Rotational partition function

(Classical and quantum)

One important property of gaseous system is the specific heat of the gas. Classically (Dulong and Petit) specific heat is independent of temperature. But experimentally at low temperatures specific heat depends upon temperature and falls to zero at zero degree Kelvin.

Translational degrees of freedom - 3

Rotational degrees of freedom - 2

- Energy for each degree of freedom is (1/2)kT from law of equipartition of energy. The translational energy is, therefore, (3/2)kT and for n molecules it will be (3/2)nkT~(3/2)RT, whereas rotational energy for n molecules will be nkT~RT.
- Single particle rotational partition function is given by $q(r) = \sum exp.(-E_r/kT)$

  where Er is the rotational energy.

- Since the diatomic molecule has two rotational degrees of freedom and conjugate momenta are p(theta) and p(phi), the rotational energy is given by

Er = [p(theta)square+p(phi)square/sin(theta)square]/2I

where I is the moment of inertia along the axis of rotation.

I = m1m2x r square/m1+m2

- The molecules of diatomic gas may be visualized as a pair of mass points connected together at a distance r apart. The system can be considered to be a rigid rotator.
- Since all the variables can be considered to vary continuously the sign of summation can be converted to that of integration.
- As a result we get

qr = 8π(square)IkT/h(square)

- This is the case when the temperature is very high. Here $\Theta r = h(\text{square})/8\pi(\text{square})Ik$ is called the rotational characteristic temperature.
- When $\Theta r >> T$ i.e. In the low temperature region $qr = \sum(2j+1)\exp.-j(j+1)\,\Theta r/T$
- $= 1 + 3\exp.-2\,\Theta r/T + 5\exp.-6\,\Theta r/T + ...$
- Now $Q = q(r).q(r).q(r)........N$ times.

$\text{Log } Q = N.\log q(r)$

$E_r = 6kN\,\Theta_r.\exp.-2\,\Theta_r/T + \ldots\ldots\ldots$

$C_v = 12kN(\Theta_r/T)\text{square}.\exp.-2\,\Theta_r/T + \ldots\ldots$

Hence the specific heat is a function of temperature .