

E: Boltzmann's Constant

The simplest system for relating microscopic features to macroscopic observations is a dilute gas of N atoms. There are four steps:

- a. For this system, the fundamental equation for energy simplifies to

$$dE = -pdV + TdS \quad (\text{G1})$$

- b. For this system, the ideal gas law applies, such that

$$P = nRT/V \quad (\text{G2})$$

where n = the number of moles of atoms and R = the gas constant. Therefore

$$-PdV = -\left(\frac{nRT}{V}\right)dV \quad \text{and} \quad dE = -\left(\frac{nRT}{V}\right)dV + TdS \quad (\text{G3})$$

- c. In this system, the number of ways to place an atom is proportional to the available volume V and, because they don't interact, the number of ways of placing all N atoms is proportional to V^N , i.e.,

$$W = cV^N \quad (\text{G4})$$

where c is a proportionality constant. Therefore,

$$S = k \ln(cV^N) = k[\ln(c) + N \ln(V)] \quad (\text{G5})$$

and, for a volume change dV , the change in entropy is

$$dS = kN \left(\frac{1}{V}\right) dV \quad (\text{G6})$$

Substituting into Equation G3, the change in energy due to a volume change dV is

$$dE = -\left(\frac{nRT}{V}\right)dV + TkN \left(\frac{1}{V}\right)dV \quad (\text{G7})$$

- d. A monatomic gas has only kinetic energy which, according to kinetic theory, is

$$E = \left(\frac{3}{2}\right)PV = \left(\frac{3}{2}\right)nRT \quad (\text{G8})$$

independent of volume. In other words, for any volume change, dV , $dE = 0$.

Thus, from Equation G7,

$$0 = -\left(\frac{nRT}{V}\right)dV + \left(\frac{TkN}{V}\right)dV = (-nR + Nk) \left(\frac{T}{V}\right)dV \quad (\text{G9})$$

This can only hold for all possible volume changes, dV , if

$$(-nR + Nk) = 0, \quad \text{i.e.,} \quad k = \left(\frac{n}{N}\right)R = \frac{R}{N_A} \quad (\text{G10})$$

where N_A is Avogadro's constant. In other words, Boltzmann's constant k and the gas constant R are the same constant in different units (per particle in k and per mole of particles in R).

This page titled [E: Boltzmann's Constant](#) is shared under a [CC BY-NC-ND 4.0](#) license and was authored, remixed, and/or curated by [Judith Herzfeld](#).