

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.

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Contents

<i>Preface</i>	<i>page</i> ix
<i>List of Symbols</i>	xii
1 Thermodynamics and the Earth system	1
1.1 A thermodynamic basis for Earth system science	1
1.2 Thermodynamics in a nutshell	3
1.3 Disequilibrium, life, and Earth	6
1.4 Thermodynamic limits	8
1.5 Thermodynamics, evolutionary dynamics, and structures	11
1.6 Connecting Earth system processes	15
1.7 Structure of this book	17
2 Energy and entropy	19
2.1 The central roles of energy and entropy	19
2.2 Defining thermodynamic systems	21
2.3 Forms of energy	24
2.3.1 Radiative energy	24
2.3.2 Thermal energy	26
2.3.3 Uncompensated heat	28
2.3.4 Potential energy	30
2.3.5 Kinetic energy	32
2.3.6 Binding energy	33
2.3.7 Chemical energy	34
2.4 Forms of entropy	35
2.4.1 Entropy as probability	37
2.4.2 Illustrations of the three forms of entropy	41
2.4.3 Linkages between forms of entropy	44
2.5 Energy and entropy budgets of the Earth system	44

vi	<i>Contents</i>	
3	The first and second law of thermodynamics	46
3.1	The rules for energy conversions	46
3.2	The first law of thermodynamics	48
3.3	The second law of thermodynamics	51
3.4	Thermodynamic equilibrium and disequilibrium	56
3.5	Free energy and thermodynamic potentials	60
3.6	Dynamics as energy conversion	63
3.7	Thermodynamic laws in the Earth system	69
4	Thermodynamic limits	72
4.1	Limits to energy conversions	72
4.2	The Carnot limit	74
4.3	The Carnot cycle	77
4.4	The dissipative heat engine	84
4.5	The maximum power limit	86
4.6	Maximum power limits for non-thermal energy conversions	90
4.7	Maximum entropy production (MEP) and other thermodynamic principles	94
4.8	Thermodynamic limits in the Earth system	97
5	Dynamics, structures, and maximization	99
5.1	Energy conversions, maximization, and evolution	99
5.2	Dynamics of an evolving heat engine	102
5.3	Dynamic feedbacks and maximum power	104
5.4	Evolutionary dynamics and power	106
5.5	Feedbacks, maximum power, and dynamic stability	107
5.6	Structural organization of flow	109
5.7	Maximization by structures	112
5.8	Structures and maximization in the Earth system	119
6	Radiation	121
6.1	The main driver of the Earth system	121
6.2	Thermodynamics of radiation	124
6.3	Solar radiation	129
6.3.1	From Sun to Earth	130
6.3.2	Scattering	131
6.3.3	Absorption	133
6.3.4	Estimates	135
6.4	Terrestrial radiation	137
6.5	Limits to converting radiative energy	141
6.6	Limits to converting radiative heating	143

	<i>Contents</i>	vii
	6.7 Sensitivity to radiative forcing	146
	6.8 Radiation and the Earth system	150
7	Motion	154
	7.1 Transporting mass on the planet	154
	7.2 Depletion of potential energy	158
	7.3 Maintaining motion	162
	7.4 Limits to atmospheric and oceanic motion	166
	7.5 Inferring mass exchange from maximum power	172
	7.6 Maximum power and geostrophic motion	174
	7.7 Limits to motion in the Earth’s interior	178
	7.8 Thermodynamic consequences of motion	182
	7.9 Motion in the Earth system	185
8	Hydrologic cycling	188
	8.1 Thermodynamic roles of water	188
	8.2 Thermodynamics of the phase transitions of water	192
	8.3 Saturation of water vapor	195
	8.4 Maintaining hydrologic cycling	198
	8.5 Limits to hydrologic cycling	206
	8.6 Sensitivity of hydrologic cycling	209
	8.7 Thermodynamic consequences of hydrologic cycling	213
	8.8 Hydrologic cycling in the Earth system	216
9	Geochemical cycling	219
	9.1 Drivers of chemical disequilibrium in the Earth system	219
	9.2 Thermodynamics of chemical reactions	225
	9.3 Atmospheric processes	232
	9.4 Hydrospheric processes	235
	9.5 Geologic processes	237
	9.6 Biotic processes	240
	9.7 Biospheric activity	245
	9.8 Thermodynamic consequences of geochemical cycling	251
	9.9 Geochemical cycling in the Earth system	255
10	Land	258
	10.1 The thermodynamic setting of land	258
	10.2 Limits to dry convection on land	263
	10.3 Limits to dry convection with heat storage changes	266
	10.4 Hydrologic effects on land–atmosphere exchange	272
	10.5 Convective mass exchange on land	276

viii	<i>Contents</i>	
	10.6 Limits to terrestrial photosynthesis	279
	10.7 Thermodynamic consequences of vegetated land	283
	10.8 Land in the Earth system	288
11	Human activity	291
	11.1 Human activity as a thermodynamic process	291
	11.2 Energy and human activity	295
	11.3 Limits to food acquisition	299
	11.4 Limits to primary energy acquisition	306
	11.5 Thermodynamic consequences of human activity	314
	11.6 Human activity in the Earth system	319
12	The thermodynamic Earth system	323
	12.1 Thermodynamic foundations of the whole Earth system	323
	12.2 The thermodynamic Earth system	326
	12.3 Habitable planets and life	331
	12.4 Planetary evolution, optimization, and regulation	337
	12.5 Human activity and a sustainable future	344
	12.6 Perspectives	348
	<i>Glossary</i>	351
	<i>References</i>	356
	<i>Index</i>	375

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

Preface

xi

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
α	albedo	frac.	-	sec. 6.3.3
A	chemical affinity of a reaction	J mol^{-1}	-	sec. 9.2
A	area (typically surface area)	m^2	-	
B	geometric factor	-	-	
c	speed of light	m s^{-1}	$3 \cdot 10^8$	chap. 6
c	heat capacity	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_{sat}	partial pressure of water vapor at saturation	Pa	-	
E	evaporation rate	$\text{kg m}^{-2} \text{s}^{-1}$ or mm d^{-1}	-	
ϵ	dilution factor	-	-	chap. 6
ϵ_{lue}	light use efficiency	$\mu\text{mol CO}_2 (\mu\text{mol PAR})^{-1}$	-	sec. 10.6

List of Symbols xiii

Symbol	Description	Units	Value	Primary use
ϵ_{wue}	water use efficiency	$\text{g CO}_2 (\text{kg H}_2\text{O})^{-1}$	-	sec. 10.6
η	efficiency (= power/flux)	frac.	-	
f	fraction	frac.	-	
f	feedback factor	-	-	chap. 5
f	Coriolis parameter	s^{-1}	-	sec. 7.6
f_w	water limitation factor	frac.	-	sec. 10.4
F	Helmholtz free energy	J	-	sec. 3.5
F	force	kg m s^{-2}	-	sec. 4.6
ϕ	geopotential	$\text{m}^2 \text{s}^{-2}$		sec. 2.3.4
ϕ	latitude	°		chap. 7
g	gravitational acceleration	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
ΔG_r	Gibbs free energy of a reaction	J	-	chap. 9
γ	psychrometric constant	Pa K^{-1}	≈ 65	
Γ_d	dry adiabatic lapse rate	K m^{-1}	$9.81 \cdot 10^{-3}$	
Γ_{dew}	lapse rate of the dew point	K m^{-1}	$1.8 \cdot 10^{-3}$	
H	enthalpy	J	-	sec. 3.5
H	sensible heat flux	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_{in}	influx of energy	W	-	
J_{out}	outflux of energy	W	-	
J_s	entropy flux	W K^{-1}	-	chap. 2
J_m	mass flux	kg s^{-1}	-	
J_{mom}	momentum flux	kg m s^{-3}	-	
k	conductivity	W K^{-1}	-	
k	friction coefficient	(depends)	-	sec. 4.6
k_b	Boltzmann's constant	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_ν	spectral energy density	$\text{J sr}^{-1} \text{m}^{-2}$	-	sec. 6.2
K_{eq}	equilibrium constant	-	-	sec. 9.2
L	length	m	-	
L_ν	spectral entropy density	$\text{J sr}^{-1} \text{m}^{-2} \text{K}^{-1}$	-	sec. 6.2
λ	wavelength	m	-	chap. 6
λ	latent heat of vaporization	J kg^{-1}	$2.5 \cdot 10^6$	chap. 8, chap. 10
λE	latent heat flux	W m^{-2}	-	

xiv

List of Symbols

Symbol	Description	Units	Value	Primary use
μ	chemical potential	J mol ⁻¹		
m	mass	kg	-	
n	molar mass	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
ν	frequency	s ⁻¹	-	
Ω	solid angle	sr	-	chap. 6
Ω_{sun}	solid angle of the Sun in the Earth's sky	sr	$6.8 \cdot 10^{-5}$	chap. 6
Ω	Earth's angular velocity	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	kg m ⁻² s ⁻¹ or mm d ⁻¹	-	chap. 8
π	osmotic pressure	Pa	-	
q	specific humidity	kg kg ⁻¹	-	
Q	amount of heat added or removed	J	-	
Q	charge	C	-	sec. 4.6
Q	runoff	kg m ⁻² s ⁻¹	-	sec. 10.4
ρ	density	kg m ⁻³	-	
r_{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	J kg ⁻¹ K ⁻¹ J kg ⁻¹ K ⁻¹ J mol ⁻¹ K ⁻¹	287 (air) 461 (water vapor) 8.314 (general)	
$R_{\text{in}}, R_{\text{out}}$	radiative flux	W m ⁻²	-	
R_l	flux of terrestrial radiation	W m ⁻²	-	
$R_{l,\text{up}}$	flux of terrestrial radiation (upwards) at the surface	W m ⁻²	-	
$R_{l,\text{down}}$	flux of terrestrial radiation (downwards) at the surface	W m ⁻²	-	
$R_{l,\text{net}}$	net flux of terrestrial radiation at the surface	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	W m ⁻²	1370	
R_s	flux of solar radiation	W m ⁻²	-	
$R_{s,a}$	absorbed solar radiation in the atmosphere	W m ⁻²	≈ 75	
$R_{s,s}$	absorbed solar radiation at the surface	W m ⁻²	≈ 165	
$R_{s,\text{toa}}$	total absorbed solar radiation	W m ⁻²	≈ 240	

List of Symbols xv

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