

INTERNATIONAL GEOPHYSICS SERIES • VOLUME 6



INSTITUT
FÜR METEOROLOGIE U. KLIMATOLOGIE
DER TECHN. HOCHSCHULE

HANNOVER · HERRENHAUSER STR. 2

§. 30/849

Thermodynamics of Clouds

LOUIS DUFOUR *and* RAYMOND DEFAY

Royal Belgian *University of Brussels*
Meteorological Institute *Brussels, Belgium*
Uccle, Belgium

Translated by M. Smyth
and A. Beer

1963



ACADEMIC PRESS
New York and London

Contents

INTRODUCTION	v
I. Ideas of Capillarity	
1. Introduction	1
2. Surface Tension	1
3. Mechanical Equilibrium Conditions for a Surface	3
4. Equilibrium of an Edge	6
5. Contact Angle of a Fluid/Fluid Interface with the Surface of a Solid	7
6. Mechanical Work Done by a Capillary System	9
7. Surface Tension of a Crystal Face	11
II. Surface Model and Definitions of Adsorption, Surface Enthalpy, and Entropy	
1. The Real System and the Simplified Model	15
2. Difficulties Inherent in the Use of the Surface Model	17
III. Laws of Thermodynamics	
1. Choice of Variables	19
2. First Law of Thermodynamics	21
3. Second Law of Thermodynamics	23
IV. Fundamental Formulas in Terms of Intensive Variables	
1. Aims of the Chapter	29
2. Variables on Which the Surface Functions of State Depend	29
3. Intensive Properties of the Surface	30
4. Transformation from Intensive to Extensive Variables	31
5. Specific Surface Functions of State	32
6. Fundamental Formulas Relating to the Surface Phase	34
7. Fundamental Formulas in Terms of Intensive Variables	36
V. Equilibrium States	
1. Affinities of Adsorption	41
2. Conditions for Adsorption Equilibrium	41
3. Equilibrium Displacement	42
4. Phase Rule	44
5. Extension of Duhem's Theorem to Systems Containing Surfaces	46

VI. Adiabatic Transformations	49
VII. Examination of Some Approximations or Hypotheses	
1. Aims of the Chapter	55
2. Humid Air Can Be Treated as a Mixture of Two Perfect Gases: Dry Air and Water Vapor	55
3. The Surface Tension of a Droplet Can Be Considered Independent of the Radius of Curvature	59
4. Adsorptions Are Negligible in Comparison with the Masses Involved, and Adsorption of Atmospheric Components Has Negligible Effect on the Surface Tension	62
5. The Lateral Functions α_{γ}' , β_{γ}' , λ_{γ}' and α_{γ}'' , β_{γ}'' , λ_{γ}'' Can Be Neglected	65
6. The Heat Capacities at Constant Pressure of Dry Air and Water Vapor, of Which the Atmosphere Is Composed, Are Constants	67
7. The Heat Capacities of Pure Liquid and Solid Water Vary Only Slightly with Temperature	68
VIII. Study of a Droplet Suspended in the Atmosphere	
1. Statement of the Problem	69
2. Influence of Curvature on the Saturation Pressure of a Droplet	70
3. Influence of Other Components on the Heat of Vaporization of Water from a Plane Surface	83
4. Influence of Curvature on the Heat of Vaporization of a Droplet	84
5. Influence of Curvature on the Equilibrium Temperature of a Droplet	87
6. Stability of Equilibrium of a Droplet	91
7. Reversible Adiabatic Transformations	95
IX. Study of an Ice Crystal Suspended in the Atmosphere	
1. Statement of the Problem	103
2. Influence of Radius on the Saturation Pressure Relative to an Ice Crystal	104
3. Influence of Radius on the Heat of Sublimation of an Ice Crystal	106
4. Influence of Radius on the Equilibrium Temperature of an Ice Crystal	108
5. Stability of Equilibrium of an Ice Crystal	109
6. Reversible Adiabatic Transformations	110
X. Temperature of Coexistence of a Droplet of Solution and a Crystal of Ice in the Atmosphere	
1. Statement of the Problem	117
2. Droplet of Solution and Crystal of Ice Suspended in the Atmosphere	118
3. Ice Crystal Contained within a Droplet of Solution Suspended in the Atmosphere	125
XI. Germs of Condensation and Crystallization	
1. Definition of the Germ	131
2. Calculation of Radius of Germ	134

3. Formation of Germs, or Nucleation	151
4. Free Energy of Formation of a Drop Phase	153
5. Free Energy of Formation of a Crystal Phase	156
6. Free Energy of Formation in the Case When There Is Only a Single Component in the Drop or Crystal	158
7. Choice of Shape Factor for Ice Crystals	162
XII. Equilibrium Populations of Embryos. Calculation of Number of Germs as Limiting Case of Problem of Equilibrium	
1. Introduction	165
2. Properties of Embryos Considered as Particles	165
3. Comparison between the System Containing Embryos Treated as Phases and the System of Particle Embryos	169
4. Equilibrium Populations of Embryos in a Liquid Mother Phase	171
5. Embryos and Germs of Ice in Pure Water	173
6. Embryos and Germs of Ice in Salt Water	177
7. Equilibrium Populations of Embryos in a Gaseous Mother Phase	179
XIII. Nucleation Rate	
1. Definition of Nucleation Rate	183
2. Ratio of the Forward Rate \vec{w} to the Reverse Rate \overleftarrow{w} per Unit Surface Area	186
3. Kinetics of Nucleation	189
4. Nucleation of Water or Ice in Humid Air	195
5. Review of the Basic Elements of the Theory of Viscosity	208
6. Nucleation in a Pure Liquid	211
7. Nucleation in a Liquid Mixture	213
8. Experimental Tests in a Liquid Mother Phase	214
9. Calculation of Mean Freezing Temperature of Water Droplets	216
10. Values Used in Calculating Nucleation Rate and Freezing Temperature	219
11. Determination of Ice/Water Surface Tension	225
12. Comparison of Values of Ice/Water Surface Tension Given by Various Authors	228
LIST OF SYMBOLS	237
BIBLIOGRAPHY	243
AUTHOR INDEX	249
SUBJECT INDEX	251