

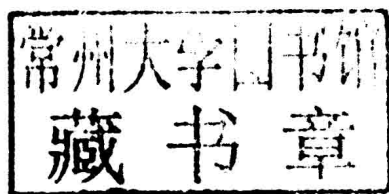
# **Thermodynamic Foundations of the Earth System**

Axel Kleidon

# THERMODYNAMIC FOUNDATIONS OF THE EARTH SYSTEM

AXEL KLEIDON

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## THERMODYNAMIC FOUNDATIONS OF THE EARTH SYSTEM

Thermodynamics sets fundamental laws for all physical processes and is central to driving and maintaining planetary dynamics. But how do Earth system processes perform work, where do they derive energy from, and what are the ultimate limits?

This accessible book describes how the laws of thermodynamics apply to Earth system processes, from solar radiation to motion, geochemical cycling and biotic activity. It presents a novel view of the thermodynamic Earth system that explains how it functions and evolves, how different forms of disequilibrium are being maintained, and how evolutionary trends can be interpreted as thermodynamic trends. It also places human activity into a new perspective in which it is treated as a thermodynamic Earth system process.

This book uses simple conceptual models and basic mathematical treatments to illustrate the application of thermodynamics to Earth system processes, making it ideal for researchers and graduate students across a range of Earth and environmental science disciplines.

AXEL KLEIDON leads a research group in Biospheric Theory and Modelling at the Max-Planck-Institute for Biogeochemistry, Jena, Germany. He uses thermodynamics to quantify natural energy conversions within the Earth system and their limits, and applies this approach to understand atmosphere-biosphere interactions, Earth system responses to global change, and the natural limits of renewable energy.



## Preface

This book is about how thermodynamics applies to the Earth system. It is less about thermodynamics itself, but rather about how it applies to Earth system processes, their interactions, and the operation of the Earth system as a whole.

The motivation for writing this book stems from my interest in gaining a better, and more profound understanding of the Earth system, of the role that life plays within the system, and of how human activity changes the Earth system at a time when humans increasingly alter the operation of the planet. One way to deal with this challenge is to build increasingly comprehensive, yet also increasingly incomprehensible models of the Earth system. The other way is to search for a fundamental missing constraint that describes in comparably simple terms how systems operate and evolve. Since my doctoral work I have increasingly concentrated on this search. I looked into optimality approaches in vegetation, the Gaia hypothesis, and worked on the proposed principle of maximum entropy production (MEP). Over the years, I had many discussions with colleagues and took part in several workshops on these topics. I am tremendously thankful for these stimulating discussions, as these ultimately helped to shape my understanding that is now described in this book.

Today I think the answer to this missing constraint lies in the second law of thermodynamics. This law formulates a fundamental direction in physics that requires entropy to increase, at the small scale of an engine as well as at the scale of the whole Universe. Yet, its application to Earth system processes is almost absent, particularly when dealing with the whole Earth system. The second law, jointly with a thermodynamic formulation of the different processes yields a foundation to Earth system science that expresses processes in the same units of energy; it allows us to describe evolutionary dynamics as a thermodynamic direction imposed by the second law, and it sets fundamental limits and constraints on the emergent dynamics and interactions within the system. These limits can be quantified and yield estimates for Earth system processes that are largely consistent with observations, but require hardly any empirical parameters, substantiating that the second law provides

missing constraints. It thus yields a grand picture of the Earth system in which its dynamics and evolution are a manifestation of the second law, a picture that is largely consistent with current descriptions yet yields a few critical insights that are not apparent from common formulations of the Earth system.

I think that these profound insights from thermodynamics should be accessible to a broad audience in the geosciences. Unfortunately, most books on non-equilibrium thermodynamics are only accessible to a highly specialized readership. Over the years I encountered several colleagues who studied thermodynamics yet still found it difficult to grasp, and this includes myself. Yet, I find this really unfortunate because thermodynamics can be fun and provides an elegant and simple way to look at the Earth system. For this view, it does not require much thermodynamic details to recognize its relevance and to use it for first-order estimates. In this book I aim to make thermodynamics accessible and thus describe only the bare essentials that are needed to formulate Earth system processes in thermodynamic terms.

To accomplish such an interdisciplinary, thermodynamic description of the whole Earth system, from radiation to human activity, poses a challenge as it requires a broad range of processes to be described. I therefore decided to focus on the mere minimum of thermodynamics and of Earth system processes to understand how thermodynamics applies to them and how these processes relate to each other. The book is thus not a comprehensive review of thermodynamics and its applications to Earth system processes. The text then includes references to related literature, and I apologize to those that I may have missed or that I may not have represented adequately. This led to a structure in which after the introduction, Chapters 2–5 provide the background in thermodynamics while the major processes of the Earth system are covered in Chapters 6–11. Chapter 12 closes with a synthesis to yield the perspective of the thermodynamic Earth system and how it can yield insights for Earth system science. Each chapter aims to be relatively self-contained and follows a similar format. It starts with a general introduction and closes by placing the material of the chapter back into the context of the Earth system and describes the linkages to the other chapters. By describing a broad range of processes across disciplines, one practical challenge was the mathematical formulation, as the letters of the alphabet are used for different variables in different disciplines. The letter *G*, for instance, is used for the gravitational constant, but also for Gibbs free energy. I tried to compromise and used mostly the convention of the different disciplines, so that some symbols refer to different aspects in different chapters. To help avoid confusion, the symbols are summarized in a table at the beginning of the book. Furthermore, a glossary includes brief explanations of the most central terms.

Even though the book was not written as a textbook, it is written at a level accessible to an audience in Earth and environmental sciences and is suitable for a course

at the graduate level. As it involves the physical formulation of the different Earth system processes, the reader does require a certain level of familiarity with basic physics. The book illustrates the basic concepts associated with thermodynamics at a qualitative level supported by illustrations, and then uses comparatively simple models to demonstrate the application of thermodynamics and to estimate limits that predict magnitudes of different Earth system processes. These simple models are certainly not meant to be complete, but rather provided as an illustration of how thermodynamics is applied and how it can be used to establish magnitudes of Earth system processes.

This book would have been impossible to write without the substantial support and many stimulating discussions on various aspects of the Earth system as well as thermodynamics with colleagues and within my research group over the years. The number of colleagues are too many to list here, but I am very thankful for the stimulating discussions we had, for the disciplinary knowledge they provided, and for answering the seemingly strange questions that I sometimes asked. From my research group, I particularly thank James Dyke, Fabian Gans, Lee Miller, Philipp Porada, Maik Renner, Stan Schymanski, Eugenio Simoncini, and Nathaniel Virgo for the many discussions we had on entropy, life, Earth, and the universe. I thank Uwe Ehret and Christian Reick for thoroughly reading through the draft of the book, providing constructive feedback, identifying unclear passages, and finding errors. I thank Cambridge University Press, particularly Susan Francis and Zoë Pruce, for their support and insistence to bringing this book to completion. Last, but not least, I thank my partner, Anke Hildebrandt, for her support at critical points and times in this and other projects. She and our kids were very patient, tolerated entropy discussions at the dinner table over the years, and accepted the time I spent in the last year to complete this book.

I hope you will find this book useful in providing a starting point to more applications of thermodynamics to Earth system science. I would be curious to hear back from the reader about any comments, suggestions, or activities to which this book may have helped to contribute.

*Axel Kleidon*



# Symbols

Overview of the most frequently used symbols in the book, which may be supplemented by additional indices. For those symbols that are used to describe more than one property, the section or chapter where the respective symbol is being used is also given. Note that some variables, such as fluxes, are also used in reference to unit area.

Symbol	Description	Units	Value	Primary use
$\alpha$	albedo	frac.	-	sec. 6.3.3
$A$	chemical affinity of a reaction	$\text{J mol}^{-1}$	-	sec. 9.2
$A$	area (typically surface area)	$\text{m}^2$	-	
$B$	geometric factor	-	-	
$c$	speed of light	$\text{m s}^{-1}$	$3 \cdot 10^8$	chap. 6
$c$	heat capacity	$\text{J K}^{-1}$	-	
$c_p$	specific heat capacity at constant pressure	$\text{J kg}^{-1} \text{K}^{-1}$	-	
$c_v$	specific heat capacity at constant volume	$\text{J kg}^{-1} \text{K}^{-1}$	-	
$C$	energy conversion rate (within Lorenz cycle)	W	-	sec. 7.3
$C$	condensation rate	$\text{kg m}^{-2} \text{s}^{-1}$	-	sec. 8.2
$C_d$	drag coefficient	-	-	sec. 7.3
$d_e$	mean distance of Earth to Sun	m	$150 \cdot 10^9$	
$D$	dissipation rate	W	-	
$e$	partial pressure of water vapor	Pa	-	
$e_{\text{sat}}$	partial pressure of water vapor at saturation	Pa	-	
$E$	evaporation rate	$\text{kg m}^{-2} \text{s}^{-1}$ or $\text{mm d}^{-1}$	-	
$\epsilon$	dilution factor	-	-	chap. 6
$\epsilon_{\text{lue}}$	light use efficiency	$\mu\text{mol CO}_2 (\mu\text{mol PAR})^{-1}$	-	sec. 10.6

Symbol	Description	Units	Value	Primary use
$\epsilon_{wue}$	water use efficiency	$\text{g CO}_2 (\text{kg H}_2\text{O})^{-1}$	-	sec. 10.6
$\eta$	efficiency (= power/flux)	frac.	-	
$f$	fraction	frac.	-	
$f$	feedback factor	-	-	chap. 5
$f$	Coriolis parameter	$\text{s}^{-1}$	-	sec. 7.6
$f_w$	water limitation factor	frac.	-	sec. 10.4
$F$	Helmholtz free energy	J	-	sec. 3.5
$F$	force	$\text{kg m s}^{-2}$	-	sec. 4.6
$\phi$	geopotential	$\text{m}^2 \text{s}^{-2}$	-	sec. 2.3.4
$\phi$	latitude	$^\circ$	-	chap. 7
$g$	gravitational acceleration	$\text{m s}^{-2}$	9.81	
$G$	gravitational constant	$\text{m}^3 \text{kg}^{-1} \text{s}^{-2}$	$6.67 \cdot 10^{-11}$	sec. 2.3.4
$G$	generation rate (power)	W	-	
$G$	Gibbs free energy	J	-	sec. 3.5, chap. 9
$\Delta G_r$	Gibbs free energy of a reaction	J	-	chap. 9
$\gamma$	psychrometric constant	$\text{Pa K}^{-1}$	$\approx 65$	
$\Gamma_d$	dry adiabatic lapse rate	$\text{K m}^{-1}$	$9.81 \cdot 10^{-3}$	
$\Gamma_{\text{dew}}$	lapse rate of the dew point	$\text{K m}^{-1}$	$1.8 \cdot 10^{-3}$	
$H$	enthalpy	J	-	sec. 3.5
$H$	sensible heat flux	$\text{W m}^{-2}$	-	chap. 10
$h$	Planck's constant	J s	$6.63 \cdot 10^{-34}$	
$I$	current	A	-	
$i$	van't Hoff factor	-	-	
$J$	heat flux	W	-	
$J_{\text{in}}$	influx of energy	W	-	
$J_{\text{out}}$	outflux of energy	W	-	
$J_s$	entropy flux	$\text{W K}^{-1}$	-	chap. 2
$J_m$	mass flux	$\text{kg s}^{-1}$	-	
$J_{\text{mom}}$	momentum flux	$\text{kg m s}^{-3}$	-	
$k$	conductivity	$\text{W K}^{-1}$	-	
$k$	friction coefficient	(depends)	-	sec. 4.6
$k_b$	Boltzmann's constant	$\text{J K}^{-1}$	$1.38 \cdot 10^{-23}$	
$k_f$	forward constant for chemical reactions	$\text{mol l}^{-1} \text{s}^{-1}$	-	sec. 9.2
$k_r$	reverse rate constant for chemical reactions	$\text{mol l}^{-1} \text{s}^{-1}$	-	sec. 9.2
$k_r$	radiative linearization constant	$\text{W m}^{-2} \text{K}^{-1}$	-	
$K_\nu$	spectral energy density	$\text{J sr}^{-1} \text{m}^{-2}$	-	sec. 6.2
$K_{\text{eq}}$	equilibrium constant	-	-	sec. 9.2
$L$	length	m	-	
$L_\nu$	spectral entropy density	$\text{J sr}^{-1} \text{m}^{-2} \text{K}^{-1}$	-	sec. 6.2
$\lambda$	wavelength	m	-	chap. 6
$\lambda$	latent heat of vaporization	$\text{J kg}^{-1}$	$2.5 \cdot 10^6$	chap. 8, chap. 10
$\lambda E$	latent heat flux	$\text{W m}^{-2}$	-	

Symbol	Description	Units	Value	Primary use
$\mu$	chemical potential	$\text{J mol}^{-1}$		
$m$	mass	kg	-	
$n$	molar mass	$\text{kg mol}^{-1}$	-	
$N$	number of particles	- or mol	-	sec. 2.4.1
$N_v$	distribution function	-	-	sec. 6.2
$N$	Nusselt number	-	-	sec. 7.7
$\nu$	frequency	$\text{s}^{-1}$	-	
$\Omega$	solid angle	sr	-	chap. 6
$\Omega_{\text{sun}}$	solid angle of the Sun in the Earth's sky	sr	$6.8 \cdot 10^{-5}$	chap. 6
$\Omega$	Earth's angular velocity	$\text{s}^{-1}$	$7.27 \cdot 10^{-5}$	sec. 7.6
$p$	pressure	Pa	-	
$p_s$	surface pressure	Pa	$1.01325 \cdot 10^5$	
$p$	radiation pressure	Pa	-	sec. 6.2
$p$	probability	-	-	sec. 3.3
$p$	precipitation	$\text{kg m}^{-2} \text{s}^{-1}$ or $\text{mm d}^{-1}$	-	chap. 8
$\pi$	osmotic pressure	Pa	-	
$q$	specific humidity	$\text{kg kg}^{-1}$	-	
$Q$	amount of heat added or removed	J	-	
$Q$	charge	C	-	sec. 4.6
$Q$	runoff	$\text{kg m}^{-2} \text{s}^{-1}$	-	sec. 10.4
$\rho$	density	$\text{kg m}^{-3}$	-	
$r_{\text{sun}}$	radius of the Sun	m	$695.8 \cdot 10^6$	
$r_e$	radius of the Earth	m	$6.372 \cdot 10^6$	
$R$	ideal gas constant	$\text{J kg}^{-1} \text{K}^{-1}$	287 (air)	
		$\text{J kg}^{-1} \text{K}^{-1}$	461 (water vapor)	
		$\text{J mol}^{-1} \text{K}^{-1}$	8.314 (general)	
$R_{\text{in}}, R_{\text{out}}$	radiative flux	$\text{W m}^{-2}$	-	
$R_l$	flux of terrestrial radiation	$\text{W m}^{-2}$	-	
$R_{l,\text{up}}$	flux of terrestrial radiation (upwards) at the surface	$\text{W m}^{-2}$	-	
$R_{l,\text{down}}$	flux of terrestrial radiation (downwards) at the surface	$\text{W m}^{-2}$	-	
$R_{l,\text{net}}$	net flux of terrestrial radiation at the surface	$\text{W m}^{-2}$	-	
$R_{\text{sun,tot}}$	solar luminosity	W	$7.6 \cdot 10^{26}$	
$R_{s,\text{in}}$	influx of solar radiation at the top of the atmosphere	$\text{W m}^{-2}$	1370	
$R_s$	flux of solar radiation	$\text{W m}^{-2}$	-	
$R_{s,a}$	absorbed solar radiation in the atmosphere	$\text{W m}^{-2}$	$\approx 75$	
$R_{s,s}$	absorbed solar radiation at the surface	$\text{W m}^{-2}$	$\approx 165$	
$R_{s,\text{toa}}$	total absorbed solar radiation	$\text{W m}^{-2}$	$\approx 240$	

Symbol	Description	Units	Value	Primary use
$R$	resistance	$\Omega$	-	sec. 4.6
$s$	slope of the saturation vapor pressure curve, $s = de_{\text{sat}}/dT$	$\text{Pa K}^{-1}$	-	
$S$	thermal entropy	$\text{J K}^{-1}$		sec. 2.3.2
$S$	radiation entropy	$\text{J K}^{-1}$	-	sec. 6.2
$\sigma$	Stefan-Boltzmann constant	$\text{W m}^{-2} \text{K}^{-4}$	$5.67 \cdot 10^{-8}$	sec. 6.2
$\sigma$	entropy production	$\text{W K}^{-1}$	-	
$t$	time	s	-	
$\Delta t$	time interval	s	-	
$T$	temperature	K	-	
$T_a$	atmospheric temperature	K	-	
$T_e$	engine temperature	K	-	
$T_r$	radiative temperature	K	$\approx 255$	
$T_s$	surface temperature	K	-	
$T_{\text{sun}}$	emission temperature of the Sun	K	5760	
$\theta$	potential temperature	K	-	
$\tau$	residence time or time scale	s	-	chap. 2, chap. 5
$\tau$	optical depth	-	-	chap. 6
$u$	energy density	$\text{J m}^{-3}$	-	chap. 6
$u$	velocity (zonal component)	$\text{m s}^{-1}$	-	chap. 7
$U$	internal energy	J	-	
$U_{\text{rad}}$	radiative energy	J	-	
$U_{\text{te}}$	thermal energy	J	-	
$U_{pV}$	uncompensated heat	J	-	
$U_{\text{pe}}$	potential energy	J	-	
$U_{\text{ke}}$	kinetic energy	J	-	
$U_{\text{be}}$	binding energy	J	-	
$U_{\text{other}}$	other, non-thermal form of energy	J	-	
$U$	voltage	V	-	sec. 4.6
$U$	heat storage	$\text{J m}^{-2}$	-	sec. 10.3
$v$	velocity (general, or meridional component)	$\text{m s}^{-1}$	-	chap. 7
$v$	reaction velocity	$\text{mol l}^{-1} \text{s}^{-1}$	-	sec. 9.2
$V$	volume	$\text{m}^3$	-	
$W$	number of possible arrangements	-	-	sec. 2.4.1
$W$	work	J	-	
$W_s$	soil water content	$\text{kg m}^{-2}$	-	sec. 10.4
$x$	horizontal dimension	m	-	
$\xi$	extent of reaction	mol	-	
$X$	dilution effect on entropy	-	-	sec. 6.3
$y$	horizontal dimension	m	-	
$\Delta z$	vertical thickness	m	-	
$z$	vertical coordinate	m	-	
$z_0$	scaling height in the barometric formula	m	$\approx 8425$	



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