

# Essentials of Thermodynamics

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**Essentials of Thermodynamics**  
Published by SRI Books,  
an imprint of the Simplicity Research Institute,  
Singapore  
[www.simplicitysg.net](http://www.simplicitysg.net)  
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# Dedication

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I dedicate this book to my beloved high school teacher Sri. H. Anantha Rao (1907-2011), who lived true to the spirit of science. He opened our minds to the wonderful world of physics. Till his last days he was preoccupied with science, and in particular whether modern science was addressing the right questions.

I also dedicate this book to my parents. To my mother, Venkatalakshmi, who, despite gnawing poverty, made the education of her children her prime objective in life. She passed away on 4 Feb 2021 as this book was getting its final touches. And to my late father, Desikachar, who, despite being very orthodox religiously never hindered our choices in life.

I further dedicate this book to my uncle Professor M.V. Narasimhan(IISc)(1932-2017) for his strong influences on my scientific thinking. Being the first PhD in the family he opened my eyes to the world of research. His deep understanding of the essentials of thermodynamics, conveyed to me in numerous discussions, have shaped the many choices I made writing this book.

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# Contents

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<b>Dedication</b>	<b>v</b>
<b>Preface</b>	<b>xv</b>
<b>Guide for Readers and Teachers</b>	<b>xvii</b>
<b>1 The Beginnings</b>	<b>1</b>
1.1 Temperature and thermometry . . . . .	2
1.1.1 Uniform temperature scale . . . . .	3
1.1.2 Non-uniform temperature scales . . . . .	4
1.1.3 Materials for thermometry . . . . .	5
1.2 Ideal gas laws . . . . .	7
1.2.1 The Kelvin scale . . . . .	9
1.2.2 Non-ideal gases . . . . .	11
1.3 Heat and specific heats . . . . .	11
1.3.1 Nature of heat . . . . .	12
1.3.2 States and transformations . . . . .	13
1.3.3 Some examples . . . . .	15
1.4 Sadi Carnot and the motive power of heat . . . . .	17
1.4.1 Infinitesimal and finite cycles . . . . .	26
1.5 Steam engines and the Clapeyron Equation . . . . .	28
1.6 Problems . . . . .	32
<b>2 First Law—The <math>E = Mc^2</math> of Thermodynamics</b>	<b>35</b>
2.1 The fall of the caloric . . . . .	35
2.2 The path to the first law . . . . .	37
2.3 The first law of thermodynamics . . . . .	40
2.4 Some applications of the first law . . . . .	42
2.4.1 Internal energy of ideal gases . . . . .	43
2.4.2 Isochoric changes . . . . .	43
2.4.3 Isobaric changes . . . . .	44
2.4.4 Adiabatic changes in an ideal gas . . . . .	44
2.4.5 Isothermal changes . . . . .	45
2.4.6 Heats of transformation . . . . .	45
2.4.7 Enthalpy . . . . .	46

2.5	Problems . . . . .	50
2.6	Suggested reading for this book in general . . . . .	52
<b>3</b>	<b>The Second and Third Laws</b>	<b>55</b>
3.1	Perpetuum mobiles . . . . .	56
3.1.1	Perpetual machines of the first kind . . . . .	57
3.1.2	Perpetual machines of the second kind . . . . .	57
3.2	The entropy axiom: the first part of second law . . . . .	58
3.2.1	A bonanza from first law for ideal gases . . . . .	58
3.2.2	A consequence of the entropy axiom . . . . .	58
3.3	Entropy axiom and universality of Carnot cycles in the new Thermodynamics. . . . .	60
3.3.1	Ideal gas Carnot cycle . . . . .	64
3.3.2	Composition of Carnot cycles . . . . .	64
3.4	Historical formulations of second law . . . . .	66
3.4.1	Consequences of Clausius Inequality . . . . .	68
3.5	Second law and irreversibility . . . . .	70
3.5.1	Second law and arrow of time . . . . .	74
3.5.2	Entropy and disorder . . . . .	74
3.5.3	Entropy and information . . . . .	75
3.6	An absolute scale of temperature . . . . .	75
3.7	Applications of the first and second laws . . . . .	77
3.8	Third law of thermodynamics - the Nernst-Planck postulate . . . . .	84
3.9	Problems . . . . .	90
<b>4</b>	<b>Carnot Cycles - The Turing Machines of Thermodynamics</b>	<b>93</b>
4.1	The gas Carnot cycles . . . . .	94
4.1.1	The ideal gas cycles . . . . .	94
4.1.2	The van der Waals cycle . . . . .	94
4.2	The steam Carnot cycle . . . . .	96
4.3	The Stirling engine . . . . .	97
4.4	The Otto cycle . . . . .	98
4.4.1	The Diesel cycle . . . . .	99
4.5	The Brayton cycle . . . . .	100
4.5.1	The magnetic Brayton cycle . . . . .	100
4.6	Carnot cycle with photons . . . . .	102
4.6.1	The Thermodynamics of the radiation field . . . . .	103
4.6.2	Photon Carnot cycle . . . . .	105
4.6.3	The thermodynamic gateway to quantum world . . . . .	106
4.7	Problems . . . . .	107



<b>5</b>	<b>Specific Heats: Magnificent Bridges</b>	<b>111</b>
5.1	A brief history . . . . .	111
5.2	Varieties of specific heats . . . . .	113
5.2.1	Negative specific heats . . . . .	114
5.3	Specific heats and the third law . . . . .	115
5.3.1	Specific heats and cooling powers . . . . .	115
5.4	Specific heats and microscopics . . . . .	116
5.5	Specific heats herald quantum theory! . . . . .	117
5.5.1	Einstein and specific heats . . . . .	118
5.5.2	Debye Theory . . . . .	120
5.5.3	Specific heats of quantum ideal gases . . . . .	122
5.6	Problems . . . . .	124
<b>6</b>	<b>Structure of Thermodynamic Theories</b>	<b>127</b>
6.1	Extensive and intensive variables: general . . . . .	131
6.2	The Fundamental Equations . . . . .	132
6.2.1	Intensive variables and the fundamental equation . . . . .	133
6.2.2	The Euler relations . . . . .	134
6.2.3	The Gibbs-Duhem relations . . . . .	135
6.3	True equations of state . . . . .	136
6.4	Multicomponent systems . . . . .	137
6.5	Entropy of mixing and the Gibbs paradox . . . . .	138
6.5.1	Extensivity revisited . . . . .	140
6.6	Worked out examples . . . . .	141
6.6.1	Fundamental equations and equations of state . . . . .	141
6.6.2	Gibbs-Duhem relations . . . . .	143
6.7	Axiomatic intensive variables and equilibrium . . . . .	144
6.7.1	Stability of equilibrium . . . . .	145
6.8	Problems . . . . .	146
<b>7</b>	<b>Thermodynamic Potentials and Maxwell Relations</b>	<b>149</b>
7.1	Thermodynamic potentials . . . . .	149
7.1.1	Internal energy and enthalpy . . . . .	150
7.1.2	Helmholtz free energy . . . . .	150
7.1.3	Gibbs free energy . . . . .	152
7.2	Maxwell's relations . . . . .	153
7.2.1	How many different potentials? . . . . .	155
7.2.2	Inclusion of chemical potential . . . . .	156
7.3	Problems . . . . .	157
<b>8</b>	<b>Magnetic Systems</b>	<b>161</b>
8.1	Introduction . . . . .	161
8.2	Thermodynamic potentials . . . . .	174
8.2.1	Inclusion of PdV and $\mu dn$ terms in dU . . . . .	175

8.2.2	Magnetic Euler relations . . . . .	176
8.2.3	Counting the magnetic potentials . . . . .	176
8.2.4	Estimating PdV vs $B_e dM$ . . . . .	178
8.2.5	Equation of state for magnetic systems . . . . .	178
8.2.6	Equilibrium conditions . . . . .	181
8.3	Problems . . . . .	182
<b>9</b>	<b>Dilute Solutions</b>	<b>185</b>
9.1	General considerations . . . . .	185
9.2	Mixing revisited . . . . .	189
9.3	Osmotic pressure . . . . .	191
9.4	Vapor pressure and boiling point of solutions . . . . .	195
9.5	Freezing point of dilute solutions . . . . .	200
9.6	Problems . . . . .	201
<b>10</b>	<b>Phases and Their Equilibria</b>	<b>203</b>
10.1	The Gibbs phase rule . . . . .	204
10.2	Phases of water . . . . .	206
10.3	Salt water phase diagram . . . . .	209
10.4	Phases of Carbon . . . . .	210
10.5	Helium-3 Phase Diagram . . . . .	212
10.6	Helium-4 Phase Diagram . . . . .	213
10.7	QCD Phase Diagram . . . . .	213
10.8	Superconducting Phase Transitions . . . . .	214
10.9	High- $T_c$ Superconductor Phase Diagram . . . . .	216
10.10	Problems . . . . .	217
<b>11</b>	<b>The Clapeyron Equation</b>	<b>219</b>
11.1	Clapeyron's original treatment . . . . .	219
11.1.1	Clausius's improvement . . . . .	219
11.2	More modern approaches . . . . .	220
11.2.1	Other demonstrations . . . . .	222
11.3	Freezing curves . . . . .	223
11.3.1	Anomalous freezing curves . . . . .	224
11.3.2	Boiling and sublimation curves . . . . .	225
11.3.3	Slope near absolute zero . . . . .	225
11.4	The Clausius-Clapeyron approximation . . . . .	225
11.4.1	Dew, frost and relative humidity: An application . . . . .	226
11.5	Temperature dependence of latent heats . . . . .	229
11.5.1	Fermi's treatment . . . . .	230
11.6	Boiling points of dilute solutions . . . . .	232
11.7	Breakdown of the Clapeyron equation . . . . .	232
11.8	Magnetic Clapeyron equation . . . . .	234
11.8.1	Superconducting transitions . . . . .	235

11.9 Problems . . . . .	241
<b>12 The van der Waals Equation</b>	<b>243</b>
12.1 Thermodynamic aspects . . . . .	244
12.1.1 Thermodynamic potentials . . . . .	245
12.1.2 Various isoparametric processes . . . . .	247
12.1.3 Properties of the vdW isotherms . . . . .	250
12.2 Existence of Phases in the vdW system . . . . .	254
12.2.1 The Maxwell construction . . . . .	256
12.2.2 Stable and unstable states of the vdW system . . . . .	259
12.2.3 Phases of the vdW system . . . . .	260
12.3 Negative pressures in vdW systems . . . . .	261
12.4 Surface tension . . . . .	262
12.5 Thermodynamics of inhomogeneous substances. . . . .	265
12.5.1 van der Waals theory of surface tension . . . . .	266
12.5.2 Surface thermodynamics in vdW theory . . . . .	268
12.6 Revisiting the bubble pressure . . . . .	269
12.7 Problems . . . . .	271
<b>13 The Critical Point</b>	<b>273</b>
13.1 Overview . . . . .	273
13.2 Critical properties of water: data . . . . .	275
13.2.1 The coexistence curve . . . . .	275
13.2.2 Latent heat . . . . .	276
13.2.3 Surface tension . . . . .	277
13.3 Critical behaviour of van der Waals theory . . . . .	278
13.3.1 Critical exponents of vdW theory . . . . .	282
13.3.2 Even more exponents . . . . .	282
13.3.3 Beyond the critical region of vdW theory . . . . .	283
13.3.4 From van der Waals to Wilson via Landau . . . . .	285
13.3.5 The renormalization group . . . . .	286
13.3.6 Renormalization group inspired thermodynamics . . . . .	287
13.4 Problems . . . . .	288
<b>14 Approach to Absolute Zero</b>	<b>291</b>
14.1 Standard methods of refrigeration . . . . .	292
14.1.1 Cooling power . . . . .	292
14.2 Helium cryostats . . . . .	293
14.2.1 He4 cryostat . . . . .	294
14.2.2 He3 cryostat . . . . .	295
14.3 Dilution refrigeration . . . . .	296
14.3.1 Thermodynamics of He3-He4 mixtures . . . . .	296
14.3.2 Cooling power of dilution refrigerators . . . . .	300
14.3.3 The dilution refrigerator . . . . .	301

14.3.4	Dilution refrigeration: skeletal designs . . . . .	302
14.4	Magnetic cooling . . . . .	304
14.4.1	Principles of adiabatic cooling . . . . .	305
14.4.2	Adiabatic demagnetization . . . . .	305
14.4.3	Electronic demagnetization: some results . . . . .	309
14.4.4	Nuclear demagnetization: some results . . . . .	310
14.4.5	Cascade nuclear demagnetization . . . . .	311
14.4.6	Further lows! . . . . .	311
14.5	Pomeranchuk cooling . . . . .	312
14.5.1	The principle of cooling . . . . .	313
14.5.2	Ends or means? . . . . .	314
14.6	Problems . . . . .	315
<b>15</b>	<b>Entropy Constants</b>	<b>317</b>
15.1	Gaseous reactions . . . . .	318
15.2	Entropy constants for solids . . . . .	321
15.3	Two experimental verifications of the Sackur-Tetrode formula . . . . .	325
15.4	The entropy constants for diatomic gases . . . . .	328
15.5	Problems . . . . .	329
<b>16</b>	<b>Some Mathematical Aspects of Thermodynamics</b>	<b>331</b>
16.1	Introduction . . . . .	331
16.2	Differentials and derivatives . . . . .	332
16.2.1	Partial derivatives . . . . .	332
16.2.2	Important properties of partial derivatives . . . . .	333
16.2.3	Pfaffian forms . . . . .	334
16.3	Jacobian matrices and Jacobians . . . . .	335
16.3.1	Some important properties of Jacobians . . . . .	336
16.3.2	Half-Jacobians! . . . . .	336
16.3.3	Maxwell relations and Jacobians . . . . .	337
16.3.4	Thermodynamic potentials and Jacobians . . . . .	338
16.3.5	Another application to thermodynamics . . . . .	338
16.4	Differential forms in thermodynamics . . . . .	338
16.4.1	Some applications to thermodynamics . . . . .	339
<b>17</b>	<b>References</b>	<b>341</b>
	<b>Index</b>	<b>347</b>

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## Preface

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The great German physicist Arnold Sommerfeld, in the preface to his book *Thermodynamics and Statistical Mechanics*, had this to say: “*In contrast to classical mechanics, thermodynamics has withstood the quantum revolution without having its foundations shaken.*” A similar sentiment is echoed in the American physicist Arthur Wightman’s tribute to Gibbs that “his contributions have survived 100 years of turbulent developments in theoretical physics.” It is this resilience that makes a study of thermodynamics such a rewarding experience. In fact, not only did thermodynamics survive the revolutionary developments of quantum theory, it, in the hands of the great masters Planck and Einstein, played midwife to the very birth of quantum theory. Behind this resilience lies the great generality of the principles of thermodynamics. Usually when principles are too general, their effectiveness gets limited. But in the case of thermodynamics, its impact both on scientific thought as well as its practical impact have been unmatched by any other field of science. As for the latter aspect, the applications of thermodynamics range over physics, chemistry and engineering, and of late over biology and even black holes!

With the epoch-making developments in *Statistical Mechanics*, there is an increasing trend among physicists to treat thermodynamics as some sort of a second fiddle. This is unfortunate indeed as in reality the powers of thermodynamics remain undiminished. Of course, the two complement each other, making both of them even stronger. It is also unfortunate in another sense that young readers get the mistaken impression that statistical mechanics is easier while thermodynamics is nearly incomprehensible. This is partly because at that level, statistical mechanics is almost algorithmic, while thermodynamics seems to require constant revision of its basic tenets. In fact, one often needs, as for example in the case of magnetism, the guidance of thermodynamics in proper applications of statistical mechanics.

In this book( this is a thoroughly revised version of a previous book by the author which is no longer in print) the focus is entirely on what Pippard calls *Classical Thermodynamics*. My intention is certainly not to belittle the greatness of statistical mechanics. It is more to highlight the elegance, power, and conceptual economy of thermodynamics. To see how much of natural phenomena can be comprehended, even highly quantitatively, by thermodynamics on its own. I find it gratifying that Max Planck, Fermi, and Pippard have written their great books in a similar spirit. That this classical thermodynamics can be successfully applied even to a manifestly quantum state like the Bose-Einstein condensate is yet another example of the resilience mentioned above.

All this granted, I am sure many would like to ask “Why yet another book on thermodynamics?.” It is true that there are many many books on this subject, and some of them are classics. I would say, in response, that first of all there should always be space for more books. No two serious authors will have the same perspective and emphasis. But on a more serious note, I found, while teaching courses on this subject at the Chennai Mathematical Institute, that even the classics were not uniform in their choice of topics. By this I do not mean the applications part. They are too vast anyway to be included in any single book. I mean that even when it came to the basic aspects there was this non-uniformity. It was, therefore, my desire to distill in one book the essence of many of these classics, and more. It is unlikely that this book is ever going to replace the classics. But my hope is that it will single handedly complement most of them. As can be gleaned both from the Table of Contents and the extensive subject index, I have given detailed coverage to a number of basic topics. I have also included historical background without interfering with the scientific content, as I strongly believe that a history of ideas is as important as the ideas themselves. My second goal was to help enlarge the scope of thermodynamics for teaching purposes. My third goal was to produce a handy reference for experts. I hope I have succeeded, at least to some measure, in these aspects. Needless to say, I have not only relied on the great classics, but also on some pedagogically excellent sources, which I have described at the end of chapter 2. I have devoted an entire chapter, right in the beginning, to an overview of the book along with a reading guide to help teachers, students as well as experts and researchers.

Writing a book is a venture that can not be undertaken without the support and encouragement of many. Firstly, I thank my daughter Shantala for prevailing over me, time and time again, to write books to make my pedagogical skills available to a larger audience. I thank both her and my wife, Jayanthi, for all the difficulties on the personal front that had to be endured during the writing, and for the continuous enthusiasm they showed throughout. I thank Prof. Dr. Gmehling and Prof. Joerg Krafczyk of the Dortmund Data Bank for their immense help and permission to use their data on water. I am indebted to Rama Murthy of Indian Institute of Science for his meticulous drawing of the figures, and for his patience with many redrawings. I thank my uncle Prof. M.V. Narasimhan (passed away in 2017) for innumerable discussions on heat engines and entropy. I would like to thank the students of the 2010 batch of BSc Honours (Physics) at the Chennai Mathematical Institute for sensitizing me as to how to teach a subject like thermodynamics properly! The books arose out of this interaction. I am grateful to Naresh Kumar at TCIS, Hyderabad, for intense discussions on chapter 3 which resulted in correcting a subtle but major flaw in its earlier version.

Mysore, December 2020

N.D. Hari Dass



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# Guide for Readers and Teachers

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I have written this book with the objective that it can address i) beginning undergraduate students, ii) more advanced undergraduate or beginning graduate students, iii) teachers, and iv) experts and researchers. The entire material should be easily accessible to all except the beginning undergraduate students. In this guide, I wish to point out a practical road map to each one of these categories.

A basic knowledge of calculus is essential for all. My suggestion is to start with chapter 16; the beginning undergraduates must first master the first two sections of this chapter. After that, depending on their interest, they can master the rest of the sections. For the other categories, I would recommend reading this entire chapter thoroughly.

## Teachers

Teachers can use this book in a variety of ways. They can use it to augment the courses they are already teaching by using selective portions of the book as per their requirements. They will benefit from the large number of solved examples and problems in each chapter. Alternately, they can split the material into two courses a) a beginning undergraduate course, and b) an advanced course.

For the beginning undergraduate course: the first three sections of chapter 1, all of chapter 2, skip sections 3.2 and 3.3 but otherwise cover all other sections of chapter 3, all of chapter 4, skip chapter 5 and chapter 6, cover all of chapter 7, skip chapter 8, cover all of chapters 9 and 10, cover only the first three sections of chapter 11, only the first two sections of chapter 12, skip chapter 13, cover the first two sections of chapter 14, and skip chapter 15.

For the more advanced course, whatever was skipped above can all be covered.

## Students

Beginning undergraduate students can follow the same guidelines as given to the teachers above in designing a beginning undergraduate course. The more advanced students will be able to follow the entire book.

It is highly recommended to understand the solved examples as well as attempt as many problems as possible. It is also very important to follow the suggested reading at the end of chapter 2.

## **Experts and Researchers**

This category should find the entire book very useful. In several places, reference has been made to original literature.

## **Solution manual**

A solution manual will be made available to instructors upon request in which solutions to all the problems will be given. For lack of space many important topics like chemical reactions, saturated solutions, surface tension of solutions, equilibrium in external force-fields etc. could not be adequately discussed in the main text. These have been addressed in the solution manual. At any time, the author may be contacted at [ndhari.dass@gmail.com](mailto:ndhari.dass@gmail.com) for your suggestions, comments, and any help.

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## The Beginnings

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Like all sciences, the subject of thermodynamics too grew out of systematizing *empirical data*. Needless to say, data has no meaning unless viewed within a reasonably well-defined *conceptual framework*. The beginnings of such a framework is of course in day-to-day sense perceptions and experiences. The notion of *hotness* and *coldness* must have been around for a very long time. An important part of this experience is also the recognition that upon contact, the hotter body grows colder and the colder body grows hotter.

Another very important, though somewhat abstract, empirical notion is that of *equilibrium*. Taking the example of mixing, say, hot water with cold water, it was recognized that after some *reasonable time*, the bodies reach a common hotness, and left to themselves, would continue in that situation. In fact, experience tells us that this property of equilibrium holds even when several objects are brought in contact. So, for example, if three samples of water all with different hotnesses are mixed together, they would all reach the same hotness. This is true if instead of mixing the same substance at different hotnesses, one brings in contact totally different materials. For example, if a chunk of iron, a chunk of copper and a volume of water, all with different hotnesses, are brought together, they would all reach the same hotness eventually.

This leads to the following highly non-trivial property of thermal equilibrium: if bodies A and B are in thermal equilibrium, and bodies B and C are also in thermal equilibrium, then A and C are necessarily in thermal equilibrium. This obvious sounding, innocuous looking property is so essential for the consistency of the subject of thermodynamics that Fowler [17] has suggested elevating it to the status of a law, and consequently it is often called *The Zeroth Law*.

There are a few subtle points that are worth emphasizing in the context of thermal equilibria. In the example of the mixing two substances mentioned above, it is clear that some time has to elapse before equilibrium is reached. But how much time? This is strictly speaking beyond the purview of thermodynamics discussed in this book, which is called *equilibrium thermodynamics*. It turns out to be a very difficult question anyway. For example, if we live in a static universe (which we do not) and if the basic laws are laws of classical mechanics, the two systems will eventually go out of equilibrium! Of course, one has to wait for *super-astronomical times*, but in classical mechanics this is among the very few exact results. The phenomenon is

called *Poincaré Recurrence*. So, one has to wait long enough for equilibrium to set up, but not wait too long. Even ignoring the Poincaré Recurrence, the very fact that systems are not perfectly isolated can also take them out of equilibrium.

The other point is that the nature of the *contact* between systems has to be qualified more carefully. Whatever has been said so far only holds when contacts are such that only heat can be exchanged between the two systems. Such conditions are usually called *constraints*, or more picturesquely called *walls*.

## 1.1 Temperature and thermometry

A real progress in this process of theorizing and conceptualizing was the recognition of the notion of *temperature* as a *measure of hotness*. The main bases for this concept are the following empirical facts: i) The fact that when bodies are in equilibrium they acquire the same hotness would mean that they will also have the same temperature. ii) The property of thermal equilibrium mentioned above has the important consequence that it would be possible to decide if two bodies would be in thermal equilibrium without having to bring them into actual contact; this can be done by simply measuring their respective temperatures. If their temperatures are the same, they have to be in thermal equilibrium.

That raises the question as to how to *measure* the temperature of a body. Since the abovementioned aspects of thermal equilibrium do not depend on the relative sizes of objects, an important corollary is that by making one of the objects, to be eventually called a *thermometer*, very small, so that its contact with the bigger object does not in any appreciable manner affect the thermal condition of the bigger object, it would be possible to monitor the hotness of the bigger object by simply monitoring the hotness of the smaller system or, in other words, its temperature.

That still leaves open the question as to how to decide what the temperature of the smaller body, the thermometer, is. The empirical fact that heat affects the material state of bodies can be exploited for answering this. It can be done by measuring one of the properties of the thermometer, like its volume. For example, bodies expand upon being heated (mostly, but there are very important exceptions like ice on heating actually shrinks in volume). Therefore, properties like the volume of an object at some prescribed pressure can be used as a measure of its temperature. This is the basis of the so called *thermometry*.

But it may come as a shock to know that how this is to be done, i.e define the temperature of the thermometer in terms of, say, its volume, is essentially *arbitrary*. This can lead to troubling thoughts as to how a temperature scale that is fixed arbitrarily can play any role in a scientific theory. In particular, it can lead to worries as to how, say, two different scales of temperatures so defined can still be compatible with each other? We shall address these important concerns with an explicit model for a thermometer. But it is worth pointing out that such basic difficulties are necessarily there in every branch of physics. If we take time as an example, and a clock in place of the thermometer, questions like what defines the quantity one calls time and how exactly should the markings on a clock be determined are precisely

the sort of questions we are encountering in thermometry!

Let  $X(t)$  be some temperature-dependent property of some system as a function of its temperature  $t$ . It could, for example, be the volume of a gas under some fixed pressure  $P_0$ . But let us keep the discussion general and not specify what  $X(t)$  is. The thermometer can essentially be thought of as a measuring device for  $X(t)$ , the difference being that its readings give out temperatures in place of values of  $X$ .

The first thing one has to do is choose two *fiducial* points on the thermometer. In simple words this means we should mark two positions on the thermometer which correspond to the temperatures, according to this particular thermometer, of two standard states. For example, these can be taken to be the freezing point of water and the boiling point of water, both at one atmospheric pressure. Thus, thermometry is a relation giving  $t$  in terms of the higher fiducial temperature  $T_H$ , lower fiducial temperature  $T_L$ , where the scale agrees with some standard scale, along with the measured values of  $X$  at these three temperatures.

Let us *arbitrarily* mark the freezing point as 0 and the boiling point as 100 (as for example in the *Centigrade* scale; in the *Fahrenheit* scale these would be 32 and 212 respectively) on *all* thermometers. Let the values of the quantity  $X$  at these fiducial temperatures be  $X_0$  and  $X_{100}$ . Next, one subdivides this interval in  $X$ -space into  $N$  *uniform* divisions with  $N+1$  points. The value of  $X$  at the point labelled  $n$  is given by  $X^{(n)} = X_0 + \frac{(n-1)}{N} \cdot (X_{100} - X_0)$ . There should be no confusion between the numbers in the superscript and those in the subscript. The numbers in the subscript refer to the temperatures of the fiducial points (on the centigrade scale in this example), while the superscripts refer to the marker positions. The important point to bear in mind is that the markers on the thermometer corresponding to these values will also be *equally spaced* as the thermometer is just a measuring device for  $X$ .

So far we made several arbitrary choices, even after fixing the substance to be used in the thermometer as well as its property used for measuring temperatures. There is one more arbitrariness, which may come as a surprise to some. Even though we have  $N+1$  equally spaced markers on the thermometer, it is not *necessary* to assign numerical values to these markers in a *uniform* way! These numerical values will be the 'temperatures' read out by the thermometer. Let us look at two concrete examples to clarify the situation.

### 1.1.1 Uniform temperature scale

The simplest is to adopt a *uniform* or *linear* scale. In this case, the numerical values attached to the markers (temperatures) are given by

$$X^{(n)} = X_0 + \frac{n-1}{N} (X_{100} - X_0) \quad (1.1)$$

Thus we can mark one hundred points separated by  $\Delta t = 1$  or two hundred points separated by  $\Delta t = 0.5$  etc. with  $\Delta t = 1/N$  in general. The larger the number of subdivisions, i.e the value of  $N$ , the more accurately can the temperature be measured by this thermometer. We can work out the temperature dependence of  $X$  when this

temperature scale is used:

$$X(t) = X_0 + \frac{X_{100} - X_0}{100} t \quad (1.2)$$

which says that  $X$  increases *linearly* with  $t$ . But it should be borne in mind that this linear behaviour of  $X$  is an artifact of the way this particular temperature scale was defined. It is easy to generalize these considerations when the fiducial temperatures are arbitrary, and even on an arbitrary scale and not just on the centigrade scale as exemplified here.

For many students, this can be a source of great confusion. Often it is asked, does  $X$  really vary linearly with temperature? The point is that this question does not have much content. To specify temperatures, one must say which scale of temperature has been used. Depending on that, the same physical quantity may show different temperature-dependence. In the above example,  $X(t)$  varies linearly with temperature simply because the temperature scale was as defined in eqn.(1.1). But we have to show that physically sensible conclusions, like whether a body A is hotter than B, or whether C and D are in equilibrium etc. are indeed *independent* of the arbitrary definition of the temperature scale.

### 1.1.2 Non-uniform temperature scales

To clarify these, let us define another scale of temperature, and for ease of comparison take the same fiducial states, i.e freezing and boiling points of water at one atmospheric pressure. Let us still call these 0 and 100 degrees respectively. But instead of defining temperature according to eqn.(1.1), let us define it according to the admittedly more complex

$$\frac{t^*}{100} = \sqrt{\frac{(X - X_0)}{X_{100} - X_0}} = \sqrt{\frac{n - 1}{N}} \quad (1.3)$$

Even according to this new scale, when  $X = X_0$  the temperature  $t^* = 0$  and likewise when  $X = X_{100}$ ,  $t^* = 100$ . Therefore at the fiducial states, by design, all temperature scales agree. But they generally do not agree elsewhere. The temperature dependence of  $X$  according to the new scale is

$$X(t^*) = X_0 + (X_{100} - X_0) \left( \frac{t^*}{100} \right)^2 \quad (1.4)$$

Now we see that the same physical quantity  $X$  has a quadratic temperature dependence according to  $t^*$ -scale. It should be kept in mind that  $X_{100}, X_0$  are physical values of  $X$  and are therefore *independent* of any temperature scale.

Suppose we have two bodies A and B, and that our thermometer shows values  $X_A, X_B$  when brought in contact with them. As already stressed,  $X_A, X_B$  in themselves do not depend on any temperature scale. Further, let  $X_A > X_B$  when A is hotter than B. Then, according to the  $t$ -scale,  $t_A > t_B$  and indeed  $t$  is a good measure of hotness. But it is easily seen that  $t_A^* > t_B^*$  also, so that the  $t^*$ -scale, which has

nothing to do with the  $t$ -scale, is also an equally good measure of hotness. Finally, if according to  $t$ -scale the two bodies are in equilibrium, i.e.  $t_A = t_B$ , then from eqn.(1.2)  $X_A = X_B$ . But from eqn.(1.4),  $t_A^* = t_B^*$ . This means that even according to the  $t^*$ -scale, the two bodies are in equilibrium.

Finally, note that it is possible to convert from one scale to another:

$$\frac{t^*}{100} = \sqrt{\frac{t}{100}} \quad \frac{t}{100} = \left(\frac{t^*}{100}\right)^2 \quad (1.5)$$

and this conversion is such that a given value of  $t$  corresponds to a unique value of  $t^*$ , and vice versa. Because of this, one can, without any loss of generality, always adopt the uniform scale. But it should be stressed that the natural scale to be adopted depends on the function  $X(t)$ . For example, if  $X(t) = at^2$ , it is obviously better to adopt the non-uniform scale (quadratic in this case).

### 1.1.3 Materials for thermometry

Can any physical quantity play the role of  $X(t)$  as long as it is temperature-dependent? The answer is no. Before answering this in mathematical terms, note that water has a peculiar behaviour at  $4^\circ\text{C}$ . Its density is *maximum* at this temperature, and decreases both as the temperature increases or decreases from this value. So if we had used the density (or equivalently the volume) of water in a *water thermometer*, we would have had the peculiar situation that the temperature would be ambiguous. More precisely, it is two-valued, one of them above  $4^\circ\text{C}$  and the other below. Hence the mathematical criterion for  $X(t)$  to be admissible for thermometry is that  $t = t(X)$  must be *single-valued* which also means that  $X(t)$  itself must be a monotonically increasing or decreasing function of  $t$ . Here  $t$  can be with respect to some other thermometer. While we have illustrated these important properties of thermometry with just two examples, it is clear that there are infinitely many temperature scales all equally valid.

Clearly the temperatures so measured will depend on the material used in the thermometer, on how its properties depend on temperature as well as on the temperature scale chosen. An apparent circularity at this stage can be removed by using several types of thermometers, i.e. depending not only on different materials but also on different properties used for thermometry. Then different thermometers can be *calibrated* against each other. The properties of the substances used in thermometers must, however, obey the general mathematical criteria spelled above.

It is very important to emphasize that though temperature is a measure of hotness or coldness of a body, there is no *absolute quantification* of hotness of a body. This is because of the inherent arbitrariness in the choice of a temperature scale.

It will also become clear that no one substance or one property will suffice to define a temperature scale with arbitrary range of parameters. At temperatures low enough that a certain gas will liquefy, a gas thermometer based on this gas can not obviously be used at low temperatures. In fact under extreme conditions of temperature and pressure, radically different methods of thermometry will come

into play. Their design, the task of their accurate calibration etc. forms a fascinating part of thermodynamics.

For a very illuminating account of the history of thermometers, including the very early ones based on human physiology, see [48]. Thermometers based on gases at low pressures and average temperatures were found to agree rather well with each other. We shall also see later that thermodynamics provides a very elegant way of defining a *universal scale of temperature* which is independent of all such material details.

### Example 1.1 Comparing thermometers

Consider two constant volume thermometers, one of which is based on an ideal gas, and the other on a substance whose pressure at fixed volume follows the law  $P(T) = aT + bT^2$ ,  $T$  being the absolute scale. Find expressions for the two temperatures  $T_1$  and  $T_2$  in terms of  $T$ . Show that the temperature (on the absolute scale) at which the discrepancy between the scales is maximal is always the mid-point between the fiducial temperatures.

Let us take the ideal gas law to be  $P = cT$ , where  $c$  depends on the molar fraction of the ideal gas used in the thermometer and its volume. Let the fiducial points for both the thermometers be at  $T_A, T_B$  with  $T_A < T_B$ .  $T_1$  read on this scale is

$$T_1 = T_A + (T_B - T_A) \frac{P(T) - P_A}{P_B - P_A} = T \quad (1.6)$$

irrespective of  $c$ . Likewise, the temperature  $T_2$  read on the thermometer with the second material is

$$T_2 = T_A + (T_B - T_A) \frac{P(T) - P_A}{P_B - P_A} = T_A + (T_B - T_A) \frac{aT + bT^2 - aT_A - bT_A^2}{aT_B + bT_B^2 - aT_A - bT_A^2} \quad (1.7)$$

It is easy to see that  $T_2$  can be recast as

$$T_2 = T + b'(T - T_A)(T - T_B) \quad (1.8)$$

where  $b'$  is a constant depending on  $T_A, T_B$  and  $b/a$  (but not on  $b$  and  $a$  individually). Therefore the maximum deviation i.e  $T_2 - T_1$  occurs at  $T = (T_A + T_B)/2$ . This is to be expected as everything is symmetric between  $T_A$  and  $T_B$ .

### Example 1.2 Uniform and nonuniform scales

Consider two constant pressure thermometers both of which use an ideal gas as the material. One adapts a uniform scale while the other adapts a quadratic scale. Take the fiducial temperatures to be 0 and 100 on the celsius scale. If there are  $N$  subdivisions in both cases, find  $T_1^{(n)}$  and  $T_2^{(n)}$ .

On the uniform scale the temperature corresponding to the marker  $n$  is

$$T_1^{(n)} = 100 \frac{n - 1}{N} \quad (1.9)$$



while on the quadratic scale

$$T_2^{(n)} = 100 \sqrt{\frac{n-1}{N}} \quad (1.10)$$

Thus with 100 subdivisions the first nonzero marking will occur at a temperature of  $10!$  Clearly, on the nonuniform scale one must take  $N$  to be sufficiently large. If the first nontrivial reading is to be at  $t=1$ ,  $N$  should be  $10^4$ . For that case, the second nontrivial reading will be at  $t_3 = \sqrt{2}$ , the next at  $\sqrt{3}$  etc..

### Example 1.3 A water thermometer

Water has its maximum density at  $4^\circ\text{C}$ . Denoting this density as  $\rho_4$  and the density of liquid water at  $0^\circ\text{C}$  as  $\rho_0$ , the variation of density can be modelled as  $\rho(t) = \rho_0 + t(\rho_4 - \rho_0)/4$  for  $0 < t < 4$ , and by  $\rho(t) = \rho_4 + (t - 4)(\rho_0 - \rho_4)/4$  for the range  $t \geq 4$ . Discuss the peculiarities of this water based thermometer.

It is clear that density as a function of temperature is not single valued in this case. In fact, densities at temperatures  $t + \tau$  and  $t - \tau$  (on the centigrade scale) are both equal. Thus a thermometer based on water will not be able to distinguish these temperatures when  $\tau \leq 4$ . However, when  $\tau > 4$ , i.e when  $t > 8$ , density becomes a single valued function of temperature and water qualifies to be a good thermometer material as per our earlier discussion. Else, one will have to use separate water thermometers for the respective temperature ranges above. However, it must be stressed that the differences in density are very small in practice. The density at  $0^\circ\text{C}$  is  $0.9999 \text{ g/cc}$  while the density at  $4^\circ\text{C}$  is  $1.0000 \text{ g/cc}$  (definition).

## 1.2 Ideal gas laws

We now turn to a discussion of the thermal properties of the so called *Ideal Gases*. An understanding of these is important from many different perspectives including their relevance for the *Gas Thermometers*. Historically, long before these empirically determined gas laws were established, thermometry had already reached a good degree of sophistication. The gas thermometer designs shall be based on these laws. At this stage it may be hard to motivate what one means by an *ideal gas*, but that should become clearer as we proceed.

The immediate temptation for a modern reader is to think of  $PV = nRT$ , where  $P$  and  $V$  are the pressure and volume respectively, while  $T$  is the temperature,  $n$  the number of *moles* of the gas, and finally  $R$  is the so called *Gas Constant* (it is said that the letter  $R$  is in honour of Regnault, whose work will appear prominently in any discussion on the development of thermodynamics). But one should resist that for several reasons, both historical as well as scientific. That this is so can immediately be seen on noting that temperatures in this equation refer to the *Kelvin* or *Absolute* scale, something that came much after the gas laws were discovered. Equally importantly, this single equation is a concatenation of three distinct, and equally important, laws of gases. Each of these is conceptually different and each was discovered at very different times. It is necessary to pay attention to these nuances

to get a proper understanding of what is collectively called the ideal gas law. That will also turn out to be crucial to the understanding of gas thermometry.

Denoting temperatures by  $t$  (say, as measured by some thermometer according to some chosen temperature scale), the first relevant law in this connection is the *Boyle-Mariotte* law (Boyle 1658, Mariotte 1676; but in those days scientists often discussed their researches in monographs published many years after their work), which states that

$$P^{(i)}V^{(i)} = \theta^{(i)}(t) \quad (1.11)$$

This law states that for a given mass of a gas, the product  $PV$  depends only on its temperature. In the above, we have labelled the gases by an index  $i$  to allow for the possibility that while for each species pressure is in inverse proportion to its volume, the product  $PV$  could vary from gas to gas.

In most modern texts, this point is glossed over and the product is taken to be the same for all gases. But careful historical accounts [43] have asserted that that was not what Boyle had claimed in actuality. Though Boyle was careful enough to clearly point out that the said relationship had only been established in a narrow range of pressures and temperatures, it appears as if his experiments were done only on air. Therefore the logical possibility that the functions  $\theta^{(i)}$  could be different must be allowed for in a careful enunciation of the Boyle-Mariotte law.

For gas thermometry, it makes a considerable difference whether  $\theta^{(i)}$  is different for different gases or not. In the physical ranges where  $\theta(t)$  satisfy the conditions for consistent thermometry discussed above, if these products are not the same, any one of them can be used to construct a bona-fide gas thermometer, and in general these thermometers will not agree with each other, though all of them can be calibrated against each other. Further, as explicitly shown in section 1.1 on thermometry, each of them can be brought to the linear form, a form associated with the text book formulations, by choosing the thermometer material appropriately. But mention had been made of the fact that a large number of gas thermometers agree rather well with each other. This is only possible if for this class of gases the function  $\theta(t)$  is the same to a good accuracy. Boyle's law does not claim any such universality.

In fact, the source of that universality lies in yet another of the gas laws, the so called *Gay-Lussac-Charles's Law*. Gay-Lussac announced his results in 1802 in the journal *Ann. de Chimie* but even then he acknowledged the fact “..citizen Charles had noticed the same property in these gases 15 years ago..”[20]. Therefore, it is appropriate to call this law as the *Gay-Lussac-Charles's law*. But what exactly did this law claim, and what exactly is its impact on gas thermometry?

Unfortunately, textbooks and other modern accounts of this miss the essentials. They also wrongly attribute to this law conclusions that were never claimed, and what is worse, conclusions that obfuscate important scientific issues. For example, many of them claim that according to this law, 'for a given mass at constant pressure,  $\frac{V}{T}$  is the same for all gases.' As commented before, the Kelvin scale was unknown at the time, and consequently this could not have been the original formula. Some others say that according to this law 'the fractional change in volume for a given mass of any gas at constant pressure is proportional to the change in temperature'

while yet another source claims that according to this law 'the fractional change in volume at constant pressure for a change in temperature of 1 °C is the *same* for all gases.'

Fortunately, the English translation of Gay-Lussac's original French paper is available [20]. He has recorded his claims in such a precise way as to be far more useful for the current purposes than any of the modern renderings. It turns out that Gay-Lussac did not study any detailed temperature dependence of volumes of gases at constant pressure, nor did he study the the fractional changes in volume per degree Celsius. What he did show was, in his own words, *All gases, whatever may be their density and the quantity of water which they hold in solution, and all vapors expand equally between the same degrees of heat.* In this context, *equal expansion* should be understood as the *ratio* of the change in volume to the original volume, and the phrase *same degrees of heat* meaning given initial and final temperatures. In fact, he studied the expansion as gases were heated, according to him, between temperatures of melting ice and boiling water. In other words, the precise statement of the Gay-Lussac-Charles's law should be taken to be

$$\frac{V_{100}^{(i)} - V_0^{(i)}}{V_0^{(i)}} = f(P) c(0, 100) \quad (1.12)$$

for all gases when their masses are held fixed. Here  $c(0, 100)$  is a number that depends on the two temperatures of 0 and 100 on the centigrade scale. Combining eqn.(1.12) with the Boyle-Mariotte law of eqn.(1.11) would give

$$\frac{\theta^{(i)}(100) - \theta^{(i)}(0)}{\theta^{(i)}(0)} = f(P) c(0, 100) \quad (1.13)$$

for all  $i$ . That is possible only if  $f(P)$  is a constant independent of  $P$ , and  $\theta^{(i)}(t) = \theta(t)$  for all  $i$ . Furthermore,  $f(P)$  can be taken to be 1 without loss of generality and in that case  $c(0, 100) = \frac{\theta(100) - \theta(0)}{\theta(0)}$ . Therefore, the true import of Gay-Lussac-Charles law is that the product  $PV$  is indeed the same function of temperature for all gases.

This has the profound consequence that if Gay-Lussac-Charles and Boyle-Mariotte laws are exact, *all gas thermometers* based on volumes of gases would agree with each other. Gases for which these laws are exact will be called *Ideal*. When any of the ideal gases is used as a material for a thermometer and a *linear* scale is chosen,  $\theta(t) = \theta_0(1 + \alpha t)$ . In that case, the *equal expansion* of Gay-Lussac is simply  $100\alpha$ .

### 1.2.1 The Kelvin scale

Now we come to the second result of Gay-Lussac as declared by himself. according to him, the *equal expansion* for all the gases was found to be  $100/266.66$  on the centigrade scale [20]. Equating this to  $100\alpha$  yields  $\alpha = 1/266.66$ . Now,  $\theta(t) = \theta_0(1 + \alpha t)$  can be reexpressed as  $\theta(t) = (\theta_0\alpha)(\alpha^{-1} + t)$ . Hence, the temperature scale can be taken to be  $T(t) = 266.66 + t$ . The modern value of the zero of Kelvin scale expressed in Celsius is 273.13 as against Gay-Lussac's value of 266.66. But

considering his times, his value is pretty close indeed. In terms of this new scale the gas law will take the form  $PV = kT$ .

This new scale was introduced by Lord Kelvin and hence carries the name *Kelvin Scale*. The Kelvin and centigrade scales are related by just a *constant shift*. Hence temperature differentials on both scales are the same. Whereas in the earlier scale, changes in volume at constant pressure were proportional to changes in temperature, in the Kelvin scale, volumes of ideal gases are themselves proportional to temperature. The zero on this scale has the interpretation of being the temperature at which volumes of *all* ideal gases vanish if the pressure is kept nonzero. It is yet another matter that before such a temperature almost every known gas becomes a liquid to which the gas laws are no longer applicable.

In reality neither of the above mentioned laws is exact and deviations, even if small, are frequent. Then the gas thermometers will not all agree with each other, and there is really no criterion to choose one over the other. For each of them, a Kelvin-like scale can be introduced, and for each of them their zero on the centigrade scale will be somewhat different. The same Lord Kelvin also showed how a temperature scale can be introduced without reference to any material, not even perfect gases (and therefore independent of any gas law), which shall be called the *Absolute Scale* of temperature. In practice, the Kelvin scales of ideal gases is very close to this absolute scale.

The last ingredient in the gas law is the *Avogadro's law* formulated in 1811. Avogadro's law, as formulated by him, said *equal volumes of gases under the same external conditions of pressure and temperature contain equal number of corpuscles*. In modern terminology Avogadro's *corpuscles* are the *molecules*. The seeds for this law were laid in Dalton's *law of multiple proportions* for chemical compounds and Gay-Lussac's *law of integral volume ratios* for gases.

Avogadro formulated this law with an atomistic view of matter. Though today we know that the nature of matter is indeed atomistic, at the time of Avogadro, and to even much later times, atomism remained a speculation. Even at the time of Boltzmann it remained so, and the first vindication of this age-long and profound conjecture came only in the wake of Albert Einstein's work on *Brownian Motion* in 1905. As emphasized earlier, the spirit of thermodynamics is to involve as little as possible of microscopic details, whether empirically well established or merely speculative, in its description. On the other hand, it would be futile to completely ignore the microscopic reality. Therefore, what is needed is a very minimalistic attitude towards microscopics.

With this in mind, the famous physical chemist Ostwald, a long time critic of atomism, suggested to use the concept of *moles* instead of molecules. A *gram-mole* of a gas would be a certain mass characteristic of the gas. For Hydrogen it is 2gms etc. The Ostwald reformulation of Avogadro's law would then read *equal volumes of gases under the same external conditions of pressure and temperature contain equal moles of the gas*. Stated this way, and with an operational way of determining the number of moles in a given mass, all reference to atomism has been removed. Another equivalent formulation is to say that all gases under the same external conditions

have the same *molar volumes*.

As an example of molar volumes, consider Hydrogen gas whose molar weight is 2gms. The density of Hydrogen gas at 0°C and 1 atm. of pressure is about  $9.0 \times 10^{-2}$  g/liter. The molar volume is easily calculated to be 22.2 liter. What is remarkable is that a gram-mole of every gas occupies this very volume at the said pressure and temperature. This is really a first glimpse into the atomic nature of matter.

The final form of the ideal gas law after combining all the three laws is

$$PV = nRT \quad (1.14)$$

where  $n$  is the number of moles,  $T$  the temperature in Kelvin, and  $R$  the so called *gas constant* with a numerical value of 8.31 Joules/K.

### 1.2.2 Non-ideal gases

As already mentioned, in reality no gas is perfectly ideal and departures from the gas laws discussed earlier are the rule rather than the exception. Many alternative equations have been proposed, each with its positive as well as negative features. Here are just a few of the most prominent ones.

**van der Waals equation**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (1.15)$$

**Clausius equation**

$$\left(P + \frac{an^2}{T(V + nc)^2}\right)(V - nb) = nRT \quad (1.16)$$

**Dieterici equation**

$$P(V - nb) = nRT e^{-\frac{an}{VRT}} \quad (1.17)$$

Of these the van der Waals equation played a major role in explaining the liquefaction of gases. In a separate chapter we show how this equation provides a simple model for almost everything that one needs to learn and understand in thermodynamics.

## 1.3 Heat and specific heats

As we saw earlier a hotter body on contact with a colder body becomes itself colder, while at the same time the colder body gets hotter. So it is legitimate to think in terms of an *exchange of heat* between the two bodies. This is where the notion of *heat* enters the subject. The above process, then, is described as the hotter body giving up a certain amount of heat to the colder body. The concept at this stage is only intuitive and heuristic. A quantification of this concept and finally an elucidation of the *nature* of heat are among the prime objectives of thermodynamics.

The quantification is done through the following, arbitrarily chosen, criterion: the unit of heat is a Kcal or kilocalorie, and it is the amount of heat needed to raise the temperature of 1 Kg of water under one atmospheric pressure from  $14.5^{\circ}\text{C}$  to  $15.5^{\circ}\text{C}$ .

For any body, the *specific heat*  $c$  is given by the amount of heat required to raise the temperature of 1 kg of the substance by 1K. Denoting the amount of heat by  $dQ$ , the definition of specific heat is  $c = \frac{dQ}{dT}$ . Note that while defining the calorie, the heat transferred to water was at the constant pressure of one atmosphere. It will turn out that the amount of heat required to raise the temperature of a body by a given amount depends on the external conditions. Consequently there are many types of specific heats. All this will be clarified in great detail as we go along.

### 1.3.1 Nature of heat

One of the most important questions in thermodynamics concerns the *nature of heat*. It is interesting that none of the gas laws required any understanding of heat for their formulation. In fact their statement only involves the mechanical notion of pressure, the geometrical notion of volume in addition to that of temperature and molar content. While temperature is a measure of hotness, it is not heat *per se*. This is indeed a fortunate circumstance as far as the gas laws are concerned, as their validity is not entangled with the correctness or otherwise of any particular *theory of heat*.

One of the earliest such was the *Phlogiston* theory. We shall not discuss this at all. For one thing, this theory was discarded long ago, and more importantly it had no *predictive power* whatsoever. The next serious contender was the *Caloric* theory, chiefly propounded by Lavoisier. Unlike the Phlogiston theory, the caloric theory was capable of making specific and some very sophisticated predictions. The fundamental and pioneering works of the genius Sadi Carnot were all based on this theory. We shall describe Carnot's seminal work in detail.

The basis of the caloric theory was the following: while heat may be added or subtracted from bodies, it is not obvious whether a concept of a *total heat contained* by a body in some thermodynamic state makes sense or not. The caloric theory claims it does. This theory goes further and states that heat is an indestructible fluid. Consequently, the total heat of a body is the sum total of all heat that has flown in and flown out, there being no other mechanism to alter the amount of heat in the body. More precisely, the caloric theory claims that *heat is a state function* very much like pressure, volume, temperature etc. This aspect of caloric theory can be expressed in a mathematically precise manner as then  $dQ$  is a *perfect differential*. We shall first describe Carnot's work based on this theory in detail, then discuss various arguments and experiments that were put forward in its criticism before going on to develop the theory of heat as understood by post-Carnot thermodynamics. Carnot's theory is remarkable in that even in a cyclic process where total heat absorbed has to be necessarily zero in accordance with the caloric theory, net work can be produced.



The modern theory of heat, in contrast, refutes the caloric theory by claiming heat can be created and destroyed by other agencies, principally work of various kinds like *mechanical, electrical, magnetic* etc. Since it can easily be shown that work can not be a state function, and in fact depends on the history of how one state was transformed to another as a result of work performed, it follows that heat can not be a state function either. The post-Carnot view is that heat is yet another form of energy interconvertible with other forms of energy like mechanical, electrical etc. Furthermore, the *new thermodynamics* specifies a precise conversion factor between heat and work, a development as revolutionary as Einstein's famous  $E = mc^2$ , in both its conceptual depth as well as its scientific impact. Subsequently, the principle of conservation of energy takes form as *the First Law of Thermodynamics*. Contrary to the impression created that heat can be freely and completely converted to work, thermodynamics imposes *an absolute upper limit* to the efficiency with which heat can be converted to work. This is the content of *the Second Law of Thermodynamics*, a law unsurpassed in its depth and a law that has impact even on the most modern branches of physics today.

Before turning to a description of Carnot's work, we shall introduce in more precise terms notions very basic to the thermodynamic description as *thermodynamic states and their transformations, constraints and walls*, and finally the notion of *reversible and irreversible changes*. Carnot uses all these notions in a precise manner in a way that is completely consistent with their post-Carnot meanings. It appears to the author that precise formulations of the notion of a state, of reversible and irreversible process may indeed be due to Carnot himself.

### 1.3.2 States and transformations

**States:** By a *Thermodynamic State* we shall mean the *equilibrium* states of a system. Though it would seem natural to include only stable equilibrium states, it turns out useful to include even unstable and metastable equilibrium states also in the thermodynamic state space. So, a thermodynamic state of a *single component system* is characterized by well defined values of temperature, pressure and volume. If it is a *multicomponent system*, in addition to P, V and T, additional parameters like the *molar fractions* are needed to specify the state. If the system is also *magnetic*, then the magnetic degrees should also be included.

**Equations of State:** These are relations between the parameters of a thermodynamic state that lead to a *complete thermodynamic specification* of the system. For example, in the ideal gas case  $PV = nRT$  is one such equation. For a more structural meaning of these equations, please see chapter 6. There are as many equations of state as there are *independent* degrees of freedom.

**Transformations:** Any change of state is a *transformation*. The changes in the parameters during a general transformation could be anything subject to the equations of state. When the transformation connects states whose degrees of freedom are very close (neighbouring states), the transformation is called infinitesimal. For both kinds of changes (transformation) a further, very important, distinction should

be made between so called *irreversible* and *reversible* changes.

**Reversible and Irreversible changes:** We can try to illustrate these concepts by considering a cylinder filled with a gas and fitted with a piston. Imagine the cylinder in contact with a *heat reservoir* which is nothing but a body much larger than the cylinder, kept at a constant temperature. We can imagine loading the piston with enough weights to completely balance the gas pressure. If we increase the pressure by a very small amount, the gas will quickly come to a new equilibrium position at a slightly smaller volume. This is an example of an infinitesimal transformation. Now reduce the pressure and the gas will start expanding; one can go on reducing the pressure gently so that after some large number of steps both the volume and pressure have changed substantially. This would amount to a change that is not infinitesimal.

Now imagine that there is friction between the piston and the cylinder walls. Irrespective of which way the changes are made, i.e increase of pressure or decrease of pressure, the moving piston will dissipate heat. So a sequence of changes in pressure  $P \rightarrow P + \Delta P \rightarrow P$  will dissipate energy both ways, and even though the gas has been brought back to its original state, the surroundings have certainly undergone some change. When that happens, we say the change is *irreversible*. While reversible changes are always infinitesimal, infinitesimal changes can be both reversible as well as irreversible.

But for Carnot's times this would not be a good example as it presupposes that friction can lead to generation or *creation* of heat. Though admittedly correct from the point of view of modern thermodynamics, such an assertion would not be tolerated by the caloric theory. So we should characterize reversible and irreversible changes in a way that would be insensitive to the actual nature of heat. Such a characterization would be: *a reversible change, whether finite or infinitesimal, should be such that at the end of the combined operation of the original process and its exact reverse, no changes should have occurred in the surroundings.* Any process not fulfilling this will be deemed *irreversible*. Carnot indeed used such a refined notion in his seminal work.

In the specific example of the steam engine, he cited effects such as the heating of the boiler walls through conduction to be the ones that would spoil the reversibility of the changes made on the water-steam system. Clearly if the system is expanded to include not just steam and water, but also various surrounding elements including the boiler walls, the seemingly irreversible nature of changes to the subsystem of steam and water can be reconciled with reversible changes of the larger system. Precisely such nuances concerning reversibility and irreversibility also show up in the seemingly unconnected case of *Quantum Measurements!*

There is another aspect of irreversibility that is important to highlight; while reversible changes have necessarily to be slow (quasi-static) though the reverse is not true, i.e not every slow change is reversible, sudden changes are, as a rule, irreversible. Imagine reducing the pressure on the piston suddenly and by a large amount. The gas will go through various stages before eventually settling to a final equilibrium state. But the path from the initial state to the final is not representable as a se-



quence of intermediate equilibrium states. So in the, say, PV-diagram, an irreversible change will appear as a sudden jump. The conceptually cleanest characterization of irreversible changes is given in the context of the second law of thermodynamics, but in the present context that would be like putting the cart before the horse.

**Walls and Constraints** Very often, useful and interesting changes are such that some parameter is held fixed. For example, if we enclose gas in a box of fixed volume, only P and T are variable and because of the gas law only one of them is an independent variable. So the set of possible changes is *one-dimensional* in contrast to the full, *unconstrained* changes, which in this case are *two-dimensional*. Such changes are called *constrained* and the *constraint* in this case is  $V = \text{const.}$ . As in this example, it is the walls that enforce the constraint, Callen picturesquely calls all constraints as arising due to *Walls* even though literally that may not be the case. Changes that maintain volume are called *isochoric*. Likewise, we can think of changes under constant pressure, called *isobaric*. Changes at the same temperature are called *isothermal*. Systems can also be completely thermally insulated from their surroundings and changes are then called *adiabatic* (care should be taken not to confuse this word with what is used in classical mechanics). Such changes are also called *isentropic*, i.e the constraint being constant entropy, but we have to wait till we have discussed the second law of thermodynamics for its justification. Lastly, it is possible to consider transformations that do not change the number of moles. In what follows, we shall focus only on such changes. We shall consider changes of molar concentrations while dealing with *phase equilibria*.

### 1.3.3 Some examples

We now present some examples, based on the ideal gas law, to illustrate the concepts discussed above. Let us start with *reversible isochoric* processes. Then the only independent variable for a simple single-component system is either P or T. Changing one changes the other. An observable associated with such changes is the *pressure coefficient* defined as  $\beta_P = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V$ . For one mole of an ideal gas this can easily be worked out using the ideal gas law to be  $\frac{1}{T}$ . At close to freezing point of water this is close to  $\frac{1}{273}$ , the expansion coefficient used in gas thermometry.

Likewise, if we consider *reversible isobaric* processes, i.e processes under constant pressure, the independent variables are now V and T. An observable associated with such changes is the *expansion coefficient* defined by  $\beta_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ . It again follows from ideal gas law that this is also  $\frac{1}{T}$ , same as the pressure coefficient.

The observable associated with *reversible isothermal* processes is the fractional change of volume per unit change of pressure, i.e  $-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ . It is defined with a negative sign as the volume is expected to *decrease* with increased pressure. Called the *isothermal compressibility* and denoted by  $\kappa_T$ , for ideal gases it equals  $1/P$ , as can easily be checked.

An example of an *irreversible isothermal process* is the mixing of two samples of a gas at the same temperature but each sample having different volume and different mass. Likewise, an example of an *irreversible isobaric process* is the mixing

of two samples of gas at the same pressure but different temperatures. The last two examples bring out yet another aspect of irreversibility, namely a process is irreversible if it can proceed *spontaneously* but not its reverse.

Actually, there are relationships between quantities characterizing these different constrained processes. That follows from the *triple product rule* of partial derivatives:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \quad (1.18)$$

On using the other very important property of partial derivatives, namely,

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1} \quad (1.19)$$

it is easy to show that

$$\frac{\beta_V}{\kappa_T} = P\beta_P \quad (1.20)$$

It is to be noted that these relations are valid for all thermodynamic systems whether they are solids, liquids, or gases. Among gases they hold for ideal as well as non-ideal gases. It is the existence of such very general relationships that makes thermodynamics so powerful. For example, knowing  $\beta_V, \beta_P$  would immediately determine  $\kappa_T$  without a need for its independent determination.

#### Example 1.4 Work by ideal gases

Calculate the work done by an ideal gas for i) an isothermal expansion from volume  $V_1$  to  $V_2$  at  $T$ ; ii) an isothermal rarefaction from pressure  $P_1$  to pressure  $P_2$  at  $T$ ; iii) from volume  $V_1$  to  $V_2$  during an isobaric process at  $P$ ; iv) from temperature  $T_1$  to  $T_2$  during an isobaric process at  $P$ , and finally, v) from volume  $V_1$  to  $V_2$  during an adiabatic process.

For the ideal gas  $PV = nRT$  where  $n$  is the number of moles present. The infinitesimal work done by the system is  $PdV$ , and the total work done is the integral of this along the path describing the process. Without specifying a path, it is meaningless to talk of the work done as the latter is path-dependent.

i) For isothermal processes  $T$  is constant. Since the question specifies the changes in volume, pressure  $P$  is eliminated in favor of  $V$  according to  $P = nRT/V$ . This gives the work done in going from  $V_1$  to  $V_2$  to be  $W = \int nRT(dV/V)$  to be  $nRT \ln(V_2/V_1)$ .  
 ii) In calculating the work done in this case, we should eliminate the volume in favor of pressure. This leads to  $dW = -nRTdP/P$  and the total work done is  $W = -nRT \ln(P_2/P_1)$ . It should be recognized that this is the same expression as in i) but expressed in terms of the pressures. iii) It is trivial to find out the work done in this case as  $P$  remains constant, i.e  $W = P(V_2 - V_1)$ . iv) Now we eliminate  $V$  in terms of  $T$  to get  $dW = nRdT$ , therefore the work done is  $W = nR(T_2 - T_1)$ . v) In this case the adiabatic relation gives  $PV^\gamma = c$ , where the constant is determined by the initial pressure and volume. Straightforward integration yields  $W = c(V_2^{1-\gamma} - V_1^{1-\gamma})/(1-\gamma)$ .

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## Some Mathematical Aspects of Thermodynamics

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### 16.1 Introduction

In this chapter we discuss some mathematical aspects of thermodynamics. This is not going to be an extensive account of the foundations and applications of a mathematical theory of thermodynamics. It is instead intended in the first place as a guide to the mathematics that has already been extensively used so far in the book like the properties and uses of the *partial derivatives*, *integrability conditions* etc. Therefore, the first parts of this chapter will explain, in as straightforward a manner as possible, these aspects. Readers who were unfamiliar with these concepts and could not therefore fully appreciate the scope of this book (and others of this nature) are urged to gain full familiarity with these parts. They are absolutely essential for a proper understanding of the full powers of thermodynamics.

A logical next step to the introduction of partial derivatives is the so called *Pfaffians*, a short name for *Pffafian form of differential equations*. An important issue in this context is the solvability of these differential equations which leads to the notion of *integrability conditions*. Again, this is crucial for a proper appreciation of thermodynamics. Many of these properties have already been widely used in the book and the reader is urged to use the material in the text as examples of these concepts. Most of the properties of thermodynamic potentials including the Maxwell relations are particular applications of these concepts.

After this, we shall explore interesting structures like *Jacobian matrices* and their determinants called *Jacobians*. There is an intimate relationship between partial derivatives and Jacobians, which will be explained in reasonable detail. We shall then introduce what we call *half-Jacobians*. Though this is a purely formal device, it has amazing applications in thermodynamics. Examples will be given of their use in getting Maxwell relations as well as their use in getting various properties of the thermodynamic potentials. As an application we shall show how Jacobians provide compact and elegant means of proving some results that were shown using the properties of partial derivatives.

Then we shall introduce the powerful notions of *differential forms* and their properties. These provide extremely compact codifications of the various laws of

thermodynamics. We shall again provide examples of their use in thermodynamics. It should be emphasized that while all these mathematical techniques enable one to derive results known earlier in compact, succinct and elegant ways, they do not really add anything significant towards a deeper physical understanding of thermodynamics. Nevertheless, they offer very powerful techniques which should be part of the 'armory' of any serious student of thermodynamics.

## 16.2 Differentials and derivatives

This section must be well known to most readers, but it is still included for the sake of completeness, and also to help the few who are not familiar with it. If we have a function  $f(x)$  of a single variable  $x$ , the differential  $df(x)$  of  $f(x)$  is

$$df = f(x + dx) - f(x) \quad (16.1)$$

The derivative of  $f(x)$  with respect to  $x$  is defined as  $(f(x + dx) - f(x))/dx$  in the limit in which  $dx \rightarrow 0$ :

$$\frac{d}{dx} f(x) = \frac{df}{dx} \text{ as } dx \rightarrow 0 \quad (16.2)$$

This allows  $df$  to be written, to first order, as

$$df = \frac{d}{dx} f(x) \cdot dx \quad (16.3)$$

Now the first derivative is a function of  $x$  and one can construct its derivative which is the second derivative  $\frac{d^2}{dx^2} f(x)$  of  $f(x)$  and so on.

### 16.2.1 Partial derivatives

Suppose we have a function of two variables,  $f(x,y)$ ; then the above considerations can be generalized. To first order we expect  $df = a dx + b dy$ . Now there is a new question that we can ask, i.e, how  $f(x,y)$  changes when, say,  $x$  is changed to  $x+dx$ , but not changing  $y$ . Then  $df = a dx$  allowing a new type of derivative to be identified with  $a$ . It is denoted by  $\left(\frac{\partial f}{\partial x}\right)_y$  and is called a *partial derivative* of  $f(x,y)$  with respect to  $x$ . Likewise we can have the partial derivative  $\left(\frac{\partial f}{\partial y}\right)_x$  and the relation, to first order,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad (16.4)$$

Now the partial derivatives are themselves functions of  $(x,y)$  and one can construct various second derivatives of  $f(x,y)$ . Consistency requires

$$\frac{d^2}{dx dy} f(x, y) = \frac{d^2}{dy dx} f(x, y) \quad (16.5)$$

leading to the important consequence

$$\frac{\partial}{\partial x} \left( \left( \frac{\partial f}{\partial y} \right)_x \right)_y = \frac{\partial}{\partial y} \left( \left( \frac{\partial f}{\partial x} \right)_y \right)_x \quad (16.6)$$

Here  $\dots|_x$  means the quantity evaluated while  $x$  is held fixed etc.

### Example

Let  $f(x, y) = 2xy^2 + 7x^2y + x^2 + 3xy + 6y^2 + 2x + 4y + 5$ . Let us evaluate the partial derivative  $\left( \frac{\partial f}{\partial x} \right)_y$ . This means we must find the derivative of  $f(x, y)$  with respect to  $x$ , while keeping  $y$  fixed. In other words, as far as  $x$ -dependence is concerned  $y$  will act like a constant whose derivative wrt  $x$  is zero. Then,  $\left( \frac{\partial f}{\partial x} \right)_y = 2y^2 + 14xy + 2x + 3y + 2$ . Likewise,  $\left( \frac{\partial f}{\partial y} \right)_x = 4xy + 7x^2 + 3x + 12y + 4$ . The partial derivative of  $\left( \frac{\partial f}{\partial x} \right)_y$  with respect to  $y$ , keeping  $x$  fixed, is therefore  $14x + 3$ , while the partial derivative of  $\left( \frac{\partial f}{\partial y} \right)_x$  wrt  $x$ , keeping  $y$  fixed is also  $14x + 3$ . This is the meaning of eqn.(16.6).

### Example from thermodynamics

Consider the specific heat  $C_V$ . Its physical meaning is that while keeping the volume of the system fixed, say by enclosing a gas in a rigid container, the amount of heat that must be added to increase the temperature by  $dT$  is  $C_V dT$ . As we have seen, partial derivatives abound in thermodynamics.

#### 16.2.2 Important properties of partial derivatives

Let us consider a quantity  $u$  that changes by  $du$  when another quantity  $v$  is changed by  $dv$ , while a third quantity  $w$  is held fixed. By our previous considerations  $\left( \frac{\partial u}{\partial v} \right)_w = du/dv$  in the limit both  $du$  and  $dv$  tend to zero. On the other hand,  $\left( \frac{\partial v}{\partial u} \right)_w$  is  $dv/du$  in the same limit. Therefore, it must follow that

$$\left( \frac{\partial u}{\partial v} \right)_w = \left( \frac{\partial v}{\partial u} \right)_w^{-1} \quad (16.7)$$

So far we talked about partial derivatives as derivative wrt one independent variable, say  $x$  in the above example, while another independent variable,  $y$  in the above example, was held fixed. But things can be more general and we can talk about partial derivatives when some function of the two variables is held fixed. To illustrate this, consider a function  $f(x, y)$  of two independent variables  $(x, y)$ , so that

$$df(x, y) = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \quad (16.8)$$

which always holds. Now consider varying  $x$  and  $y$  in such a way that  $f(x, y)$  is fixed, i.e  $df=0$ . The ratio  $dy/dx$  in the limit both  $dx, dy$  tend to zero while keeping  $f$  fixed

is by definition  $\left(\frac{\partial y}{\partial x}\right)_f$  and one gets

$$0 = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_f \rightarrow \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1 \quad (16.9)$$

which is the *triple product rule* for partial derivatives used extensively in the book. In arriving at its final form in eqn.(16.9), note that we have made use of eqn.(16.7) twice.

What many beginners find intriguing about this rule is that a 'chain rule' for derivatives ends up with a negative sign! But the above derivation is so transparent that this should not be bothersome any more. Another fact that intrigues them is that the partial derivative  $\left(\frac{\partial y}{\partial x}\right)_f$  is non-vanishing even though x and y were declared to be independent. The resolution is that this partial derivative is evaluated keeping the f(x,y) fixed which makes the variations dx and dy no longer independent.

### 16.2.3 Pfaffian forms

Consider k independent variables  $x_1, x_2 \dots x_k$  and an equation of the form

$$df(\{x_i\}) = f_1(\{x_i\})dx_1 + f_2(\{x_i\})dx_2 + \dots + f_k(\{x_i\})dx_k \quad (16.10)$$

where we have used the short hand notation  $\{x_i\}$  to denote possible dependence on all the independent variables. This is called a *Pfaffian form* or *Pfaffian form of differential equation*. An important question is the conditions the coefficient functions  $f_i$  must obey in order that this differential equation can be solved (or 'integrated') to give a function f. Let us, for the sake of clarity, consider only two independent variables  $x_1, x_2$ , and consider a Pfaffian differential equation

$$df(x_1, x_2) = N(x_1, x_2)dx_1 + M(x_1, x_2)dx_2 \quad (16.11)$$

It is obvious from previous definitions that  $N = \left(\frac{\partial f}{\partial x_1}\right)_{x_2}$  and  $M = \left(\frac{\partial f}{\partial x_2}\right)_{x_1}$ , and by eqn.(16.6), one must have  $\left(\frac{\partial N}{\partial x_2}\right)_{x_1} = \left(\frac{\partial M}{\partial x_1}\right)_{x_2}$ . Therefore, unless the coefficient functions M, N in the Pfaffian form of eqn.(16.11) satisfy this *integrability condition*, there will be no solutions to the Pfaffian differential equation. This has been the basis of the many thermodynamic identities that were discussed in the book. In fact, all the Maxwell relations are integrability conditions of this type. To clarify the issues raised here, let us consider a famous example where a Pfaffian-looking form is actually not integrable!

#### The first law

Let us consider the first law for an ideal gas with constant  $C_V$  (these considerations are generally valid, not just for this example), i.e  $dQ = C_V dT + PdV$ . This superficially looks like a Pfaffian form. It would have been a Pfaffian form if instead of  $dQ$  we had  $dQ$ . Now  $C_V dT = d(C_V T)$  so integrability of this equation would

have been possible only if  $PdV$  could also have been written as a df for all  $V$  and  $T$ . But a moment's inspection shows that that would have been possible only if  $P$  were a function of  $V$  alone, which it certainly is not. The integrability condition  $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T = 0$  would also have demanded the same. Of course, the physical significance of the failure to integrate this equation is that heat  $Q$  is not a state function and is instead path-dependent. Hence the convention to denote changes in  $Q$  by  $\delta Q$  and not  $dQ$ . This is also equivalent to the notions of exact and inexact differentials introduced earlier in the book.

### 16.3 Jacobian matrices and Jacobians

Let us illustrate the relevant ideas for a case with two independent variables, say,  $x_1, x_2$ . Generalization to several variables is straightforward. Now suppose we want to work with another set of independent variables, say,  $x'_1, x'_2$ , which are functions of the older independent variables. In the thermodynamic context, an example would be working with  $P, T$  instead of  $P, V$ . In that simple example one of the variables, i.e.  $P$ , does not change but the other, say,  $T$  is changed to  $V$  but by equation of state  $V = V(T, P)$ .

The first question that arises is about the check for the independence of the new variables, as after all not every pair of functions of the old variables can form independent variables. This is answered through the properties of the *Jacobian Matrix*  $J_{ij}$ , defined as

$$J_{ij} = \left(\frac{\partial x'_i}{\partial x_j}\right)_{..} \quad (16.12)$$

where  $..$  stands for keeping fixed all independent variables other than  $x_j$ . For the specific example of the two variable case, the Jacobian matrix is given by

$$J_{11} = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2} \quad J_{12} = \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1} \quad J_{21} = \left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \quad J_{22} = \left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} \quad (16.13)$$

The *Jacobian*  $J$  is the determinant of this Jacobian matrix:

$$J = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2} \left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} - \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1} \left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \quad (16.14)$$

In answer to the question about the independence of  $(x'_1, x'_2)$ , the answer is that they will be independent only if  $J \neq 0$ , i.e. if the Jacobian matrix is *non-singular*. There are many notations used for the Jacobian. We shall use the notation  $J = \frac{\partial(x'_1, x'_2)}{\partial(x_1, x_2)}$  i.e.

$$J = \frac{\partial(x'_1, x'_2)}{\partial(x_1, x_2)} = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2} \left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} - \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1} \left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \quad (16.15)$$



### 16.3.1 Some important properties of Jacobians

It is immediately obvious that Jacobians satisfy

$$\frac{\partial(x, y)}{\partial(a, b)} = -\frac{\partial(y, x)}{\partial(a, b)} \rightarrow \frac{\partial(x, x)}{\partial(a, b)} = 0 \quad (16.16)$$

A non-trivial property of the Jacobians is their *composition law*

$$\frac{\partial(x, y)}{\partial(a, b)} \cdot \frac{\partial(a, b)}{\partial(c, d)} = \frac{\partial(x, y)}{\partial(c, d)} \quad (16.17)$$

It is difficult to establish this directly from the definition of the Jacobian given above. If the independent variables are thought of as *coordinates* of a two-dimensional manifold, the invariant area element is given by  $dA = \sqrt{g} dx dy$  where  $g$  is the determinant of the *inverse metric* on the manifold. Under changes of coordinates from  $(x, y)$  to, say  $(a, b)$ , this changes according to

$$g(x, y) = \left\{ \frac{\partial(x, y)}{\partial(a, b)} \right\}^{-2} g'(a, b) \quad (16.18)$$

The area  $dA$  being a geometrical quantity does not depend on the choice of coordinates and one gets the important relation

$$dx dy = \frac{\partial(x, y)}{\partial(a, b)} \cdot da db \quad (16.19)$$

Considering the sequence of transformations  $(x, y) \rightarrow (a, b) \rightarrow (c, d)$  and directly comparing to the transformation  $(x, y) \rightarrow (c, d)$ , and making use of eqn.(16.19) at every step leads to eqn.(16.17).

Yet another important property of Jacobians is that every partial derivative can itself be expressed as a Jacobian:

$$\frac{\partial(x, z)}{\partial(y, z)} = \left( \frac{\partial x}{\partial y} \right)_z \quad (16.20)$$

This can easily be shown from the definition of the Jacobian itself.

### 16.3.2 Half-Jacobians!

Let us first introduce a convenient shorthand for Jacobians [60]:

$$\frac{[x, y]}{[a, b]} = \frac{\partial(x, y)}{\partial(a, b)} \quad (16.21)$$

Then the composition law of eqn.(16.17) can be recast as

$$\frac{[x, y]}{[a, b]} \cdot \frac{[a, b]}{[c, d]} = \frac{[x, y]}{[c, d]} \quad (16.22)$$



Now consider the independent variables (c,d) to be arbitrary, in principle specifiable, but never specified in practice. Furthermore, introduce yet another notation via

$$\{x, y\} = \frac{\partial(x, y)}{\partial(c, d)} \quad (16.23)$$

We can call objects like  $\{x, y\}$  *half-Jacobians* as only half the information required to compute the Jacobian is explicitly available, i.e (x,y). But it must be kept in mind that  $[x,y]$  takes on definite value once (c,d) is specified. As a Jacobian, it never vanishes. This will turn out to be very important. Because of this, eqn.(16.17), or equivalently eqn.(16.22) can be recast in terms of half-Jacobians as

$$\frac{\partial(x, y)}{\partial(a, b)} = \frac{\{x, y\}}{\{a, b\}} \quad (16.24)$$

Let us consider an interesting application of half-Jacobians by rewriting eqn.(16.8) with the help of eqn.(16.20) and eqn.(16.24) as

$$df = \frac{\{f, y\}}{\{x, y\}} dx + \frac{\{f, x\}}{\{y, x\}} dy \quad (16.25)$$

which, on using  $\{x, y\} = -\{y, x\}$ , can be written as

$$\{x, y\} df + \{f, x\} dy + \{y, f\} dx = 0 \quad (16.26)$$

### 16.3.3 Maxwell relations and Jacobians

Now we illustrate the powerfulness of Jacobians by showing the equivalence of the four Maxwell relations to a *single* Jacobian condition. Consider the Maxwell relation  $(\frac{\partial V}{\partial S})_P = (\frac{\partial T}{\partial P})_S$  and rewrite it in terms of half-Jacobians as

$$\frac{\{V, P\}}{\{S, P\}} = \frac{\{T, S\}}{\{P, S\}} \rightarrow \{T, S\} = \{P, V\} \quad (16.27)$$

In other words this Maxwell relation is equivalent to the statement that the transformation (T,S) to (P,V) is *area preserving*, i.e the corresponding Jacobian is unity. This is the familiar result that the Carnot cycle represented in (P,V) or (S,T) coordinates has the same area! Now it can be shown that  $\{T, S\} = \{P, V\}$  also reproduces the other three Maxwell relations. We show one of them explicitly:

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{\{S, T\}}{\{P, T\}} = -\frac{\{P, V\}}{\{P, T\}} = -\left(\frac{\partial V}{\partial T}\right)_P \quad (16.28)$$

### 16.3.4 Thermodynamic potentials and Jacobians

As a prelude, let us consider the Pfaffian  $dz = M(x, y)dx + N(x, y)dy$ , from which it follows that, for some other choice of independent variables (a,b)

$$\left(\frac{\partial z}{\partial a}\right)_b = M(x, y)\left(\frac{\partial x}{\partial a}\right)_b + N(x, y)\left(\frac{\partial y}{\partial a}\right)_b \rightarrow \{z, b\} = M\{x, b\} + N\{y, b\} \quad (16.29)$$

This holds for arbitrary choice of b and can be used to efficiently generate a number of identities. Of course, N and M must satisfy the integrability conditions characteristic of the Pfaffian forms.

This result can be readily applied when z can be taken to be any of the thermodynamic potentials. Let us illustrate by taking z to be U, H, F and G respectively, yielding

$$dU = TdS - PdV \rightarrow \{U, X\} = T\{S, X\} - P\{V, X\} \quad (16.30)$$

$$dH = TdS + VdP \rightarrow \{H, X\} = T\{S, X\} + V\{P, X\} \quad (16.31)$$

$$dF = -SdT - PdV \rightarrow \{F, X\} = -S\{T, X\} - P\{V, X\} \quad (16.32)$$

$$dG = -SdT + VdP \rightarrow \{G, X\} = -S\{T, X\} + V\{P, X\} \quad (16.33)$$

X can be taken to be any independent variable, and these can yield a host of identities.

### 16.3.5 Another application to thermodynamics

We close this discussion with another application to thermodynamics. Following Rao [60] we apply the method of Jacobians to derive eqn.(3.51) from chapter 3. Let us first recall that equation:

$$TdS = C_V dT + \frac{T\alpha}{\kappa_T} dV \quad (16.34)$$

From our earlier discussion, it is easy to see that

$$dS = \frac{\{S, V\}}{\{T, V\}} dT + \frac{\{S, T\}}{\{V, T\}} dV \quad (16.35)$$

The specific heat at constant volume  $C_V$ , the coefficient of expansion  $\alpha$ , and the isothermal compressibility  $\kappa_T$  can be expressed in terms of Jacobians as follows:

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = T \frac{\{S, V\}}{\{T, V\}} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \frac{\{V, P\}}{\{T, P\}} \quad \kappa_T = -\frac{1}{V} \frac{\{V, T\}}{\{P, T\}} \quad (16.36)$$

On using  $\{S, T\} = \{V, P\}$ , it is easy to see that eqn.(16.35) and eqn.16.36) are indeed the same.

## 16.4 Differential forms in thermodynamics

Now we very briefly present the uses of *differential forms* in thermodynamics. As structures, differential forms are even more formal than Jacobians, and a full discussion of all their nuances is beyond the scope of this book. Let us begin with some

definitions. All functions  $f$  are said to be *0-forms*. Their differentials,  $df$ , are said to be *1-forms*. There is an operation, called the *exterior derivative*, denoted by  $\mathbf{d}$  which acts on all forms and increases their rank by one. For example, acting on functions, which are 0-forms, exterior derivative yields the 1-form  $df$  i.e  $\mathbf{d}f = df$ . At this level, and only at this level, the exterior derivative coincides with the differential. If  $\omega$  is a  $p$ -form,  $\mathbf{d}\omega$  is a  $p+1$ -form.

A crucial property of exterior derivatives is that  $\mathbf{d}(\mathbf{d}(\text{anything})) = 0$ . In this respect  $\mathbf{d}$  differs fundamentally from differentials, and this is a frequent source of confusion in this subject. The next structure of importance is the so called *wedge product* of differential forms. If  $\omega$  is a  $p$ -form, and  $\eta$  is a  $q$ -form,  $\omega \wedge \eta = (-1)^{pq} \eta \wedge \omega$  is a  $p+q$ -form.

A very important rule to remember is for the exterior derivative of wedge products. If  $\omega$  is a  $p$ -form, and  $\eta$  is a  $q$ -form, the rule is

$$\mathbf{d}(\omega \wedge \eta) = \mathbf{d}\omega \wedge \eta + (-1)^p \omega \wedge \mathbf{d}\eta \quad (16.37)$$

Let us pause and consider a few examples. Let us consider two functions  $f$  and  $g$ ; as per our earlier discussion, both are 0-forms, and their wedge product should also be a 0-form. Indeed, the product function  $fg$  is a 0-form, being another function. Next consider the wedge product of  $f$  with  $dg$ , the latter being a one form. This gives the 1-form  $fdg$ . If we apply eqn.(16.37) to the product  $fg$ , we get  $d(fg) = df \cdot g + f \cdot dg$ , which is again familiar. But let us apply it to  $fdg$ :

$$\mathbf{d}(fdg) = df \wedge dg \quad (16.38)$$

as  $\mathbf{d}^2g = 0$ . This is a 2-form.

### 16.4.1 Some applications to thermodynamics

Consider the 1-form  $dU = TdS - PdV$ , which is nothing but the first law. Applying the exterior derivative to this

$$\begin{aligned} \mathbf{d}(dU) &= 0 = dT \wedge dS - dP \wedge dV \\ &= \left( \left( \frac{\partial T}{\partial V} \right)_S dV + \left( \frac{\partial T}{\partial S} \right)_V dS \right) \wedge dS - \left( \left( \frac{\partial P}{\partial S} \right)_V dS + \left( \frac{\partial P}{\partial V} \right)_S dV \right) \wedge dV \\ &= \left( \left( \frac{\partial T}{\partial V} \right)_S + \left( \frac{\partial P}{\partial S} \right)_V \right) dV \wedge dS \end{aligned} \quad (16.39)$$

This is nothing but the Maxwell relation M.1!

As yet another example, consider the same first law but written as  $dS = (dU +$   
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$PdV)/T$ , and consider  $0 = \mathbf{d}(dS)$  i.e

$$\begin{aligned}
 0 &= \mathbf{d}\left(\frac{dU}{T} + \frac{P}{T}dV\right) \\
 &= -\frac{1}{T^2}dT \wedge dU + \frac{1}{T}dP \wedge dV - \frac{P}{T^2}dT \wedge dV \\
 &= -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T dT \wedge dV + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V dT \wedge dV - \frac{P}{T^2}dT \wedge dV \\
 &= \left\{-\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2}\right\} dT \wedge dV \quad (16.40)
 \end{aligned}$$

This is nothing but the fundamental equation encountered earlier in eqns.(3.9,3.11, 3.43):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (16.41)$$

As a last application of the differential forms we now consider the relationship of the wedge products and Jacobians. Let us restrict ourselves to the case of two independent variables. In particular, let us consider the transformation taking two independent variables  $(x,y)$  to two other independent variables  $(a,b)$ . Let us start with the 2-form  $dx \wedge dy$ :

$$\begin{aligned}
 dx \wedge dy &= \left(\left(\frac{\partial x}{\partial a}\right)_b da + \left(\frac{\partial x}{\partial b}\right)_a db\right) \wedge \left(\left(\frac{\partial y}{\partial a}\right)_b da + \left(\frac{\partial y}{\partial b}\right)_a db\right) \\
 &= \left(\left(\frac{\partial x}{\partial a}\right)_b \left(\frac{\partial y}{\partial b}\right)_a - \left(\frac{\partial x}{\partial b}\right)_a \left(\frac{\partial y}{\partial a}\right)_b\right) da \wedge db \\
 &= \frac{\partial(x,y)}{\partial(a,b)} \cdot da \wedge db \quad (16.42)
 \end{aligned}$$

From this we can easily deduce the composition law of Jacobians of eqns.(16.17, 16.22). For that, consider the sequence of transformations  $(x,y) \rightarrow (a,b) \rightarrow (p,q)$  and we have

$$dx \wedge dy = \frac{\partial(x,y)}{\partial(a,b)} \cdot da \wedge db = \frac{\partial(x,y)}{\partial(a,b)} \frac{\partial(a,b)}{\partial(p,q)} \cdot dp \wedge dq = \frac{\partial(x,y)}{\partial(p,q)} \cdot dp \wedge dq \quad (16.43)$$

The composition law then follows.

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# Index

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- $C_P - C_V$ 
  - ideal gas, 44
  - vdW theory, 245
- $He_3$  Phases, 212
  - Pomeranchuk point, 212
  - solid phase more disordered, 212
- $He_4$  Phases, 213
- $\lambda$ -transition, 124, 213
- $\lambda$ -transitions, 234
- 23 Maxwell relations, 157
- Absolute temperature scale, 75
  - and ideal gas scale, 76
  - Carnot cycle, 76
  - Carnot theory, 77
  - practical utility, 76
  - uniform and nonuniform, 77
- Absolute zero, 84, 291
  - BEC limits, 314
  - adiabatic is not isentropic, 86
  - attainability, 84
  - Carnot cycle argument, 84
  - isotherm is isentrope, 88
  - isothermal equals adiabatic, 85
  - unattainability in finite steps, 88
- Acoustic refrigeration, 292
- Adiabatic and isothermal atmosphere, 49
- Adiabatic cooling, 305
- Adiabatic demagnetization, 305
  - and third law, 306, 309
  - cascade, 311
  - efficiency at low T, 307
  - nuclear, 310
  - paramagnetic, 307
- Adiabats
  - vdW theory, 247
- Anomalous freezing curves, 224
  - lowering of freezing point, 224
- Atomic nature, 11
- Avogadro number, 191
- Avogadro, A., 10
- Bardeen, J., 216
- BCS theory, 216
- Bérard, J., 18, 37, 112
- Berthelot, P., 86, 87
- Black Joseph, 112
- Blackbody radiation vs ideal gas, 104
- Bohr, N., 111, 118, 119
- boiling of water
  - changes in U, Q and W, 48
- Boltzmann, L., 10, 39, 104, 118, 122, 243, 244, 256
- Born, Max., 121
- Bose, S.N., 107, 122, 123, 314
- Bose-Einstein condensates, 107, 123, 314
- Bose-Einstein statistics, 107
- Boyle, Robert, 8, 128
- Boyle-Mariotte law, 8
  - universality of temperature, 8
- Brayton cycle, 100
  - magnetic, 100
- Brownian motion, 10
  - Avogadro's number, 10
- Bubble pressure, 270
  - large bubbles, 270
  - small bubbles, 271

Callen, H.B., 2, 15, 127, 129, 132,  
133, 136, 142

Caloric theory, 12

and Carnot's work, 12

basics, 12

heat as a state function, 12

successes, 18

Capillarity

Gibbs theory, 265

interface thickness, 282

vdW exponent, 282

vdW exponent, 282

vdW theory, 263, 265, 282

Carathéodory, 133

Carbon dioxide

critical temperature, 273

Carnot cycle, 23

air engine, 23

and Turing machine, 18, 93

Clapeyron's analysis, 28

graphical analyses, 24

Kelvin improvement, 24

Kelvin reanalysis, 27

Maxwell improvement, 24

operational definition, 23

operational problems, 24

steam engine, 24, 28

Carnot cycle composition

caloric theory, 66

net efficiency, 66

serial and parallel, 65

Carnot cycle universality, 60

and perpetual machines, 60

entropy axiom, 60

equivalence to entropy axiom, 62

general conditions, 61

Carnot theory, 17–32

$C_P - C_V$ , 31

analog of first law, 32

analogy with waterwheels, 20

Carnot's scepticism, 18

Clapeyron equation, 17

concept of cycles, 19

efficiency of heat engines, 19

Kelvin's exposé, 17

lessons for scientific method, 18

logarithmic  $C_V$ , 31

Mathematical treatment, 29–32

motive power, 19

notion of reversibility, 20

simplified presentation, 26

specific heats, 25

style of analysis, 25

the universal function  $\mu(t)$ , 29

Carnot, S., 12–14, 17–32, 39–41, 60,

61, 93, 97, 98, 112, 113

Casimir, H., 239

Chandrasekhar, S., 123

Charles, J., 8, 18

Chemical potential, 39, 131

equals Gibbs potential, 132

Euler relation, 135

Gibbs-Duhem relations, 135

Clapeyron equation, 96, 219, 221

a misnomer?, 220

a skating myth, 223

and Pomeranchuk point, 233

anomalous freezing curves, 224

as a shorthand, 62, 220

boiling point shift, 223

Clapeyron's graphical method,

219

critical phenomena, 274

Fermi's method, 222

freezing curves, 223

freezing point shift, 223

Gibbs potential approach, 220

Huang's derivation, 222

magnetic, 235

mathematical aspects, 221

original derivation, 219

reduced form, 281

superconducting transitions, 238

Clapeyron, P., 17, 23, 24, 28, 29, 32,

61, 113, 219

Clausius gas equation, 285

corresponding states, 271

critical compressibility, 285

inversion curve, 272  
 Clausius inequality, 62  
     entropy, 69  
     entropy axiom, 62  
     entropy increase, 70  
     incompleteness, 141  
     second law, 62  
 Clausius postulate, 66  
     temperature, 66  
 Clausius, Rudolf., 11, 32, 38–42, 56, 58, 61–64, 66–69, 93, 96, 97, 112, 113  
 Clausius-Clapeyron approximation, 212, 225  
 Clausius-Clapeyron equation, 62, 208, 220  
 Clément, N., 18, 32, 51, 112  
 Coalescing bubbles, 264  
 Coexistence curve, 225  
     Fermi's treatment, 231  
     slope near 0 K, 225  
 Common tangent method, 258  
 Complete thermodynamic description, 128  
 Composition of Carnot cycles, 27  
     serial and parallel, 27  
 Compressibilities  $\kappa_T$ ,  $\kappa_S$ , 82  
 Compressibility factor  
     vdW gas, 271  
 Compressibility factor  $Z$ , 251  
 Container filling, 51  
 Cooling power, 292  
     at 0 K, 294  
     dilution refrigerators, 300  
     Pomeranchuk cooling, 314  
 Cooper, L., 216  
 Cornell, E., 314  
 Counting Maxwell relations, 156  
 Critical  
     isobar, 283  
     isochore, 283  
     isotherm, 283  
 Critical compressibility factor  $Z_c$ , 251  
     vdW theory, 251, 285  
     water, 251, 285  
 Critical data  
      $C_P$  for steam, 277  
      $C_P$  for water, 277  
     carbon dioxide, 275  
     carbon monoxide, 275  
     water, 275  
     xenon, 275  
 Critical exponents  
     surface tension, 277  
     classical, 286  
     Landau theory, 286  
     vdW theory, 282  
 Critical field  $H_c$ , 237  
 Critical Opalescence, 286  
 Critical phenomena  
     beyond Ehrenfest, 274  
     Landau theory, 286  
     specific heats, 123  
 Critical phenomenon  
     exponents, 285  
     universality, 285  
 Critical point  
     overview, 273  
 Critical point of  $He_4$ , 213  
 Critical points  
     superconducting, 238  
     vdW theory, 251  
 Cryostats, 293  
      $He_3$ , 296  
      $He_4$ , 294  
     limitations of  $He_4$ , 295  
 Curie law, 179, 308  
     and third law, 179  
 Curie, P., 116  
 Current density, 162  
 Cusp in BEC specific heat, 123  
 Cycles, 19  
     importance in thermodynamics, 19  
     in Carnot theory, 19  
 Dalmia Cements., 98  
 Dalton, J., 10, 18, 243

Davy, H., 36  
 Debye frequency, 121  
 Debye temperature, 321  
 Debye theory  
     high T, 322  
 Debye theory of specific heats, 120  
 Debye, P., 120, 121, 324  
 Delaroche, F., 18, 37, 112  
 Dependencies among Maxwell  
     relations, 154  
 Desalination, 139, 194  
 Desormes, C., 18, 32, 51, 112  
 Dewar, J., 118  
 Dews and Frosts, 226  
 Diamagnetic substances, 166  
 Diamonds are not forever, 211  
 Diatomic gases, 328  
     Sackur-Tetrode relation, 328  
 Diesel cycle, 99  
     nonuniversal efficiency, 100  
 Difference in G for vapor and solvent,  
     197  
 Differential forms, 338  
     in thermodynamics, 339  
 Differential susceptibility, 168  
 Dilute solutions, 185  
     boiling point elevation, 196  
     chemical potential, 198  
     entropy, 186, 187  
     free energy F, 188  
     freezing point depression, 200  
     Gibbs potential G, 189  
     lowering of vapour pressure, 195,  
         196  
     mixing entropy, 187  
     surface tension, 289  
 Dilution refrigeration, 301–304  
 Dry static energy, 51  
 Dulong, P., 37, 112, 117, 118  
 Dulong-Petit law, 117  
     superconducting transitions, 240  
 Ehrenfest, P., 219, 233, 240  
 Einstein and Gibbs, 39  
 Einstein theory of specific heats, 118,  
     119  
 Einstein, A., 10, 13, 22, 35, 87–89,  
     103, 106, 107, 111, 112,  
     117–120, 122, 123, 243, 262,  
     286, 294, 314, 321  
 Elevation of boiling points, 199, 232  
 Energy and work in magnetic  
     systems, 163  
 Energy conservation, 37  
     Mayer's ideas, 37  
 Energy density of magnetic fields, 163  
 Energy representation, 129  
 Enthalpy, 46, 80, 150  
     and  $C_P$ , 47  
     and flows, 46  
     at 0 K, 300  
     mixing, 189  
     porous plug expt., 46  
 Enthalpy diagrams, 51  
 Entropy, 58  
      $He_3$  near Pomeranchuk T, 313  
     and disorder, 74  
     and information, 75  
     another state function, 58  
     helium mixtures, 298  
     magnetic, 236  
     mixing, 138  
     Photons, 107  
     radiation field, 104  
     Shannon, 75  
     superconducting phase, 237  
     surface, 269  
     units, 73  
     vdW theory, 246  
 Entropy and photons, 107  
 Entropy axiom, 58  
     and Sommerfeld, 56  
     Clausius inequality, 62  
     from first law, 58  
     mathematical form, 59

- restrictions on U, 59
- U for ideal gas, 59
- U for vdW gas, 59
- universality of Carnot cycles, 60
- Entropy constants, 317
  - and quantum theory, 320
  - and sublimation, 324
  - and vapor pressure, 325
  - in Debye's theory, 321
  - in Einstein's theory, 322
  - in gaseous reactions, 318, 319
  - scaling properties, 328
- Entropy of radiation, 106
- Entropy representation, 129
- Equilibrium, 144
  - matter-flow, 145
  - Stability, 145
  - Thermal, 144
  - thermo-mechanical, 145
  - Thermodynamic, 144
- Euler relations, 134
  - chemical potential, 132
  - magnetic analog, 176
- Euler relations in entropy rep., 135
- Evaporative cooling, 292
- Extensive and intensive variables, 131
- Extensivity in multicomponent systems, 138
- External magnetic field, 166
- Fall of caloric theory, 36
  - Davy's expts., 36
  - Rumford's expts., 36
- Fermi liquid, 299
- Fermi, E., 196, 222, 230, 231, 256, 319, 323–325
- Ferromagnetic substances, 166
- First law, 35–40
  - adiabaticity for ideal gas, 45
  - Carnot's influence, 41
  - conservation of energy, 35
  - for magnetic systems, 163
  - heat as energy, 35
  - internal energy, 39
  - mathematical form, 42
  - surfaces, 265
  - two new forms of energy, 35
  - U for ideal gas, 43
- First law for magnetic systems, 167
- Flory-Huggins theory, 189
  - mixing entropy, 191
- Fowler, R.H., 1
- Free expansion
  - finite, in vdW, 249
- Freezing curves, 223
  - and Clapeyron eqn., 224
- Freezing mixtures, 201
- Fugacity, 272
- Fundamental equations, 132
- Gas constant R, 7, 73
  - units and value, 73
- Gas equations
  - Clausius equation, 285
- Gas laws, 7
  - Avogadro's law, 10
  - Boyle-Mariotte, 8
  - Clausius, 11
  - Dieterici, 11
  - Gay-Lussac and Charles, 8
  - ideal, 7
  - precise form of Gay-Lussac law, 9
  - van der Waals, 11, 129
- Gay-Lussac, J., 8–10, 18, 26, 38, 128
- Gay-Lussac-Charles law, 9
  - and Kelvin scale, 10
  - universality of ideal gas scales, 9
- Gibbs paradox, 138, 187, 297
  - helium mixtures, 297
- Gibbs paradox for dilute solns., 187
- Gibbs potential
  - G, 153
- Gibbs potential and chemical potential, 132
- Gibbs potential barrier, 211
- Gibbs potential G, 152
- Gibbs, J.W., 39, 152, 203, 204, 265, 268

Gibbs-Duhem relations, 135, 143  
     entropy representation, 135  
     vdW theory, 246  
 Gorter, C.J., 239  
 Gradient demagnetization, 312  
 Griffith, R., 162, 164, 165  
 Guggenheim, E.A., 1  
  
 Half Jacobians, 336  
 Hari Dass, N.D., 32  
 Hawking, S., 114  
 Heat, 11  
     and  $E = mc^2$ , 13  
     Caloric theory, 12  
     friction, 14  
     modern theory, 12  
     nature of, 12  
     Phlogiston theory, 12  
 Heat Engine universality, 22  
     Caloric theory, 22  
     Einstein equivalence principle, 22  
     thermodynamics, 22  
 Heat Engines, 21  
     ideal, 21  
     universal efficiency, 21  
 Heat of reaction, 319  
 Height of atmosphere, 50  
 Helium mixtures, 296  
     dilution refrigeration, 298  
     no Gibbs paradox, 297  
     quantum mechanics, 297  
     third law, 297  
 Helium-4 enthalpy, 300  
 Helmholtz free energy  $F$ , 150  
     bound on maximum work, 152  
     vdW theory, 246  
 Helmholtz, H., 37, 38, 150  
 High  $T_c$  superconductivity, 216  
 Higher order Clapeyron eqns., 240  
 History of second law, 66  
 Hoff, van't., 194, 289  
 How many eqns. of state?, 128  
 Huang, K., 222  
  
 Ideal Fermi gas, 299  
 Inhomogeneous media, 265  
     equilibrium conditions, 266  
     meaning of  $P$ , 267  
     surface and bulk, 268  
 Interface chemical potential, 268  
 Internal energy, 150  
     Clausius formulation, 39  
     Clausius's integrability condition, 42  
     nonvanishing if  $C_V \neq 0$ , 40  
     water vs ice, 50  
 Internal energy of liquids, 188  
 Irreversibility, 20  
     importance of the notion, 20  
     in Carnot theory, 20  
     operational meaning, 20  
     perpetual machines, 21  
 Irreversible processes, 15  
     mixing, 16  
 Ising model, 275  
     three dimensional, 275  
     water exponents, 286  
 Isobaric processes  
     heat as a state function, 46  
     uses of enthalpy, 46  
 Isothermal changes of  $S$ , 85  
  
 Jackson, J.D., 163, 164, 167  
 Jacobians, 335  
     in thermodynamics, 337  
     properties, 336  
 Jaynes, E.T., 141  
 Jeans, J., 106  
 Joule coefficient  
     van der Waals, 249  
 Joule expansion, 38  
     Joule coefficient  $\eta$ , 47  
 Joule's free expansion expt., 38  
 Joule, J., 36–38, 43, 46, 58, 61, 128, 129  
 Joule-Kelvin process, 38  
     enthalpy, 46  
     integral, 272



- inversion curve, 272
- Joule-Thomson coefficient  $\mu_{JT}$ , 47
- Joule-Thomson coefficient
  - general expression, 249
- Kadanoff, L., 286
- Kammerlingh Onnes, H., 214, 239, 252
- Kammerlingh Onnes, J., 285
- Kanada, 243
- Keesom, W.H., 239
- Kelvin, 7–10, 23, 24, 27–29, 36, 38, 41, 42, 46, 47, 56, 66–69, 75, 77, 93, 97, 113, 128, 144
  - William Thomson, 17
- Kelvin postulate, 67
  - and Clausius formulation, 67
  - perfect heat engines, 67
- Ketterle, W., 311
- Kinetic theory, 39, 74
- Kogut, J.B., 286
- Kurti, N., 311
- Land and sea breezes, 44
- Landau theory
  - exponents, 286
  - order parameter, 286
- Landau, L., 268, 269, 285, 286
- Langevin function, 183, 315
- Langevin, P., 116, 183
- Laplace, P.S., 18, 30, 49, 113
- Latent heat
  - decrease with T, 230
  - in Fermi model, 231
- Lavoisier, A., 12
- Law of corresponding states, 252, 286
  - any three parameter equation, 286
  - Clausius equation, 286
  - vdW equation, 286
- Law of mass action, 318, 319
- Le Chatelier principle, 319
- Legendre transforms and more
  - potentials, 156
- Levelt Sengers, J., 285
- Lewis, G.N., 107, 272
- Lifshitz, E.M., 268, 269
- Lindeman, F.L., 87
- Liquids, 187
  - activity, 189
  - entropy, 188
  - ideal, non-ideal, 189
- Lounasmaa, O.V., 311
- Low T specific heats, 116
  - $T^3$  dependence, 117
  - $T^{3/2}$  in BEC, 123
  - exponential dependence, 117
  - linear dependence, 116
- Mach, E., 243
- Magnetic enthalpy, 170
- Magnetic entropy, 179
- Magnetic flux density, 165
  - induction, 165
- Magnetic Maxwell relations, 175, 177
  - explicit calculations, 180
- Magnetic specific heat identities, 181
- Magnetic susceptibility, 165
- Magnetic systems, 161
  - $\vec{B}$  vs  $\vec{H}$ , 165, 167
  - eqns. of state, 178
- Magnetic vs mechanical systems, 167
- Magnetization current, 164
- Magneto-caloric effect, 304
- Magnus-Teten equation, 228
- Marcet, F., 118
- Mariotte, E., 8, 18, 128
- Maris, H., 286
- Mathematical aspects, 331
- Maxwell construction, 256
  - based on F, 258
  - based on G, 257
  - geometrical method, 256
  - Maxwell line, 257
- Maxwell line, 257
- Maxwell relations, 81, 153
  - integrability conditions, 154
  - M.1, 154

M.2, 154  
 M.3, 154  
 M.4, 154  
     superconducting transitions, 237  
 Maxwell's equations, 162  
 Maxwell, J.C., 23, 24, 39, 56, 66–69,  
     81, 103, 153, 164, 165, 256  
 Mayer, R., 37, 112  
 Mechanical eqn. of state, 130  
 Mechanical equivalent of heat, 35, 36  
     analog of  $E = mc^2$ , 35  
     Joule's apparatus, 38  
     Joule's estimate, 37  
     Mayer's estimate, 37  
 Medley, P., 311  
 Meissner, W., 214  
 Meissner-Ochsenfeld effect, 214  
 Microscopic aspects of specific heats,  
     116  
 Mixing, 137, 189  
     entropy, 138  
     dilute solutions, 187  
     enthalpy, 189  
     Gibbs paradox, 138  
     Gibbs potential, 138  
     spontaneous, 190  
 Mixing entropy  
     liquids, 189  
     perpetual machine, 139  
     polymers, 189  
 Molar volume, 11  
 Moles vs Molecules, 10  
 Müller, Ingo, 37, 112  
 Müller, Ingo, 40  
 Multiplicity of roots and phases, 256  
  
 Negative pressures, 262  
 Negative specific heats, 114  
 Negative temperatures, 85  
 Nernst heat theorem, 86  
 Nernst, W., 84, 86–89, 114, 120  
 Newton, Isaac, 19, 49, 113, 130, 149,  
     244  
 Number of Maxwell relations, 155  
 Ochsenfeld, R., 214  
 Onsager, L., 86  
 Ordering temperature, 312  
 Osmotic pressure, 192  
     and surface tension, 289  
     van't Hoff law, 194  
 Ostwald, W., 10, 39, 243  
 Otto cycle, 98  
     compression ratio, 99  
     efficiency, 99  
 Otto, N., 98  
  
 Parabolic law for  $H_c$ , 238  
 Paramagnetic substances, 166  
 Partial derivatives  
     triple product rule, 235  
 Partial derivatives and their  
     properties, 16  
 Partial derivatives as Jacobians, 336  
 Partial pressures, 140  
 Perfect engines  
     perfect heat engine, 68  
     perfect refrigerator, 68  
 Perpetual machines, 21, 22, 56  
     and irreversibility, 21  
     and universality of Carnot cycles,  
         60  
     first kind, 57  
     Helmholtz's criticism, 39  
     obvious kind, 56  
     second kind, 57  
     second law, 56  
     those that are not, 58  
     universality of heat engines, 22  
 Perrin, J., 243  
 Petit, A.T., 112, 117, 118  
 Pfaffian forms, 334  
     in thermodynamics, 334  
 Phase diagram of vdW theory, 261  
 Phase equilibrium, 203  
     Gibbs phase rule, 204, 206  
     magnetic systems, 234  
 Phases of Carbon, 210  
     triple points, 211

Phases of helium mixtures, 298  
 Phases of QCD, 213  
     critical point, 214  
 Phases of vdW theory, 260  
     meaning of  $T_c$ , 260  
 Phases of water, 206  
     anomalous freezing curve, 208  
     the critical point, 209  
     triple point, 207  
 Photon Carnot cycle, 105  
 Pippard, A.B., 46, 154, 163, 178, 212, 274  
 Planck, Max., 55, 56, 66–69, 71, 84, 87–89, 106, 114, 118–120, 122  
 Poincaré, 2  
 Poincaré recurrence, 2  
 Poisson equation, 247  
 Poisson, S., 25, 30  
 Polymers, 189  
     mixing enthalpy, 189  
 Pomeranchuk cooling, 117, 312  
 Pomeranchuk, I., 212, 213, 224, 312  
 Positivity of temperature, 134  
 Pressure dependence of  $H_c$ , 237  
 Pruss, A., 229  
  
 Quantum Chromodynamics, 274  
     phases, 274  
 Quantum Chromodynamics, critical point, 274  
 Quantum mechanics  
     mixing entropy of He, 297  
 Quark Gluon Plasma, 214  
  
 Raman, C.V., 121  
 Rankine, W., 39  
 Raoult's law, 187, 196  
 Rayleigh, Lord, 106  
 Rayleigh-Jeans law, 106  
 Refrigeration, 292  
     control parameters, 292  
 Refrigerators, 66, 67  
     and Carnot efficiency, 67  
     as heaters, 72  
     as reverse heat engine, 67  
         coefficient of performance, 67, 71  
 Regnault, H.V., 7, 29, 112, 113, 118  
 Relative humidity, 226  
 Renormalisation Group, 286  
     thermodynamics from, 287  
 Reversibility, 20  
     importance of the notion, 20  
     in Carnot theory, 20  
     operational meaning, 20  
 Reversible and irreversible melting, 74  
 Reversible cycles, 93  
     efficiencies, 93  
     Rankine cycle, 93  
 Reversing reversible engines, 70  
 Rive, A., 118  
 Rubber bands, 108, 158  
  
 Sackur, O., 320, 327–329  
 Sackur-Tetrode formula, 320, 325  
     mercury, 326  
     neon, 327  
 Saturated solutions, 201  
 Schrieffer, R., 216  
 Second law, 55  
     and directionality, 55, 74  
     and irreversibility, 70  
     Clausius formulation, 56, 66  
     Clausius inequality, 62  
     entropy axiom, 58  
     impossibility of derivation, 56  
     impossibility of perpetual motion, 56  
     Kelvin formulation, 67  
     Maxwell postulate, 68  
     obvious facts, 55  
     perfect refrigerators, 67  
     Planck postulate, 67  
     two parts, 56  
 Shannon, C., 75  
 Significance of  $s_S = s_N$ , 239  
 Solvay, E., 88, 111  
 Sommerfeld, A., 42, 55, 56, 58, 62, 114, 165  
 Sound velocity, 19

Laplace's theory, 19, 49  
 Newton's incorrect theory, 19  
 Specific heat  
     Clement Desormes method, 51  
 Specific heat of BEC, 123  
 Specific heat of diamond, 118  
     Born-Raman controversy, 122  
     experimental anomalies, 118  
 Specific heats, 11, 80  
      $C_P$ , 150  
      $C_V$ , 150  
      $C_V$  of vdW theory, 245  
     a brief history, 111–113  
     and Carnot theory, 29  
     and cooling powers, 115  
     and third law, 115  
     BCS theory, 239  
     Clement-Desormes expt., 18  
     critical phenomena, 123  
     Einstein at Solvay, 88  
     magnetic, 169  
     quantum ideal gas, 123  
     Regnault's work, 29  
     rotational contributions, 328  
     solids and liquids, 113  
     superconducting, 216, 239  
     units, 11  
     varieties of, 113  
 Specific heats and kinetic theory, 118  
 Specific heats and quantum theory, 117  
 Specific heats at absolute zero, 87  
 Srinivasan, J., 32  
 Srinivasan, R., 291  
 Steam Carnot cycle, 96  
 Stefan, J., 104  
 Stefan-Boltzmann law, 104  
 Stell, G., 275  
 Stirling cycle, 97  
 Stirling cycle efficiency, 97  
     and regeneration, 98  
     lack of universality, 97  
 Stirling, R., 97  
 Sublimation, 225  
     Fermi model, 230  
 Super leak, 304  
 Superconducting transitions, 234  
     and Clapeyron equation, 234  
     entropy changes, 236  
     P independence of  $T_c$ , 241  
 Superconductivity  
     origin of the name, 239  
 Superconductor transitions, 214  
     critical field, 215  
     critical temperature, 215  
     parabolic law, 216  
 Supersaturated vapor, 255  
 Surface enthalpy, 269  
 Surface entropy, 269  
 Surface free energy, 269  
 Surface Gibbs potential, 269  
 Surface tension, 262  
     restriction on exponent, 277  
     bubble pressure, 264  
     dilute solutions, 289  
     first law, 265  
     IAPS table, 278  
     interface G, 269  
     interpolation formula, 278  
 TdS equations, 80  
     magnetic systems, 170  
     specific heats, 83  
 Temperature, 2  
     arbitrariness in definition, 3  
     lack of absolute value, 6  
     measurement, 2  
 Temperature scales, 6  
     absolute, 75  
     centigrade, 10  
     Kelvin, 7, 10, 75  
     material dependence, 10  
     nonideal, 10  
     universal, 6  
     validity of laws, 75  
 Tetrode, H., 320  
 Thermal equilibrium, 1, 152  
     dilute solutions, 197

- empirical facts, 2
- magnetic systems, 181
- minimum F, 152
- minimum G, 153
- the zeroth law, 1
- variational principle for, 267
- Thermo-magnetic potentials, 176
- Thermocouples, 32
- Thermodynamic eqn. of state, 130
- Thermodynamic potentials
  - magnetic systems, 174
  - vdW theory, 245
- Thermodynamic potentials U,H,F,G, 155
- Thermodynamic prepotential, 154, 156
- Thermodynamic processes, 15
  - compressibility  $\kappa$ , 15
  - expansion coefficient  $\beta_V$ , 15
  - isobaric or fixed pressure, 15
  - isochoric or fixed volume, 15
  - isothermal or fixed temperature, 15
  - pressure coefficient  $\beta_P$ , 15
- Thermodynamics, 1
  - axiomatic formulations, 133
  - Carnot's precise formalism, 13
  - degrees of freedom, 13
  - empirical nature of, 1
  - equations of state, 13
  - extensivity, 131
  - gateway to quantum world, 106
  - hotness and coldness, 2
  - inhomogeneous substances, 265
  - power of, 84
  - radiation field, 103
  - renormalisation group inspired, 287
  - reversible and irreversible processes, 14
  - rubber bands, 108, 158
  - salt water phases, 200
  - second law, 13
  - states, 13
  - structure of, 127
  - the beginnings, 1
  - time, 2
  - transformations, 14
  - walls and constraints, 2, 15
- Thermodynamics of magnetic systems, 167
- Thermometers, 2
  - and clocks, 3
  - dependence on material, 5
  - history, 6
- Thermometry, 2
  - comparing different scales, 4
  - general principles, 3
  - linear and nonlinear scales, 4
  - mathematical requirements, 5, 76
  - meaning of a scale, 4
- Third law, 84, 291, 293
  - adiabatic demagnetization, 309
  - and Einstein, 87
  - and quantum theory, 321
  - Bertholot-Thomsen, 87
  - consequences, 89
  - cooling rates, 90
  - entropy constants, 88, 317
  - magnetic entropy, 308
  - Nernst's initial conjecture, 87
  - Nernst-Planck statement, 88
  - Planck, on, 89
  - Planck's refinement, 88
  - scope of, 89
  - vdW theory, 245
- Thomsen, J., 86, 87
- Thomson, B. (Rumford), 36
- Throttling, 47
- Time, 74
  - in thermodynamics, 74
- Torquato, S., 275
- Triple point
  - carbon dioxide, 275
  - water, 275
- Triple points of  $He_4$ , 213
- Turing, A., 18, 93

Universal Maxwell line, 257  
 Unphysical aspects of vdW theory, 253  
 Unstable states in vdW theory, 255  
 van der Waals equation, 11, 136, 243  
     critical points, 273  
     entropy, 246  
     free energy  $F$ , 246  
      $G$  and  $H$ , 246  
     Gibbs-Duhem relation, 247  
     internal energy  $U$ , 244  
     isotherms, 278  
     Joule coefficient, 249  
     law of corresponding states, 278  
     Maxwell construction, 278  
     negative pressures, 261  
     phase coexistence, 278  
     phases, 278  
     physical basis, 244  
     reduced form, 252, 279  
     reduced variables, 279  
     stable and unstable states, 259  
     states of, 250  
     thermodynamic potentials, 245  
     two phases of, 256  
      $V$  independence of  $C_V$ , 245  
     value of  $\frac{P_c V_c}{RT_c}$ , 251  
 van der Waals, J.D., 94, 243, 244, 252, 265–268, 273, 275, 282, 285  
 Van Hove, L., 122  
 Vapor pressure  
      $V$  independence, 221  
 Vapor pressure and entropy  
     constants, 325  
 Vapor pressure of dilute solns., 195  
 vdW Carnot cycle, 94  
 vdW critical point  
     and Ehrenfest second order theory, 283  
     diverging  $C_P$ , 283  
     various exponents, 283  
 vdW equation  
     critical points, 251  
 vdW exponents  
      $\alpha = 0$ , 283  
      $\delta = 3$ , 282  
      $\gamma = 1$ , 283  
 vdW isotherms, 250  
      $P_{max}$  and  $P_{min}$ , 253  
      $V_{max}$  and  $V_{min}$ , 253  
     unstable state, 258  
 VdW potentials in reduced form, 252  
 Venkataraman, G., 122  
 von Karman, T., 121  
 Wagner, A., 229  
 Walls and constraints, 15  
 Water dissociation, 190  
 Water thermometer, 7  
 Watt, James., 36  
 Weber, H.F., 118, 119  
 Weimann, C., 314  
 White dwarfs and neutron stars, 123  
 Wien's law, 106  
 Wien, W., 106  
 Wightman, A.S., 39  
 Wilson, K.G., 285, 286

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