

**A TREATISE ON THE
KINETIC
THEORY OF GASES**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649482672

A Treatise on the Kinetic Theory of Gases by S. H. Burbury

Except for use in any review, the reproduction or utilisation of this work in whole or in part in any form by any electronic, mechanical or other means, now known or hereafter invented, including xerography, photocopying and recording, or in any information storage or retrieval system, is forbidden without the permission of the publisher, Trieste Publishing Pty Ltd, PO Box 1576 Collingwood, Victoria 3066 Australia.

All rights reserved.

Edited by Trieste Publishing Pty Ltd.
Cover @ 2017

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form or binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

www.triestepublishing.com

S. H. BURBURY

**A TREATISE ON THE
KINETIC
THEORY OF GASES**

A TREATISE
ON THE
KINETIC THEORY OF GASES

BY

S. H. BURBURY, M.A., F.R.S.

LATE FELLOW OF ST JOHN'S COLLEGE, CAMBRIDGE.

CAMBRIDGE :
AT THE UNIVERSITY PRESS.

1899

[All Rights reserved.]

Cambridge:

PRINTED BY J. AND C. F. CLAY,
AT THE UNIVERSITY PRESS.

PREFACE.

My object in the following treatise is to apply to the Kinetic Theory of Gases a method of analysis different from that generally employed. It has been treated always on a certain fundamental assumption, namely, that the molecules of a gas are, as regards their relative motion, *independent* of one another. As a consequence, we may say as the expression, of that independence, the law of distribution of momenta assumes the exponential form e^{-AQ} , and, so far as concerns translation velocities,

$$Q = \sum m (u^2 + v^2 + w^2),$$

m being mass, and u, v, w component velocities. From this independence and from this form of Q are deduced Boltzmann's theorems, namely the H theorem, and that of the equality of mean kinetic energy for each degree of freedom.

I propose to give to Q the more general form of a quadratic function, namely

$$Q = \sum m (u^2 + v^2 + w^2) + \sum \sum b (uu' + vv' + ww').$$

Here b is a negative function of the distance r at the instant considered between the two molecules whose velocities are u, u' , etc., which function is inappreciable except for very small values of r . I shall endeavour to prove in Chapters IV, V, that without the b coefficients the motion cannot be stationary. It has been proved abundantly that, *assuming the independence*, the motion is stationary with the usual form of Q . I question the axiom, not the demonstration.

The consequence of attributing to Q the proposed new form is, that molecules near to each other have on average a motion

in the same direction. They tend to form streams. That result, if it can be established, is worth investigation.

For ordinary gases under ordinary conditions the b coefficients are probably very small, and their effect negligible in such investigations as those of Tait and Boltzmann concerning diffusion, viscosity, etc. But I think that the law e^{-hQ} in its altered form will express the state of the system without restriction as to density, except as follows. A physical limit there must be, when the gas liquefies under pressure, if not before. For it will not be contended that the distribution of momenta among the molecules of the liquefied gas is represented by the same exponential form as in the gaseous condition. An analytical limit there is, when Q in its altered form ceases to be necessarily positive, that is when the determinant of the coefficients ceases to be positive. It can be shown that this determinant does diminish as density increases, or temperature diminishes. But I have not calculated its value. It is therefore no more than a conjecture, though perhaps a plausible conjecture, that the vanishing of the determinant may coincide with the physical change in the substance.

It appears to me that the law of equality of mean kinetic energy for each degree of freedom cannot be reconciled with my proposed form of Q ; that in fact the law holds only for the limiting case of a very rare gas.

It is no light thing to question a conclusion maintained by Boltzmann, if indeed he does maintain this conclusion for all substances, or for all gases irrespective of density. I can but state the objections to this theorem, and to a certain aspect of the H theorem, as they appear to me. The reader will judge what weight is to be attributed to them.

S. H. BURBURY.

TABLE OF CONTENTS.

CHAPTER I. Arts. 1—4. Statement of the theory. 5—10. The definition of homogeneity, density, and stream motion. 11—13. Of the pressure of a gas. 14. Of the temperature. 15. Intermolecular forces defined. 16—20. Two fundamental assumptions A and B discussed	5—10. The definition of homogeneity, density, and stream motion. 11—13. Of the pressure of a gas. 14. Of the temperature. 15. Intermolecular forces defined. 16—20. Two fundamental assumptions A and B discussed
CHAPTER II. Arts. 21—26. Clausius' theorem. 27—28. Value of $\Sigma \Sigma R$ for elastic spheres. 29—30. A vertical column of elastic sphere molecules	27—28. Value of $\Sigma \Sigma R$ for elastic spheres. 29—30. A vertical column of elastic sphere molecules
CHAPTER III. 31—37. Law of stationary motion for elastic spheres. 38. The H theorem. 39—42. Discussion of the H theorem. 43—45. Application of Boltzmann's general method, making the density proportional to $e^{-2\chi}$, where χ relates to external forces. 46. Proposed inclusion of ψ the potential of intermolecular forces. 47—52. Boltzmann and Watson's generalization. Note on the H theorem	31—37. Law of stationary motion for elastic spheres. 38. The H theorem. 39—42. Discussion of the H theorem. 43—45. Application of Boltzmann's general method, making the density proportional to $e^{-2\chi}$, where χ relates to external forces. 46. Proposed inclusion of ψ the potential of intermolecular forces. 47—52. Boltzmann and Watson's generalization. Note on the H theorem
CHAPTER IV. Arts. 53—54. An extension of Clausius' theorem. 55. Case of no intermolecular forces. 56—57. Correlation of velocities proved when intermolecular forces exist. 58. Possible case of attractive forces	53—54. An extension of Clausius' theorem. 55. Case of no intermolecular forces. 56—57. Correlation of velocities proved when intermolecular forces exist. 58. Possible case of attractive forces
CHAPTER V. Arts. 60—62. Definitions of f , ξ , etc. and M . 63—68. Treatment of $\frac{dM}{dt}$ in the case of infinitely small non-colliding molecules. 69—78. Treatment of $\frac{dM}{dt}$ for elastic spheres having finite diameters	60—62. Definitions of f , ξ , etc. and M . 63—68. Treatment of $\frac{dM}{dt}$ in the case of infinitely small non-colliding molecules. 69—78. Treatment of $\frac{dM}{dt}$ for elastic spheres having finite diameters
CHAPTER VI. Art. 79. Proposed form of solution for elastic spheres. 80. Completion of the function M . 81—82. Cases in illustration. 83—84. The form of the coefficient b not determinate, but $2b$ is determinate. 85. A suggested form of (b) ; relation of $m\Sigma u^2 + \&c.$ to the Virial of intermolecular forces	79. Proposed form of solution for elastic spheres. 80. Completion of the function M . 81—82. Cases in illustration. 83—84. The form of the coefficient b not determinate, but $2b$ is determinate. 85. A suggested form of (b) ; relation of $m\Sigma u^2 + \&c.$ to the Virial of intermolecular forces

CHAPTER VII. Arts. 86—92. Treatment of molecules under finite intermolecular forces, the encounters being supposed binary. 93. A suggested extension to non-binary encounters	pp. 89—97
CHAPTER VIII. Arts. 94—96. The general law of distribution of momenta. 97. The fundamental property of the distribution. 98—100. Boltzmann's law of equal kinetic energy. 101—102. Application of Boltzmann's general method giving for density $e^{-h^2v^2/(2\pi kT)}$. 103. The vertical column again considered. 104. Boltzmann's minimum function. 105—110. General character of the motion	pp. 98—112
CHAPTER IX. Arts. 111—112. Determination of mean free path. 113—118. The fundamental theorem for Diffusion, &c.	pp. 113—121
CHAPTER X. On the relation between temperature and kinetic energy. Arts. 119—123. Natanson's theorem. 124. Method employed by Bryan and Boltzmann. 125—126. By Professor J. J. Thomson. 127—131. The Second Law of Thermodynamics. 132—133. Original proof. 134. Modified proof. 135—142. Other proofs of the same law	pp. 122—142
APPENDIX. (a)—(p). Certain propositions relating to determinants. (q). The condition that the quadratic function Q shall be necessarily positive. (r). On the value (referring to Chapters V, VI.) of $\frac{d}{dt} \iiint a^2 \frac{d\xi}{dx} dx dy dz$	pp. 143—157

CHAPTER I.

OUTLINE OF THE THEORY.

1. A GAS according to the Kinetic Theory consists of a great number of molecules in rapid motion. And the object of the theory is to explain on this hypothesis certain of the physical properties of gases.

Any quantity of gas which can be isolated for the purpose of experiments is to be regarded as containing a number of molecules practically infinite. It is not possible to control or to observe the motions of individual molecules. But the theory assumes that such motion is subject to the usual dynamical laws. Also that if the gas, as an aggregate of molecules, be at rest, no dissipation of energy takes place.

2. A molecule may consist of one or more than one atom according to the chemical constitution of the substance to which it belongs. It may be that hereafter we shall be able to explain on dynamical principles the chemical relations of atoms as constituent parts of a molecule, and of molecules *inter se*. And some progress has been made in this direction. At present the theory is concerned not with the chemical properties, but with those properties of gases which may change without any change taking place in the chemical composition of the gas: for instance, density, pressure, and temperature. And as depending on these latter, it is concerned with the phenomena of viscosity, diffusion, and conduction of heat or electricity.