RT/P)dP$

$(G_1 < x < G_2)\square\ dG = (P_1 < x < P_2)\ RT\square\ dP/P$

$G_2 - G_1 = RT\ln(P_2/P_1)$, where $(P_2/P_1) = K$, but $(P_1/P_2) = -k$

$\Delta G = -RT\ln k$.

Relating the eqn $\Delta G = \Delta H - T\Delta S = -RT\ln k$.

$\Delta H - T\Delta S = -RT\ln k$, $k = e^{-\Delta G/RT}$

$\ln k = -\Delta H/RT + \Delta S/R$.

Therefore if one knows the value of the equilibrium constant at a number of different temperature. Then a plot of $\ln k$ vs. $1/T$ gives a straight line slope of $\Delta H/R$ from which ΔH can be found. Also it can be obtained by calculation of only 2 mole of k are known.

$\Delta H^o = (2.303RT_2T_1)/(T_2 - T_1)\log(k_1/k_2)$

$\ln(k_1/k_2) = -\Delta H/R[(T_2 - T_1)/(T_1T_2)]$

- The vapour pressure of H_2O above mixtures of $CuCl_2.H_2O$ and $CuCl_2.2H_2O$ is given in the following tables:

t°C	17.9	39.8	60.0	80.0
P atm	0.0049	0.0247	1.20	0.332

Using a graphical procedure calculate (a) the standard enthalpy ΔH^o of the reaction

Third Law of Thermodynamics

This law states that the entropy of a pure perfectly crystalline substance is zero at the absolute zero of temperature. If a crystal is imperfectly by a way of being a mixture of two or more substance, or having lattice vacancies or defects, then entropy at absolute zero will be greater than zero, although it can be small.

The third law establishes for us a reference zero of entropy. Therefore it is possible to obtained absolute values of entropy for any substance at any temperature T. The third law is of considerable importance in that it permits the calculation of absolute values of entropy of pure substances from thermal data alone. Consider a process involving the transformation of a solid from the absolute zero of temperature to some temperature T below its melting point.

$Solid_{(0ok, p)} = Solid_{(T,p)}$

The entropy change for such a process is given by $(S_o < x < S_T) \square dS = (0 < x < T) \square (C_p/T) dT$

$S_T - S_o = (0 < x < T) \square (C_p/T) dT$ where S_T is the entropy at temperature T and S_o is the entropy at 0k. Since by the third law $S_o = 0$ at $T = 0k$ one has $S_T = (0 < x < T) \square (C_p/T) dT$

$= (0 < x < T) \square (C_p d\ln T$

$\Delta S = (0 < x < T) \square (C_p \ln (T_2/T_1).$

The integral above is positive since entropy can only increase with temperature. S_T known as the absolute entropy of a substance or the third law. Third law can also be utilized to determine absolute entropies of substances that are liquid or gaseous at ordinary temperatures. This is possible because the total absolute entropy of a substance in a particular state at a given temperature is the sum of all the entropy changes the substance has to undergo in order to reach the particular state from the crystalline solid at 0k. Thus to obtain the entropy of a gas above the boiling point of the substance we have (a) the entropy change of heating the crystalline solid from $T = 0$ to $T = T_f \square C_{psolid}(dT/T)$. (b) The entropy change on fusion $\Delta H_f/T_f$. (c) the entropy change due to heating the liquid from the fusion T_f temperature to boiling temperature T_b, $\square C_{pliq}(dT/T)$ (d) the entropy change due to vaporization $\Delta H_{vap}/T_{vap}$ (e) the entropy change due to heating of the gas from T_b to the desired temperature T, $\square C_{pg}(dT/T)$. Hence,

$\Delta S_{Total} = \square Cp^s d\ln T + \Delta H_{fus}/T_{fs} + \square Cp^l d\ln T + \Delta H_{vap}/T_{vap} + \square Cp^g d\ln T)$.

The expression above is general for the evaluation of the absolute entropy for all the phases, solid, liquid, gaseous. For a solid, only the first two terms in the equation are relevant. If however, the substance is a liquid at temperature T, then use the first four terms and replace the upper limit of the fourth expression with T, When the substance is gaseouse , all terms must be used.

Debye Theory of heat capacity of crystals (or Debye third power law for heat capacities of solids at low temperatures)

This law is ;

$$C_p{}^s = a\, T^3 \qquad \text{..(1)}$$

where a is a constant The contribution to solid, s, from the curve below the   lowest experimental temperature, T' is obtained from ;

$$S(T') = (0 < x < T) \; \Box \; aT^2 dT = 1/3aT'^3 = 1/3C_p{}^s(T'). \;\text{....................(2)}$$

This means that the correction term is one-third the measured heat capacity at the lowest experimental temperature, T' provided that this temperature is within the range for which equation (1) is valid.

$$\Delta S_{Total} = \Box Cp^s dlnT + \Delta H_{fus}/T_{fs} + \Box Cp^l dlnT + \Delta H_{vap}/T_{vap} + \Box Cp^g dlnT) .$$

Calculate the entropy change in ΔS when one mole of water at 100k is heated at constant pressure of 1 atm to 500k. (Given that normal freezing point & boiling point of water to be 273k and 373k, Heat of vaporization is 40.28kJmol^{-1} latent heat of fusion 6.00kJmol^{-1}). Molar heat capacities in unit of Jmol^{-1}k^{-1}, Solid C_p = 2.092 + 0.125T, liquid C_p = 75.29, gas C_p = 30.352 + 9.621 x 10^{-3} + 1.184 x 10^{-6}T^2.

Absolute entropies may be used to calculate the entropy changes accompanying chemical reactions. The standard entropy change for a general chemical reaction is

$\Delta S^o = \sum_{ini}S^o(\text{product}) + \sum_{ini}S_i{}^o(\text{reaction})$. Where n_i is the number of moles of component i in a balanced eqn and S_i is the standard molar entropy for component i. Thus in order to determine the entropy change required for the reaction at 25°C.

$S_{(S, rhombic)} + 3/2O_{2(g)} \rightarrow SO_{3(g)}$
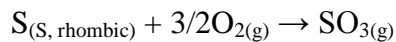
$\Delta S_{(reaction)} = S^o(SO_3) - [S^o{}_{(S, rhombic)} + 3/2S^o(O_{2(g)})]$

Since the molar entropies of SO$_{3(g)}$, S$_{(rhombic, S)}$ and O$_{2(g)}$ are 61.24, -7.62 and -49.0 respectively.

$\Delta S^o{}_{(reaction)} = -61.24 - [-7.62 + 3/2(-49.0)] = 19.9$