

## 21.6: Finding $\beta$ 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  $\epsilon_i$  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)

---

This page titled [21.6: Finding  \$\beta\$  and the Thermodynamic Functions for Distinguishable Molecules](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Paul Ellgen](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.