Ideal Gases: Thermodynamics of Non-Interacting Particles

John W Daily

University of Colorado **Boulder**

Copyright © 2019 University of Colorado

Ideal Gas Law



Jacques Charles (1746-1823)

$$PV = NRT$$

Copyright © 2019 University of Colorado

Maxwell-Boltzmann Limit

$$\ln Q_{MB} = \sum_k e^{-\beta\varepsilon_k - \gamma}$$

We can factor out the gamma term:

$$\ln Q_{MB} = e^{-\gamma} \sum_k e^{-\beta\varepsilon_k}$$

The sum

$$q \equiv \sum_k e^{-\beta\varepsilon_k}$$

is called the "molecular" partition function.

Note that it is a function only of the molecular properties and temperature.

Copyright © 2019 University of Colorado

Molecular Partition Function

First, we can separate the energy:

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{\text{int}}$$

Note in general $e^{A+B} = e^{A} e^{B}$

If A and B are independent, then

$$\sum_{A,B} e^{-A} e^{-B} = \sum_{A} e^{-A} \sum_{B} e^{-B}$$

Copyright © 2019 University of Colorado

This allows us to write:

$$\ln Q_{MB} = e^{-\gamma} \sum_k e^{-\beta \varepsilon_{tr,k}} \sum_k e^{-\beta \varepsilon_{\text{int},k}}$$

So that

$$\ln Q_{MB} = e^{-\gamma} q_{tr} q_{\text{int}}$$

The same argument applies to the internal modes:

$$q_{\text{int}} = q_{rot} q_{vib} q_{elec}$$

Therefore, the problem devolves to finding the q's.

Copyright © 2019 University of Colorado