Entropy and Temperature

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

We can get,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_V(T)dT}{T}$$

More often than not we deal with constant pressure processes.

$$dH = d(U + PV) = dU + PdV + VdP = TdS + VdP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}\ and\ \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)dT}{T}$$

If we let $T_1 = 0$

$$S(T) = S(0\ \mathrm{K}) + \int_0^T \frac{C_P(T')dT'}{T'}$$

We can therefore calculate the entropy of a substance if we know $S(0)$ and $C_P(T)$

Third Law of Thermodynamics

A perfectly crystalline substance has zero entropy at absolute zero

$$S = k_B \ln W = -k_B \sum_j p_j \ln p_j$$

Since at 0 K there is no thermal energy, only the G.S. is occupied, i.e. $p_o = 1$ and all other states are vacant, or $p_j = 0$ when $j > 0$. $\therefore S = 0$.

In case there is degeneracy of the G.S. i.e. n available states of energy E_0 then each of them has a probability $\frac{1}{n}$ to be filled.

$$S(0\,K) = -k_B \sum_{j=1}^{n} \frac{1}{n} \ln \frac{1}{n} = k_B \ln n \quad \text{... a very small number even for large value of } n$$

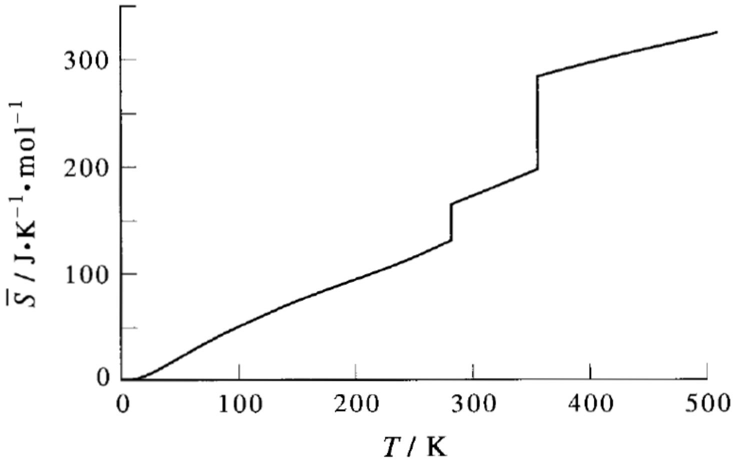
Now we can write,

$$S(T) = \int_0^T \frac{C_P(T')dT'}{T'}$$

For calculating we need to take care of phase transitions

$$\Delta_{trs}S = \frac{q_{rev}}{T} = \frac{\Delta_{trs}H}{T_{trs}}$$

$$S(T) = \int_0^{T_{fus}} \frac{C_P^s(T')dT'}{T'} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T')dT'}{T'} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_P^g(T')dT'}{T'}$$



molar entropy of benzene

Contributions to the Absolute Entropy

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = k_B \ln \frac{q^N}{N!} + k_B T \left(\frac{\partial \ln(q^N/N!)}{\partial T}\right)_V$$

$$= Nk_B \ln q - k_B \ln N! + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$

$$\text{Using Stirling}'\text{sApproximation } (\ln N! = N \ln N - N)\text{:} \quad S = Nk_B + Nk_B \ln \frac{q}{N} + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$

As an example, take the diatomic ideal gas. $\mathrm{N_2}(g)$ at 298.15 K

$$\frac{\bar{S}}{R} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\bar{V} e^{5/2}}{N_A}\right] + \ln \frac{T}{2\Theta_{rot}} - \ln\left(1 - e^{-\Theta_{\mathrm{vib}}/T}\right) + \frac{\Theta_{vib}/T}{e^{-\Theta_{\mathrm{vib}}/T} - 1} + \ln g_{e1}$$

$$\text{Using,} \qquad \Theta_{rot} = 2.88\ K, \Theta_{vib} = 3374\ K, g_{e1} = 1$$

$$\text{Standard entropy,} \qquad S^0(298.15\ K) = S^0_{trans} + S^0_{rot} + S^0_{vib} + S^0_{elec}$$

$$= 150.4 + 41.13 + 1.15 \times 10^{-3} + 0 = 191.5\ \mathrm{JK^{-1}mol^{-1}}$$

$$\textit{From heat capacity}\text{: } 191.6\ \mathrm{JK^{-1}mol^{-1}}$$

$$S(T') = \int_0^{T_{fus}} \frac{C_p^s(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_p^l(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T'} \frac{C_p^g(T)dT}{T}$$

Molecular Partition Functions

Monatomic ideal gas

$$q(V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V . g_{e1}$$

Diatomic ideal gas

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V . \frac{T}{\sigma \Theta_{rot}} . \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} . g_{e1} e^{D_e/k_B T}$$

Linear polyatomic ideal gas

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V . \frac{T}{\sigma \Theta_{rot}} . \left[\prod_{j=1}^{3n-5} \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{\mathrm{vib,j}}/T}}\right] . g_{e1} e^{D_e/k_B T}$$

Non-linear polyatomic ideal gas

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V . \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2} . \left[\prod_{j=1}^{3n-6} \frac{e^{-\Theta_{vib,j}/2T}}{1 - e^{-\Theta_{\mathrm{vib,j}}/T}}\right] . g_{e1} e^{D_e/k_B T}$$

Some useful relations

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V(T)}{T}$$

$$dH = d(U + PV) = dU + PdV + VdP = TdS + VdP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P(T)}{T}$$