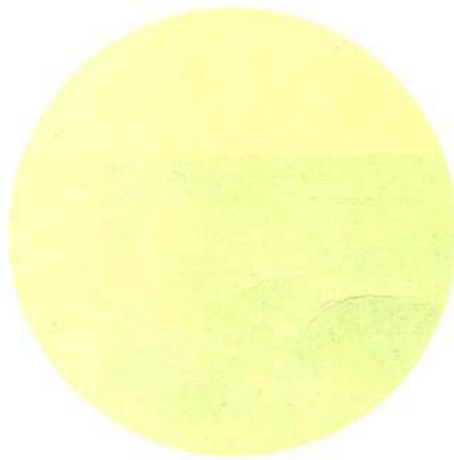


**Geophysics and Astrophysics Monographs**

# **Atmospheric Thermodynamics**

**J. V. Iribarne and W. L. Godson**

Second Edition



**D. Reidel Publishing Company**

---

# GEOPHYSICS AND ASTROPHYSICS MONOGRAPHS

AN INTERNATIONAL SERIES OF FUNDAMENTAL TEXTBOOKS

## *Editor*

B. M. McCORMAC, *Lockheed Palo Alto Research Laboratory, Palo Alto, Calif., U.S.A.*

## *Editorial Board*

R. GRANT ATHAY, *High Altitude Observatory, Boulder, Colo., U.S.A.*

W. S. BROECKER, *Lamont-Doherty Geological Observatory, Palisades, New York, U.S.A.*

P. J. COLEMAN, JR., *University of California, Los Angeles, Calif., U.S.A.*

G. T. CSANADY, *Woods Hole Oceanographic Institution, Woods Hole, Mass., U.S.A.*

D. M. HUNTEN, *University of Arizona, Tucson, Ariz., U.S.A.*

C. DE JAGER, *The Astronomical Institute, Utrecht, The Netherlands*

J. KLECZEK, *Czechoslovak Academy of Sciences, Ondřejov, Czechoslovakia*

R. LÜST, *President Max-Planck Gesellschaft für Förderung der Wissenschaften, München, F.R.G.*

R. E. MUNN, *University of Toronto, Toronto, Ont., Canada*

Z. ŠVESTKA, *The Astronomical Institute, Utrecht, The Netherlands*

G. WEILL, *Service d'Aéronomie, Verrières-le-Buisson, France*

VOLUME 6

# ATMOSPHERIC THERMODYNAMICS

*by*

J. V. IRIBARNE

*University of Toronto*

*and*

W. L. GODSON

*Atmospheric Research Directorate, Atmospheric Environment Service, Toronto*

SECOND EDITION



D. REIDEL PUBLISHING COMPANY

DORDRECHT: HOLLAND/BOSTON: U.S.A.

LONDON: ENGLAND

Library of Congress Cataloging in Publication Data

CIP

Iribarne, J. V. (Julio Victor), 1916-  
Atmospheric thermodynamics.

(Geophysics and astrophysics monographs ; v. 6)

Bibliography: p.

Includes index.

1. Atmospheric thermodynamics. I. Godson, W. L. II. Title.

III. Series.

QC880.4.T5174 1981 551.5'22 81-10674

ISBN 90-277-1296-4 AACR2

ISBN 90-277-1297-2 (pbk.)

---

Published by D. Reidel Publishing Company,  
P.O. Box 17, 3300 AA Dordrecht, Holland.

First published 1973  
Second revised edition 1981

Sold and distributed in the U.S.A. and Canada  
by Kluwer Boston Inc.,  
190 Old Derby Street, Hingham, MA 02043, U.S.A.

In all other countries, sold and distributed  
by Kluwer Academic Publishers Group,  
P.O. Box 322, 3300 AH Dordrecht, Holland.

D. Reidel Publishing Company is a member of the Kluwer Group.

All Rights Reserved

Copyright © 1973, 1981 by D. Reidel Publishing Company, Dordrecht, Holland  
No part of the material protected by this copyright notice may be reproduced or  
utilized in any form or by any means, electronic or mechanical,  
including photocopying, recording or by any informational storage and  
retrieval system, without written permission from the copyright owner

Printed in The Netherlands

## TABLE OF CONTENTS

PREFACE	IX
PREFACE TO THE SECOND EDITION	XI
LIST OF SYMBOLS	XIII
CHAPTER I. REVIEW OF BASIC CONCEPTS AND SYSTEMS OF UNITS	
1.1. Systems	1
1.2. Properties	1
1.3. Composition and State of a System	2
1.4. Equilibrium	2
1.5. Temperature. Temperature Scales	3
1.6. Systems of Units	6
1.7. Work of Expansion	8
1.8. Modifications and Processes. Reversibility	9
1.9. State Variables and State Functions. Equation of State	10
1.10. Equation of State for Gases	10
1.11. Mixture of Ideal Gases	11
1.12. Atmospheric Air Composition	12
Problems	15
CHAPTER II. THE FIRST PRINCIPLE OF THERMODYNAMICS	
2.1. Internal Energy	16
2.2. Heat	17
2.3. The First Principle. Enthalpy	21
2.4. Expressions of $Q$ . Heat Capacities	22
2.5. Calculation of Internal Energy and Enthalpy	23
2.6. Latent Heats of Pure Substances. Kirchhoff's Equation	26
2.7. Adiabatic Processes in Ideal Gases. Potential Temperature	28
2.8. Polytropic Processes	31
Problems	32



## CHAPTER III. THE SECOND PRINCIPLE OF THERMODYNAMICS

3.1. The Entropy	35
3.2. Thermodynamic Scale of Absolute Temperature	36
3.3. Formulations of the Second Principle	39
3.4. Lord Kelvin's and Clausius' Statements of the Second Principle	39
3.5. Joint Mathematical Expressions of the First and Second Principles. Thermodynamic Potentials	40
3.6. Equilibrium Conditions and the Sense of Natural Processes	43
3.7. Calculation of Entropy	45
3.8. Thermodynamic Equations of State. Calculation of Internal Energy and Enthalpy	46
3.9. Thermodynamic Functions of Ideal Gases	47
3.10. Entropy of Mixing for Ideal Gases	48
3.11. Difference Between Heat Capacities at Constant Pressure and at Constant Volume	49
Problems	51

## CHAPTER IV. WATER-AIR SYSTEMS

4.1. Heterogeneous Systems	53
4.2. Fundamental Equations for Open Systems	57
4.3. Equations for the Heterogeneous System. Internal Equilibrium	58
4.4. Summary of Basic Formulas for Heterogeneous Systems	59
4.5. Number of Independent Variables	61
4.6. Phase-Transition Equilibria for Water	62
4.7. Thermodynamic Surface for Water Substance	64
4.8. Clausius-Clapeyron Equation	65
4.9. Variation of Latent Heat Along the Equilibrium Curve	68
4.10. Water Vapor and Moist Air	69
4.11. Humidity Variables	73
4.12. Heat Capacities of Moist Air	76
4.13. Moist Air Adiabats	78
4.14. Enthalpy, Internal Energy and Entropy of Moist Air and of a Cloud	78
Problems	85

## CHAPTER V. EQUILIBRIUM WITH SMALL DROPLETS AND CRYSTALS

5.1. Vapor Pressure of Small Droplets of a Pure Substance	87
5.2. Vapor Pressure of Solution Droplets	90
5.3. Sublimation and Freezing of Small Crystals	96
Problems	97

## CHAPTER VI. AEROLOGICAL DIAGRAMS

6.1. Purpose of Aerological Diagrams and Selection of Coordinates	98
6.2. Clapeyron Diagram	99
6.3. Tephigram	99
6.4. Curves for Saturated Adiabatic Expansion. Relative Orientation of Fundamental Lines	102
6.5. Emagram or Neuhoff Diagram	104
6.6. Refsdal Diagram	106
6.7. Pseudoadiabatic or Stüve Diagram	107
6.8. Area Equivalence	107
6.9. Summary of Diagrams	109
6.10. Determination of Mixing Ratio from the Relative Humidity	110
6.11. Area Computation and Energy Integrals	110
Problems	115

## CHAPTER VII. THERMODYNAMIC PROCESSES IN THE ATMOSPHERE

7.1. Isobaric Cooling. Dew and Frost Points	116
7.2. Condensation in the Atmosphere by Isobaric Cooling	120
7.3. Adiabatic Isobaric (Isenthalpic) Processes. Equivalent and Wet-Bulb Temperatures	123
7.4. Adiabatic Isobaric Mixing (Horizontal Mixing) Without Condensation	127
7.5. Adiabatic Isobaric Mixing with Condensation	129
7.6. Adiabatic Expansion in the Atmosphere	136
7.7. Saturation of Air by Adiabatic Ascent	138
7.8. Reversible Saturated Adiabatic Process	141
7.9. Pseudoadiabatic Process	142
7.10. Effect of Freezing in a Cloud	144
7.11. Polytropic Expansion	146
7.12. Vertical Mixing	147
7.13. Pseudo- or Adiabatic Equivalent and Wet-Bulb Temperatures	149
7.14. Summary of Temperature and Humidity Parameters. Conservative Properties	151
Problems	153

## CHAPTER VIII. ATMOSPHERIC STATICS

8.1. The Geopotential Field	156
8.2. The Hydrostatic Equation	159
8.3. Equipotential and Isobaric Surfaces. Dynamic and Geopotential Height	160
8.4. Thermal Gradients	163

8.5. Constant-Lapse-Rate Atmospheres	163
8.6. Atmosphere of Homogeneous Density	164
8.7. Dry-Adiabatic Atmosphere	165
8.8. Isothermal Atmosphere	166
8.9. Standard Atmosphere	166
8.10. Altimeter	168
8.11. Integration of the Hydrostatic Equation	171
Problems	174
CHAPTER IX. VERTICAL STABILITY	
9.1. The Parcel Method	177
9.2. Stability Criteria	178
9.3. Lapse Rates for Atmospheric Ascents	180
9.4. The Lapse Rates of the Parcel and of the Environment	183
9.5. Stability Criteria for Adiabatic Processes	185
9.6. Conditional Instability	188
9.7. Oscillations in a Stable Layer	191
9.8. The Layer Method for Analyzing Stability	192
9.9. Entrainment	195
9.10. Potential or Convective Instability	197
9.11. Processes Producing Stability Changes for Dry Air	201
9.12. Stability Parameters of Saturated and Unsaturated Air, and Their Time Changes	208
9.13. Radiative Processes and Their Thermodynamic Consequences	217
9.14. Maximum Rate of Precipitation	224
9.15. Internal and Potential Energy in the Atmosphere	227
9.16. Internal and Potential Energy of a Layer with Constant Lapse Rate	230
9.17. Margules' Calculations on Overturning of Air Masses	231
9.18. Transformations of a Layer with Constant Lapse Rate	233
9.19. The Available Potential Energy	235
Problems	240
APPENDIX I: Table of Physical constants	245
BIBLIOGRAPHY	249
ANSWERS TO PROBLEMS	252
INDEX	257



## PREFACE

The thermodynamics of the atmosphere is the subject of several chapters in most textbooks on dynamic meteorology, but there is no work in English to give the subject a specific and more extensive treatment. In writing the present textbook, we have tried to fill this rather remarkable gap in the literature related to atmospheric sciences. Our aim has been to provide students of meteorology with a book that can play a role similar to the textbooks on chemical thermodynamics for the chemists. This implies a previous knowledge of general thermodynamics, such as students acquire in general physics courses; therefore, although the basic principles are reviewed (in the first four chapters), they are only briefly discussed, and emphasis is laid on those topics that will be useful in later chapters, through their application to atmospheric problems. No attempt has been made to introduce the thermodynamics of irreversible processes; on the other hand, consideration of heterogeneous and open homogeneous systems permits a rigorous formulation of the thermodynamic functions of clouds (exclusive of any consideration of microphysical effects) and a better understanding of the approximations usually implicit in practical applications.

The remaining two-thirds of the book deal with problems which are typically meteorological in nature. First, the most widely-used aerological diagrams are discussed in Chapter V; these play a vital role in the practice of meteorology, and in its exposition as well (as later chapters will testify). Chapter VI presents an analysis of a number of significant atmospheric processes which are basically thermodynamic in nature. In most of these processes, changes of phase of water substance play a vital role – such as, for example, the formation of fog, clouds and precipitation. One rather novel feature of this chapter is the extensive treatment of aircraft condensation trails, a topic of considerable environmental concern in recent years.

Chapter VII deals with atmospheric statics – the relations between various thermodynamic parameters in a vertical column. In the final (and longest) chapter will be found analyses of those atmospheric phenomena which require consideration of both thermodynamic and non-thermodynamic processes (in the latter category can be listed vertical and horizontal motions and radiation). The extensive treatment of these topics contains considerable new material, which will be found especially helpful to professional meteorologists by reason of the emphasis on changes with time of weather-significant thermodynamic parameters.

The book has grown out of courses given by both of us to students working for a degree in meteorology, at the universities of Toronto and of Buenos Aires. Most of these students subsequently embarked on careers in the atmospheric sciences – some

in academic areas and many in professional areas, including research as well as forecasting. As a consequence, the courses taught, from which the present text originates, emphasized equally the fundamental topic and practical aspects of the subject. It can therefore be expected to be of interest to engineers dealing with atmospheric problems, to research scientists dealing with planetary atmospheres and to all concerned with atmospheric behavior – either initially, as students, or subsequently, in various diverse occupations.



## PREFACE TO THE SECOND EDITION

It is now eight years since we commented that we had produced a text book on atmospheric thermodynamics to fill a rather remarkable gap in the literature related to the atmospheric sciences – namely, a general-purpose concise text in English on thermodynamics applied to the atmosphere. We have been extremely pleased with the wide acceptance of our text, and have realized that it would be worthwhile improving on this contribution to atmospheric science teaching and research by producing a revised edition. In so doing, we have taken advantage of many helpful comments made by students and colleagues.

The general subject of atmospheric thermodynamics must be regarded as extremely stable, so that there were few new concepts that we felt deserved inclusion in this edition. However, there were some topics that we considered required a more detailed treatment; moreover, it was decided that the thermodynamic aspects of cloud microphysics should now be incorporated. Thus a new chapter on equilibrium with small droplets and crystals was added, more attention was given to polytropic processes (Ch. 2, Section 8 and Ch. 7, Section 11), a section was included on the variation of latent heat along the equilibrium curve (Ch. 4, Section 9) and the last section on available potential energy was expanded; minor corrections and improvements are also to be found in many places throughout the text. This was complemented by a list of Symbols, a rather extensive Bibliography and new additional problems; for some of the latter, we acknowledge use of the WMO publication by Laikhtman *et al.* (see complete reference in Bibliography, Section 6; their problems 2-12, 24, 33, 39, 5-17 and a 'sample problem' – p. 38 – were used as such or modified for our problems VII-12, VIII-5, IX-9, 10, 11, 12).

While we were working on this revised edition, we were saddened to learn of the death, on 31 August 1980, of Prof. Jacques van Mieghem. Prof. van Mieghem was a true pioneer in atmospheric dynamics and thermodynamics, and the textbook on atmospheric thermodynamics which he co-authored (in French) is a model of elegance and precision. As a tribute to his contributions to atmospheric science, we would like to dedicate this edition to his memory.

In closing, we would like to express our thanks to all who have helped with the two editions and to express our particular gratitude to our publisher, D. Reidel, for excellence in both printing and publishing.

## LIST OF SYMBOLS

### *Roman*

### *Letters*

<i>a</i>	Work performed on the system by external forces, per unit mass.
<i>A</i>	Work performed on the system by external forces, per mole or total. Available potential energy.
<i>c</i>	Specific heat capacity. Number of components.
<i>C</i>	Molar heat capacity.
<i>d</i>	Exact differential.
<i>D</i>	Virtual differential.
<i>e</i>	Water vapor pressure.
<i>f</i>	Specific Helmholtz function. Correction coefficient.
<i>F</i>	Helmholtz function, molar or total.
<i>g</i>	Specific Gibbs function. Gravity.
<i>G</i>	Gibbs function, molar or total.
<i>h</i>	Specific enthalpy.
<i>H</i>	Enthalpy, molar or total.
<i>k</i>	Compressibility coefficient.
<i>K</i>	Kinetic energy.
<i>l</i>	Specific heat of phase change.
<i>L</i>	Molar heat of phase change.
<i>m</i>	Mass.
<i>M</i>	Molecular weight.
<i>n</i>	Number of moles. Polytropic exponent.
<i>N</i>	Molar fraction.
<i>p</i>	Pressure.
<i>P</i>	Potential energy. Rate of precipitation.
<i>q</i>	Heat received by the system, per unit mass. Specific humidity.
<i>Q</i>	Heat received by the system, molar or total.
<i>r</i>	Mixing ratio.
<i>R</i>	Specific gas constant.
<i>R*</i>	Universal (molar) gas constant.
<i>s</i>	Specific entropy.
<i>S</i>	Entropy, molar or total.
<i><math>\mathcal{S}</math></i>	Surface.
<i>t</i>	Time. Temperature, on Celsius scale.



$T$	Absolute temperature.
$u$	Specific internal energy.
$U$	Internal energy, molar or total. Relative humidity.
$v$	Specific volume.
$V$	Volume, molar or total.
$\mathcal{V}$	Volume of a drop.
$z$	Any specific property, derived from $Z$ . Height.
$Z$	Any extensive property.

*Greek**Letters*

$\alpha$	Thermal coefficient.
$\beta$	Lapse rate, referred to actual height.
$\gamma$	Lapse rate, referred to geopotential.
$\delta$	Non-exact differential. Geometric (as opposed to process) differential.
$\Delta$	Finite difference.
$\varepsilon$	Ratio of molecular weights of water and dry air.
$\eta$	Ratio of heat capacity at constant pressure to heat capacity at constant volume.
$\theta$	Potential temperature.
$\kappa$	Ratio of gas constant to molar heat capacity at constant pressure.
$\lambda$	Rate of temperature change $dT/dt$ .
$\mu$	Chemical potential.
$\nu$	Frequency. Variance of a system.
$\pi$	Length ratio of circumference to diameter.
$\varrho$	Density.
$\sigma$	Surface tension. Interfacial tension.
$\Sigma$	Area on a diagram.
$\tau$	Period.
$\varphi$	Latitude. Number of phases.
$\phi$	Geopotential.
$\omega$	Angular velocity.

*Subscripts*

$a$	Adiabatic (as in $T_{aw}$ ).
$c$	Condensed phase. Critical.
$d$	Dry air. Dry adiabatic. Dew point (in $T_d$ ).
$e$	Equivalent (as in $T_e$ ).
$f$	Fusion (in $l_f$ ). Final. Frost point (in $T_f$ ).
$g$	Gas phase.
$i$	Ice. Initial. Referred to ice (in $U_i$ ). Saturation with respect to ice (as in $e_i$ ). Isobaric (as in $T_{iw}$ ).

<i>l</i>	Liquid.
<i>m</i>	At constant composition (when using mass units). Moist.
<i>n</i>	At constant composition (when using number of moles).
<i>p</i>	At constant pressure.
<i>s</i>	Sublimation (in $l_s$ ). Solid. Saturation. Surface.
<i>t</i>	Triple point. Total.
<i>v</i>	At constant volume. Vaporization. Water vapor. Virtual (as in $T_v$ ).
<i>w</i>	Water. Referred to water (in $U_w$ ). Saturation with respect to water (as in $e_w$ ). Wet bulb (as in $T_w$ ).
<i>Bar</i>	Average (as in $\bar{T}$ ). Partial molar or specific property (as in $\bar{G}_v, \bar{g}_v$ ).
<i>Prime</i>	Parcel (as in $T'$ ).