

Appendices

- A. Review of logarithms
- B. Calculus with logarithms
- C. Summary of statistical thermodynamics
- D. Modifications due to quantum mechanics
- E. Physical constants
- F. Greek alphabet

A. Review of logarithms

Suppose that B is any positive number larger than 1. If B is raised to any power u , the result is a corresponding number x

$$x = B^u$$

where x can have any positive value (greater than 0) depending on the value of u .

Definition of logarithm. Conversely, any non-zero positive number x can be expressed in terms of some corresponding number u which is called "the logarithm of u to the base B " and denoted by $\log_B x$. The logarithm of a number x is thus defined so that

$$u = \log_B x \quad \text{if} \quad x = B^u. \quad (\text{A-1})$$

According to this definition, one can then write

$$x = B^{\log x} \quad (\text{A-2})$$

where $\log x = \log_B x$.

Correspondence between multiplication and addition. Any two numbers x and x' can be expressed in terms of their logarithms (relative to any base B) by writing

$$x = B^{\log x} \quad \text{and} \quad x' = B^{\log x'}$$

The product xx' of these numbers is then equal to

$$x x' = B^{\log x} B^{\log x'} = B^{\log x + \log x'}. \quad (\text{A-3})$$

But this product can also be expressed in terms of its logarithm, i.e., by (A-2) one can write

$$x x' = B^{\log(x x')}. \quad (\text{A-4})$$

By comparing (A-4) with (A-3), one obtains the general result that

$$\boxed{\log(x x') = \log x + \log x'} \quad (\text{A-5})$$

In other words, *the logarithm of a product of two numbers is equal to the sum of the logarithms of these numbers.*

Correspondence between exponentiation and multiplication. Suppose that the number c is used as exponent to calculate x^c . If x is expressed in terms of its logarithm (relative to any base B), one can write

$$x^c = (B^{\log x})^c = B^{(\log x) c}. \quad (\text{A-6})$$

But, x^c can also be expressed in terms of its logarithm, i.e., by (A-2) one can write

$$x^c = B^{\log x^c}. \quad (\text{A-7})$$

By comparing (A-7) with (A-6), one obtains the general result that

$$\boxed{\log x^c = c \log x}. \quad (\text{A-8})$$

In other words, *the logarithm of a number acted on by an exponent is equal to the logarithm of the number multiplied by this exponent.*

Special values of the logarithm. We know that

$$B^0 = 1 \quad \text{and} \quad B^1 = B. \quad (\text{A-9})$$

But the numbers on the right sides of these equalities can be expressed in terms of their logarithms (with respect to the base B). Hence (A-5) can also be expressed in the form

$$B^0 = B^{\log 1} \quad \text{and} \quad B^1 = B^{\log B}. \quad (\text{A-10})$$

Thus we arrive at the conclusion that

$$\log_B 1 = 0 \quad \text{and} \quad \log_B B = 1. \quad (\text{A-11})$$

Logarithms relative to the base 10. To perform calculations with numbers in our decimal system, it is often convenient to choose the base B so that $B = 10$. Indeed, it is conventional to assume that the base $B = 10$ when one writes $\log x$ without specifying the base explicitly, i.e.,

$$\log x = \log_{10} x. \quad (\text{A-12})$$

The logarithms of numbers expressed in scientific notation can then be found very simply. For example,

$$\log(5.2 \times 10^7) = \log 5.2 + \log(10^7) = \log 5.2 + 7 \log(10) = \log 5.2 + 7$$

where $\log 5.2$ is a number between 0 and 1.

Note the following corresponding values of x and its logarithm:

x	log x
1	0
10 ³	3
10 ⁶	6
10 ⁹	9

Thus it is apparent that the logarithm of a number increases much less rapidly than the number itself.

Logarithms relative to the base e. For reasons discussed in Appendix B, the analysis of many situations is greatly facilitated by using logarithms with respect to the base $B = e$ where e denotes a specially important number (whose approximate value is 2.718). Logarithms with respect to this special base are called "natural logarithm" and are conventionally denoted by \ln . Thus

The abbreviation "ln" is derived from the Latin term "logarithmus naturalis".

$$\ln x = \log_e x. \tag{A-13}$$

Relation between logarithms relative to different bases. The same number x can be expressed in terms of logarithms relative to different bases. For example, if the number is expressed relative to the base e or relative to the base 10, one can write

$$x = e^{\ln x} \text{ or } x = 10^{\log x}$$

By equating these expressions, one gets

$$e^{\ln x} = 10^{\log x}.$$

By taking the logarithm (relative to base 10) of both sides of this equation, one then gets

$$(\ln x) (\log e) = (\log x) (\log 10) = (\log x)$$

since $\log 10 = 1$. Hence

$\ln x = \frac{\log x}{\log e} \approx (2.303) \log x$
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since $\log e \approx 0.4343$.

B. Calculus with logarithms

Rates of change and the number e

Definition of derivative. Suppose that a quantity x depends on another quantity t . (For example, x might be the number of particles in a region at any particular time t .) The value x of this quantity for this value of t can then be compared with the value x' of this quantity for a slightly different value t' . The rate of change (or “derivative”) of the quantity, for this value of t , is then defined as the ratio

$$\frac{dx}{dt} = \frac{x' - x}{t' - t} \quad (\text{limiting value}). \quad (\text{B-1})$$

Here the change $dt = t' - t$ and corresponding change $dx = x' - x$ are supposed to be sufficiently small that the ratio dx/dt has reached a limiting value (unaffected if dt is made any smaller).

Equation describing a growth rate. Suppose that x denotes the number of animals in a certain region. If there are twice as many animals in the region, the number of children produced by them during some time will also be twice as large. Hence the number of offspring produced during any small time dt (and thus the increase dx in the number of animals) is proportional to the elapsed time dt and to the number x of animals present. Thus one can write

$$dx = c x dt \quad (\text{B-2})$$

or
$$\frac{dx}{dt} = c x \quad (\text{B-3})$$

where c is some constant of proportionality.

The relation (B-3), relating the rate of change of the population to the population itself, can be readily used to find the number of animals at any time. Indeed, suppose that x_0 animals are present at some initial time $t = 0$. According to (B-2), the population during a small time interval $dt = s$ increases by an amount $dx = c x_0 s$. The new population x_1 will then be

$$\text{after a time } s, \quad x_1 = x_0 + dx = x_0(1 + cs).$$

During the next small time interval s , the population increases similarly by an amount $dx = c x_1 s$. The resulting population x_2 will then be,

$$\text{after a time } 2s, \quad x_2 = x_1(1 + cs) = x_0(1 + cs)^2.$$

By repeating this argument, one can then find the population x_n after the elapse of any number n of such successive time intervals. Thus

$$\text{after a time } ns, \quad x_n = x_0(1 + cs)^n. \quad (\text{B-4})$$

By expressing this result in terms of the total elapsed time $t = ns$, one finds that the population after a time t should be

$$\text{after a time } t, \quad x = x_0(1 + cs)^{t/s}$$

By using the abbreviation $s' = cs$, this can be written in the form

$$x = x_0 (1 + s')^{ct/s'} = x_0 [(1 + s')^{1/s'}]^{ct}. \quad (\text{B-5})$$

The number e. The preceding calculation is increasingly accurate as the time interval $dt = s$ is made very small, i.e., in the limit when s' approaches zero. The quantity enclosed within the square brackets in (B-5) approaches then a definite limiting value conventionally denoted by the letter e . Thus one defines

$$e = (1 + s')^{1/s'} \quad (\text{limit as } s' \rightarrow 0). \quad (\text{B-6})$$

The approximate value of e , thus defined, is found to be

$$e \approx 2.71828. \quad (\text{B-7})$$

With this definition, the result (B-5) for the population after any time t can be simply written as

$$\boxed{x = x_0 e^{ct}}, \quad (\text{B-8})$$

i.e., the population increases exponentially with the elapsed time. (If there were no deaths, this can easily lead to overpopulation.)

Derivative of the exponential function

The quantity x in (B-8) is a solution of the equation (B-3). Hence

$$\frac{de^{ct}}{dt} = c e^{ct}. \quad (\text{B-9})$$

The derivative of the exponential function e^{ct} is thus simply a multiple of itself. In particular, if $c = 1$,

$$\boxed{\frac{de^t}{dt} = e^t} \quad (\text{B-10})$$

so that the derivative of e^t is merely the same as e^t itself.

These simple properties are widely useful in analyzing many phenomena. This is why use of the special number e simplifies many calculations and why this number serves as a specially useful base for specifying logarithms.

Derivative of the natural logarithm

The result (B-10) allows one readily to find the derivative of a natural logarithm. Indeed, suppose that

$$u = \ln t$$

so that $t = e^u$.

Equating the derivatives of both sides of this relation (and using the chain rule for the right side), one gets

$$\frac{dt}{dt} = \frac{de^u}{du} \frac{du}{dt}$$

or, using the result (B-9) on the right side,

$$1 = e^u \frac{du}{dt}.$$

Hence
$$1 = t \frac{d(\ln t)}{dt}$$

so that
$$\boxed{\frac{d(\ln t)}{dt} = \frac{1}{t}} \quad (\text{B-11})$$

Integrals

Suppose that du is an infinitesimally small change of a quantity u . Then the sum (or “integral”) of all such successive small changes, from some value u_A of the quantity to some other value u_B , is denoted by

$$\int_{u_A}^{u_B} du = u_B - u_A. \quad (\text{B-12})$$

The right side of this relation merely indicates that the sum of all these successive small changes is simply equal to the total change ($u_B - u_A$) of the quantity.

As a more complex example, consider a sum like

$$\int_{u_A}^{u_B} \frac{du}{u}. \quad (\text{B-13})$$

This is not as simple as the sum in (B-12) since it is not merely equal to the sum of successive small changes. However, the result (B-11) allows one to write

$$\frac{du}{u} = d(\ln u).$$

Hence the sum in (B-13) can again be expressed as a sum of successive small changes and thus easily calculated. Thus one finds that

$$\int_{u_A}^{u_B} \frac{du}{u} = \int_{u_A}^{u_B} d(\ln u) = \ln u_B - \ln u_A \quad (\text{B-14})$$

i.e., the sum of all the successive small changes of the logarithm is simply equal to the total change of this logarithm.

C. Summary of statistical thermodynamics

The following is a summary of the important principles and results of statistical thermodynamics (with references to the particular sections in the book where these principles or results are discussed in greater detail).

Basic hypotheses

Atomic structure of matter. Any macroscopic system consists of atomic particles described by the laws of mechanics. [Sections 1A and 8C.]

Statistical equilibrium postulate. The probabilities of finding an isolated macroscopic system in its possible basic states change with time until they reach an unchanging equilibrium situation where they are equal. [Sections 3B and 8C.]

Main definitions and principles

Thermodynamic energy law (first law of thermodynamics).

$$\Delta E = W + Q \quad (\text{C-1})$$

where ΔE = change of a systems's internal energy, W = work done on the system, Q = heat absorbed by it. [Sections 2B and 8C.]

Definition of entropy.

$$S = k \ln \Omega \quad (\text{C-2})$$

where S = entropy of a system, Ω = number of basic states available to it. [Secs. 4E and 8C.]

Probability of an equilibrium macrostate.

$$\text{For an isolated system,} \quad P \propto \Omega \propto e^{S/k} \quad (\text{C-3})$$

where S is the system's entropy in this macrostate. [Sections 4A and 8C.]

Properties of the entropy (second law of thermodynamics).

$$\text{In any small quasi-static process,} \quad dS = \frac{d'Q}{T} \quad (\text{C-4})$$

where $d'Q$ is the heat absorbed by the system in this process and T is (by definition) the system's absolute temperature.

$$\text{For any isolated system,} \quad \Delta S \geq 0. \quad (\text{C-5})$$

[Sections 4F, 8A, and 8C.]

Important results

Approach to thermal equilibrium. The absolute temperatures of the interacting systems change until they become equal. In this process, heat flows from the system at the higher absolute temperature to the system at the lower

absolute temperature (for all ordinary systems having kinetic energy). [Sections 5A and 5B.]

Mutual thermal equilibrium (zeroth law of thermodynamics). If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other.

Heat capacity and specific heat. The heat capacity C of any system is defined as

$$C_y = \left(\frac{d'Q}{dT} \right)_y \quad (\text{C-6})$$

where the quantity y (e.g., volume or pressure) is kept constant while the heat $d'Q$ is absorbed by the system.

The specific heat of a substance is the heat capacity per unit amount of the substance. (For example, if ν moles of a substance has a heat capacity C , the molar specific heat of the substance is C/ν .) [Sections 7A and 7B.]

Properties of an ideal gas.

Ideal-gas law: $pV = NkT = \nu RT$ (C-7)

where p is the pressure of the gas, V its volume, and T its absolute temperature. Here N is the number of molecules and k is Boltzmann's constant (or, equivalently, ν is the number of moles of gas and $R = N_A k$ is the gas constant). [Section 6B.]

Internal energy: E depends only on T (not on V). (C-8)

In particular, for a monatomic ideal gas, $E = \frac{3}{2} NkT$. [Section 6A.]

Adiabatic quasi-static process: $pV^\gamma = \text{constant}$ (C-9)

where $\gamma = (c + R)/c$ and c is the molar specific heat of the gas at constant volume. [Section 7E]

Probabilities of a system at constant temperature. If a system is in contact with a heat reservoir at the absolute temperature T , the probability of finding the system in any basic state r is

$$P_r \propto e^{-(E_r/kT)}. \quad (\text{C-10})$$

[Section 9C.]

D. Modifications due to quantum mechanics

For the sake of simplicity, and to avoid prerequisite knowledge of more advanced physics, this book has described atomic particles in terms of classical mechanics. The following comments indicate the modifications ensuing if they are described more correctly in terms of quantum mechanics.

Limitations of the classical description. In quantum mechanics the position and momentum of a particle cannot be simultaneously specified with unlimited precision. Instead, a particle's position coordinate x , and its corresponding momentum coordinate $p_x = mv_x$, can only be specified within uncertainties Δx and Δp_x related by the Heisenberg uncertainty principle so that

$$(\Delta x)(\Delta p_x) \geq h/2\pi. \quad (\text{D-1})$$

Here h is a fundamental constant of nature, Planck's constant, whose approximate value is 6.63×10^{-34} J s.

The classical description can be expected to become inadequate when the uncertainty Δx of a particle's position is not negligible compared to the actual separation between particles. But, according to (D-1),

$$\Delta x \geq \frac{h}{2\pi p_x} = \frac{h}{2\pi m v_x}. \quad (\text{D-2})$$

This uncertainty becomes thus increasingly large if the particle's mass is small or its velocity is small (e.g., at low temperatures where particles move with low speeds). Correspondingly, one can expect that a classical description will be nearly correct at higher temperatures, but become increasingly inaccurate below room temperature (especially when the atoms have small masses).

Basic states as quantum states. In classical mechanics, the basic states of a system are described in terms of the positions and velocities of its particles. In quantum mechanics, the basic states of a system are simply its possible *quantum states*. These states are naturally discrete and well-defined (i.e., they do not depend on any chosen precision of description, but have a precision specified by the magnitude of Planck's constant).

Unique specification of the entropy. Correspondingly, a system's entropy $S = k \ln \Omega$ has a unique value depending on the actual number Ω of available quantum states. (By contrast, in the classical description the actual value of the entropy depends on the chosen precision of description so that only entropy *differences* have a unique value.)

Validity of statistical thermodynamics. With the preceding modifications, all the discussions in this book, and all the resulting laws of thermodynamics (as summarized in Appendix C), remain equally valid. Significant differences arise only when one actually tries to infer the macroscopic properties of a system (e.g, its heat capacity) from a knowledge of its atomic constituents. For then one must treat these atomic constituents from the point of view of quantum mechanics (especially when the atoms have low masses or move with low speeds at low absolute temperatures).

E. Physical constants

The following are approximate values of some important physical constants.

Avogadro's number	$N_a = 6.022 \times 10^{23}$ particles/mole
Triple point of water	$T_t = 373.16$ K (exact by definition)
Boltzmann's constant	$k = 1.38 \times 10^{-23}$ J/K
Gas constant	$R = N_a k = 8.31$ J/(K mole)
Planck's constant	$h = 6.63 \times 10^{-34}$ J s
Mass of the electron	$m_e = 9.11 \times 10^{-31}$ kg
Mass of the proton	$m_p = 1.67 \times 10^{-27}$ kg

F. Greek alphabet

A	α	alpha	N	ν	nu
B	β	beta	Ξ	ξ	xi
Γ	γ	gamma	O	o	omicron
Δ	δ	delta	Π	π	pi
E	ϵ	epsilon	P	ρ	rho
Z	ζ	zeta	Σ	σ	sigma
H	η	eta	T	τ	tau
Θ	θ	theta	Y	υ	upsilon
I	ι	iota	Φ	ϕ	phi
K	κ	kappa	X	χ	chi
Λ	λ	lambda	Ψ	ψ	psi
M	μ	mu	Ω	ω	omega