

3.6: Finding β and the Thermodynamic Functions for Distinguishable Molecules

All of a substance's thermodynamic functions can be derived from the molecular partition function. We begin with the entropy. We consider closed (constant N) systems of independent, distinguishable molecules in which only pressure–volume work is possible. In Sections 20.10 and 20.14, we find that two different approaches give the entropy of this system,

$$S = -Nk \sum_{i=1}^{\infty} P_i \ln \rho(\epsilon_i) .$$

In Sections 20.1, 20.3, and 20.4, we find that three different approaches give the Boltzmann equation,

$$P_i = g_i \rho(\epsilon_i) = z^{-1} g_i \exp(-\beta \epsilon_i) .$$

We have

$$\ln \rho(\epsilon_i) = -\ln z - \beta \epsilon_i$$

Substituting, and recognizing that the energy of the N -molecule system is $E = N \langle \epsilon \rangle$, we find that the entropy of the system is

$$S = kN \sum_{i=1}^{\infty} P_i [\ln z + \beta \epsilon_i] = kN \ln z \sum_{i=1}^{\infty} P_i + k\beta N \sum_{i=1}^{\infty} P_i \epsilon_i = kN \ln z + k\beta E$$

In Section 10.1, we find that the fundamental equation implies that

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

Since the ϵ_i are fixed when the volume and temperature of the system are fixed, $\ln z$ is constant when the volume and temperature of the system are constant. Differentiating $S = kN \ln z + k\beta E$ with respect to S at constant V , we find

$$1 = k\beta \left(\frac{\partial E}{\partial S} \right)_V = k\beta T$$

so that

$$\beta = \frac{1}{kT}$$

This is an important result: Because we have now identified all of the parameters in our microscopic model, we can write the results we have found in forms that are more useful:

1.
$$z = \underbrace{\sum_{i=1}^{\infty} g_i \exp\left(\frac{-\epsilon_i}{kT}\right)}_{\text{molecular partition function}}$$
2.
$$P_i = g_i \rho(\epsilon_i) = z^{-1} g_i \exp\left(\frac{-\epsilon_i}{kT}\right)$$

Boltzmann's equation
3.
$$S = kN \ln z + \frac{E}{T}$$

Entropy of an N -molecule system

To express the system energy in terms of the molecular partition function, we first observe that

$$E = N \langle \epsilon \rangle = N \sum_{i=1}^{\infty} P_i \epsilon_i = N z^{-1} \sum_{i=1}^{\infty} g_i \epsilon_i \exp\left(\frac{-\epsilon_i}{kT}\right)$$

Then we observe that

$$\begin{aligned}\left(\frac{\partial \ln z}{\partial T}\right)_V &= z^{-1} \sum_{i=1}^{\infty} g_i \left(\frac{\epsilon_i}{kT^2}\right) \exp\left(\frac{-\epsilon_i}{kT}\right) \\ &= \left(\frac{1}{NkT^2}\right) Nz^{-1} \sum_{i=1}^{\infty} g_i \epsilon_i \exp\left(\frac{-\epsilon_i}{kT}\right) \\ &= \frac{E}{NkT^2}\end{aligned}$$

The system energy becomes

$$\underbrace{E = NkT^2 \left(\frac{\partial \ln z}{\partial T}\right)_V}_{\text{energy of an N-molecule system}}$$

By definition, $A = E - TS$. Rearranging our entropy result, $S = kN \ln z + E/T$, we have $E - TS = -NkT \ln z$. Thus,

$$A = -NkT \ln z$$

(Helmholtz free energy of an N-molecule system)

From $dA = -SdT - PdV$, we have

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

(Here, of course, P is the pressure of the system, not a probability.) Differentiating $A = -NkT \ln z$ with respect to V at constant T , we find

$$P = NkT \left(\frac{\partial \ln z}{\partial V}\right)_T$$

(pressure of an N-molecule system)

The pressure-volume product becomes

$$PV = NkTV \left(\frac{\partial \ln z}{\partial V}\right)_T$$

Substituting into $H = E + PV$, the enthalpy becomes

$$H = NkT \left[T \left(\frac{\partial \ln z}{\partial T}\right)_V + V \left(\frac{\partial \ln z}{\partial V}\right)_T \right]$$

(enthalpy of an N-molecule system)

The Gibbs free energy is given by $G = A + PV$. Substituting, we find

$$G = -NkT \ln z + NkTV \left(\frac{\partial \ln z}{\partial V}\right)_T$$

(Gibbs free energy of an N-molecule system)

The chemical potential can be found from

$$\mu = \left(\frac{\partial A}{\partial n}\right)_{V,T}$$

At constant volume and temperature, $kT \ln z$ is constant.

Substituting $N = n\bar{N}$ into $A = -NkT \ln z$ and taking the partial derivative, we find

$$\underbrace{\mu = -\bar{N}kT \ln z = -RT \ln z}_{\text{chemical potential of distinguishable molecules}}$$

In statistical thermodynamics we frequently express the chemical potential per molecule, rather than per mole; then,

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

and

$$\mu = -kT \ln z$$

(chemical potential per molecule)

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