Heat and Gravitation. III. Mixtures

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ABSTRACT The standard treatment of relativistic thermodynamics is not convenient for a systematic treatment of mixtures. It is proposed that a formulation of thermodynamics as an action principle may be a suitable approach to adopt for a new investigation of that and other problems in thermodynamics and astrophysics.

This third paper of the series applies the action principle to a study of mixtures of ideal gases. The action for a mixture of ideal gases is, in the first approximation, the sum of the actions for the components. The entropy, in the absence of gravity, is determined by the Gibbs-Dalton hypothesis. Chemical reactions such as hydrogen dissociation are studied, with results that include the Saha equation and that are more complete than traditional treatments, especially so when gravitational effects are included. A mixture of two ideal gases is a system with two degrees of freedom and should exhibit two kinds of sound. This is not supported experimentally and the Gibbs-Dalton lagrangian has to be modified accordingly. In the presence of gravity the Gibbs-Dalton hypothesis must be further modified to get results that agree with observation. The overall conclusion is that experimental results serve to pin down the lagrangian in a very efficient manner. It leads to a convenient theoretical framework in which many dynamical problems can be studied, and in which the incorporation of General Relativity is straightforward.

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I. Introduction

Most physical theories that have reached a high level of development are formulated as action principles. This is true of General Relativity, but it is not true of astrophysical applications of General Relativity. The reason for this historical anomaly has been the need to incorporate thermodynamics, a highly developed theory that represents the exceptions: thermodynamics is not formulated as a dynamical action principle.

This is odd, since Gibbs’ famous contributions to thermodynamics are entirely based on axioms of minimum energy and maximum entropy, stopping just short of introducing a lagrangian. That Gibbs’ “energy” can be regarded as a dynamical hamiltonian, at least in certain contexts, is well known; see Fetter and Walecka (1980).

That astrophysical problems, within a General Relativistic setting, are subject to a treatment based on an action principle was conjectured independently by Bardeen (1970), Schutz (1970) and Taub (1954). A concrete example, related to the nonrelativistic theory of Fetter and Walecka, was presented by us (Fronsdal 2007). But the absence of an established formulation of thermodynamics, suitable for the extension to the domain of General Relativity, may have led to a justifiable skepticism about the viability of this approach to astrophysical problems.

Whence the present series of papers, intended to present a view of thermodynamics that can be extended to the context of General Relativity, much in the manner in which it was done in the last cited paper, but with the thermodynamical interpretation more developed and better understood.

Our approach to thermodynamics is characterized by a complete dynamical framework based on an action principle. The action principle that describes adiabatic configurations of an ideal gas was known. Here we expand the context to include heat transfer, dissipation, mixtures and chemical reactions.

This paper is preparation for taking up one more of the issues that, it seems to us, cloud the traditional approach to relativistic thermodynamics: the treatment of mixtures. Mixtures have more degrees of freedom than those envisaged by Tolman’s relativistic equations (Tolman 1934). We begin by determining the lagrangian for a mixture of ideal gases. This requires experimental input and the first observation that is invoked is the validity of the Gibbs-Dalton hypothesis concerning the entropy of mixtures. When chemical reactions are included we obtain an expression for the degree of dissociation that is formally identical to the Saha equation. Taking the latter as a convenient, approximate summary of experimental results, we find that it places a very simple constraint on the entropy. Once the lagrangian is determined all applications are straightforward. The determination of the lagrangian by means of observation is a main strategy adopted in this paper.

A principal feature of an action principle is that all properties of a system are strongly interrelated. Having arrived at a lagrangian that is adequate for some applications, one must try to use the same lagrangian in other situations. And if other considerations require a modification of the lagrangian, then one has to accept that applications already thought to have been done will have to be revisited. For example, having found a way to account for some of the observed features of sound propagation in mixtures, we may find that difficulties arise when the theory is applied to the problem of concentrations in the atmosphere. Any modification of the lagrangian will have effects on all applications. For
another example, a polytropic model of the atmosphere cannot remain polytropic when the energy of the photon gas is taken into account, as it must for very high temperatures.

**Summary**

Section II is a brief account of the first paper in this series. The principal dynamical variables for describing a simple gas are the density, a velocity field and the temperature. Variation of the action with respect to the temperature gives a fundamental relation of the ideal gas, an expression for the entropy in terms of the density and the temperature. Any discussion of mixtures is intimately concerned with entropy. A study of simple processes, including cooling and free expansion, reveals just enough of this concept to allow us to understand mixtures, including chemical reactions.

To deal with mixtures we need additional input from experiment or from kinetic theory. A key statement that is taken from observation is the Gibbs-Dalton hypothesis about the entropy of mixtures. Traditional applications make use of general properties of the Gibbs function but all these properties are relative to the Gibbs function of a certain “reference configuration” and the investigation is hampered by the fact that this latter function is not known. For this reason, the theoretical treatment of reaction rates, for example, has limited predictive power and refers instead to a “reaction constant” that is actually a function of the temperature, to be determined by experiment. In Section III we use the experimental information that is expressed by the Gibbs-Dalton hypothesis to determine the lagrangian, thus preparing the way for many types of applications.

Turning to chemical reactions, we find that other experimental input is required. The first case studied, in Section III.3, is the simplest one, the atomization of a warm hydrogen gas. The Euler-Lagrange equations of motion lead directly to a formula for the reaction rate in terms of a single entropy parameter. This equation is formally identical to the simplest version of the Saha equation (Eggert 1919, Saha 1920). Taking this equation as a convenient summary of experimental results, we observe that this parameter is constant through the region of dissociation. That is, observation makes an especially simple statement about the lagrangian.

One could now, for example, calculate the characteristics of sound propagation in partly dissociated hydrogen. Other results that follows immediately from the equations of motion are formulas for the internal energy and the entropy. A lagrangian for more general chemical reactions is conjectured, Section III.4.

In Section IV we use this lagrangian to study the propagation of sound in a mixture. One obtains a system of two linked wave equations and two distinct normal modes, with different propagation velocities. As far as we know, this phenomenon has been recognized in the context of superfluid helium only (Putterman 1974). But this prediction of dual sound speeds is contradicted by experiment, which makes it necessary to modify the lagrangian that was built on the Gibbs Dalton hypotheses, without necessarily giving up that hypothesis, since it applies to equilibria only.

In Section V we introduce the gravitational field in the usual way, by including the gravitational potential in the hamiltonian, in each of the contexts considered and for which the lagrangian has been found. Application of the Gibbs-Dalton hypothesis to this situation is ambiguous and unsuccessful. We again turn to measurements (in the earthly
atmosphere) to determine the entropy of a mixture in the presence of gravity, obtaining density and temperature profiles in good agreement with observation.

In another paper in this series, we shall return to the context that stimulated this research, the application of relativistic thermodynamics to stellar structure and development. The generalization of the simplest lagrangian to include the effect of a generally relativistic, dynamical metric is straightforward (Fronsdal 2007).

As in all the papers of this series, viscosity is neglected and the motion is irrotational. This limitation is not as strong as it may appear to be; as may be seen from the existence of a hamiltonian formulation of a theory of turbulence (Onsager 1949).

II. The ideal gas*

II.1. The extremal principles of Gibbs

The basis for a close integration of the action principle with thermodynamics is the identification of the hamiltonian with the function

\[ H = F(V, T) + ST + PV, \]  

(2.1)

a function of 4 independent variables \( V, T, S \) and \( P \): volume, temperature, entropy and pressure. The function \( F \) is the free energy.

The states of thermodynamic equilibrium are the points in this 4-dimensional manifold at which \( H \) is extremal with respect to variations of \( T \) and \( V \),

\[ \frac{\partial H}{\partial T} \Big|_{V,S,P} = \frac{\partial F}{\partial T} \Big|_V + S = 0, \]  

(2.2)

\[ \frac{\partial H}{\partial V} \Big|_{T,S,P} = \frac{\partial F}{\partial V} \Big|_T + P = 0. \]  

(2.3)

The system is defined by the choice of the free energy function \( F \). When this function has been specified the two relations define a 2-dimensional surface in a 4-dimensional manifold with coordinates \( V, T, S, P \).

In the case of an ideal gas,

\[ F(V, T) = -RT \ln(VT^n), \]  

(2.4)

and these relations give

\[ S/R = n + \ln (VT^n), \]  

(2.5)

and

\[ PV = RT, \]  

(2.6)

* The development presented here can easily be expanded to apply, for example, to a gas with an arbitrary, cubic equation of state (Fronsdal 2010).
respectively. The on shell internal energy density is

\[ U = (F(V, T) + ST) \bigg|_{\text{on shell}} = nRT. \] (2.7)

“On shell” means that the function is restricted to the surface defined by (2.2). The last three relations define the ideal gas; we take that as sufficient proof that (2.4) is a correct and useful expression for the free energy, and that the expression (2.1) is a promising candidate to serve as hamiltonian.

The free energy is the only potential that is defined from the beginning as a function of two natural variables. The internal energy is a “variable”. It becomes a function of \( V, T \) and \( S \) by identification with \( F + TS \), restricted to the \( V, T, S \) surface. It is regarded as a function of \( V \) and \( S \), defined by the Legendre transformation \( U(V, S) = F + ST \) and elimination of \( T \) by use of the relation (2.2). The function \( F \) occupies a special position.

There is a symmetry between energy and entropy, strongly emphasized by Gibbs (1878). One can regard the entropy as a function of \( V, T, H \) and \( P \),

\[ S = \frac{1}{T}(H - F(V, T) - PV). \] (2.8)

The conditions that this function be stationary with respect to variation of the variables \( T \) and \( V \), with \( H \) fixed, are exactly the same as (2.2-3),

\[ \frac{\partial S}{\partial T} \bigg|_{V,U,P} = -\frac{1}{T} \left( S + \frac{\partial F}{\partial T} \bigg|_{V} \right) = 0 \] (2.9)

and

\[ \frac{\partial S}{\partial V} \bigg|_{T,U,P} = -\frac{1}{T} \left( \frac{\partial F}{\partial V} \bigg|_{T} + P \right) = 0. \] (2.10)

Gibbs claims that the two statements, \( \delta H = 0 \) and \( \delta S = 0 \), are equivalent. But that is not true in the local extension of the theory.

2. Local relations

The local extrapolation of thermodynamics seeks to promote these relations to field equations that describe local but stationary configurations. The functions \( F, H, S \) and \( V \) are given new interpretations as specific densities and specific volume. The mass density is \( \rho = 1/V \) and densities \( f, h, s \) are defined by

\[ f(\rho, T) = \rho F(V, T), \quad h = \rho H, \quad s = \rho S. \] (2.11)

The Hamiltonian is,

\[ \int_\Sigma d^3x \ h, \quad h = \rho \bar{v}^2/2 + \rho \phi + f(\rho, T) + sT + P. \] (2.12)

The effect of an external gravitational field is represented by the term \( \rho \phi \).
Variation with respect to $T$, with $\rho, S, T$ treated as independent variables, leads to
\[
\frac{\partial f}{\partial T} \bigg|_\rho + s = 0.
\] (2.13)

Variation with respect to $\rho$, with the mass and the volume fixed, * gives
\[
\frac{h}{\rho} + \rho \frac{\partial (f/\rho)}{\partial \rho} \bigg|_T = \lambda. \quad (\lambda = \text{constant.})
\] (2.14)

The local thermodynamic pressure is defined by
\[
\rho \frac{\partial (f/\rho)}{\partial \rho} \bigg|_T - f = p,
\]
then the last relation (2.14) reduces to
\[
\text{grad} \frac{h + p}{\rho} = 0,
\] (2.15)

In the case of the ideal gas
\[
f(\rho, T) = \mathcal{R} \rho T \ln \frac{\rho}{T^n}, \quad p = \mathcal{R} \rho T.
\]

The on shell value of $h$ is the internal energy density,
\[
h \big|_{\text{on shell}} = \rho \bar{v}^2/2 + \rho \phi + n\mathcal{R} \rho T
\]
and the variational equations reduce to
\[
S = \mathcal{R} \ln (VT^n), \quad \text{and} \quad \text{grad} \left( \bar{v}^2/2 + \phi + (n + 1)\mathcal{R}T \right) = 0.
\] (2.16)

At equilibrium ($\bar{v} = 0$), in the absence of external forces ($\phi = 0$), the temperature is uniform.

**Remark.** The Bernoulli equation, in the stationary case (all fields time independent), is
\[
\rho \text{grad} (\bar{v}^2/2) + \rho \text{grad} \phi + \text{grad} \mathcal{R} \rho T = 0.
\]

It should be noted that it is equivalent to (2.16) only if the gas is isentropic, when $\rho^n/T$ is uniform (Fronsdal 2010).

* A complimentary variation of the density, with the mass fixed but the volume not, gives the result that the internal pressure $p$ must agree with the external pressure $P$ on the boundary. See Section II.6. Any sub volume is in equilibrium with the pressure exerted by the gas outside its boundary; hence $P$ is identified with the thermodynamic pressure $p$. 
Reversing the roles of \( h \) and \( s \) we extremize the total entropy

\[
\int_{\Sigma} d^3x \, s = \frac{1}{T} \left( h - \rho \vec{v}^2/2 - f(\rho, T) - P \right).
\]

Variation with respect to \( T \), with \( \rho, T \) and \( \dot{H} = h/\rho \) treated as independent variables, gives the same result, \( \partial f/\partial T + s = 0 \), but variation with respect to \( \rho \) gives an additional constraint,

\[
\frac{s}{\rho} - \frac{P - p}{\rho T} = \text{constant}.
\]

Since \( P = p \), this tells us that the specific entropy of an isolated ideal gas is uniform. We have seen that this additional constraint is needed to identify the thermodynamic pressure \(-\partial F/\partial V\) with the gas pressure that appears in the Bernoulli equation.

The function that we referred to as the hamiltonian actually deserves the name. In order to derive hamiltonian equations of motion we need to identify canonically conjugate momenta, in particular, a variable that is conjugate to the variable \( \rho \). As shown by Fetter and Walecka (1980), a velocity potential fills the role admirably, with \( \vec{v} = -\text{grad } \Phi \) by definition. The continuity equation takes the form \( \dot{\rho} = -\delta H/\delta \Phi \), the Bernoulli equation (in integrated form) is \( \Phi = \dot{\Phi} = \delta H/\delta \rho \).

II.3. Dynamical action principle

The ideal gas is a system governed by an action

\[
A = \int dt \int_{\Sigma} d^3x L[\rho, T, \Phi, k_0, P],
\]

where \( \Sigma \subset \mathbb{R}^3 \) is connected, \( k_0 \in \mathbb{R}, \rho, T \) and \( \Phi \) are scalar fields on \( \Sigma \) and \( P \) is a scalar field on the boundary \( \partial \Sigma \) of \( \Sigma \).

For the present, the domain \( \Sigma \) is fixed and the external pressure \( P \) is irrelevant; the action is varied with respect to the density \( \rho \), the temperature \( T \) and the velocity potential \( \Phi \). The irrotational velocity field \( \vec{v} = -\text{grad } \Phi \) is subject to the boundary condition

\[
\vec{v}|_{\partial \Sigma} \quad \text{is tangential.} \tag{2.17}
\]

The lagrangian is

\[
L = \rho \dot{\Phi} - h = \rho (\dot{\Phi} - \vec{v}^2/2 - \phi + \lambda) - V(\rho, T, S),
\]

where \( \vec{v} = -\text{grad } \Phi \) and \( \lambda \) is a lagrange multiplier related to the fixing of the mass,

\[
M = \int_{\Sigma} d^3x \rho,
\]

The potential \( V \) is

\[
V(\rho, T, S) = f(\rho, T) + sT, \quad S = s/\rho = -R \ln k_0 = \text{constant}.
\]
Variation of $T$ gives Eq. (2.13),
\[ \frac{\partial V}{\partial T} = 0, \quad \frac{\partial f}{\partial T} + s = 0. \]

For the ideal gas it is
\[ \ln \frac{\rho}{T^n k_0} = n \]

Variation of $\Phi$ gives the equation of continuity (local conservation law)
\[ \dot{\rho} + \text{div}(\rho \vec{v}) = 0. \]

With the boundary condition (2.17) imposed on $\vec{v}$, it ensures the global conservation of the mass. Variation of $\rho$ leads to
\[ \dot{\Phi} - \vec{v}^2/2 - \phi + \lambda = \frac{\partial V}{\partial \rho}. \]

Taking the gradient we get, since the entropy is uniform, the differential form of Bernoulli’s equation (Bernoulli 1738),
\[ \rho \frac{D\vec{v}}{Dt} + \rho \text{grad} \phi = -\text{grad} p, \]

with the gas pressure
\[ p := \rho \frac{\partial V}{\partial \rho} \bigg|_{T,S} - V. \quad (2.18) \]

Besides the mass, the only globally conserved quantity is the hamiltonian $H = \int_{\Sigma} d^3 x \ h$, with the density
\[ h = \rho(\vec{v}^2/2 + \phi) + V[\rho]. \]

The local conservation law is
\[ \dot{h} + \text{div}(\vec{v}(h + p)) = 0. \]

The parameter $k_0$ is free, independent of volume and mass. That a free parameter must appear is evident since it must be possible to change the configuration of the system by heat transfer.

The lagrangian, for each fixed choice of $k_0$, describes configurations of an ideal gas restricted to an adiabat. The equations of motion preserve mass and energy and the system is thus in a sense isolated. It is already possible to discuss the “changes” that form the central subject of thermodynamics.

II.4. Cooling

By “cooling” is meant a slow loss of energy, as the system goes through the equilibria of a sequence of adiabatic lagrangians indexed by $k_0$, this being the only parameter available. It is regarded as a reversible process, for it is supposed that heat can be supplied, slowly so as to make the departure from equilibrium negligible, to reverse the cooling process.
The domain $\Sigma$ is supposed fixed, $\rho$ and $T$ uniform and $\Phi = 0$; hence $\rho$ is fixed, unchanged during the process of cooling.

During this process, the on shell internal energy density is $u = nRT\rho$, the total energy is $U = nRTM$, and changes in $U, T$ and $k_0$ are related by

$$dU = nRMdT, \quad dk_0 = d\frac{\rho}{T^n} = -nk_0\frac{dT}{T}.$$  

As this represents a heat loss, $\ln k_0$ is increasing. Hence

$$dU = -RTMd\ln k_0 := TdS,$$

with

$$S := -RM\ln k_0.$$  \hspace{1cm} (2.19)

This relates the parameter $k_0$ to entropy. We define the entropy density by

$$s = -R\rho\ln k_0.$$  

The specific entropy density $s/\rho$ is uniform in this case. From the point of view of thermodynamics, with its primary emphasis on equilibria, the lagrangian density is a function of the 3 independent variables $\rho, T$ and $k_0$. The on shell condition (2.5) is the fundamental relation of the ideal gas:

$$s = -R\rho\left(\ln\frac{\rho}{T^n} - n\right).$$

A dynamical description of cooling as an ongoing process may rely on the heat equation.

II.5. Free expansion

It is a process that begins (at $t = 0$) with a configuration in which the gas is uniformly distributed in a fraction $\alpha$ of the volume, with density $\rho$ and temperature $T$, at rest. From these initial conditions the gas spreads, eventually occupying the total volume. Thermodynamics deals mostly with equilibria, but the adiabatic lagrangian allows for motion as well, and it describes the agitated configurations of the expanding gas for $t > 0$. Since the equations of motion preserve energy, this predicted, adiabatic motion of the gas cannot lead to equilibria. To bring the gas to rest another process is required, involving a change in the value of $k_0$.

It is observed that the gas comes to rest, and for this to happen a non adiabatic process must take place, with a change in entropy. In order that the time development described by the adiabatic lagrangian retain its relevance, one must postulate that the additional process take place on a much longer time scale.

We thus envisage an initial, rapid, adiabatic expansion, leading to configurations of non zero kinetic energy, and a slow conversion of that kinetic energy into heat. Without attempting to describe the latter, it is nevertheless possible to predict the end result. If the energy of the asymptotic, equilibrium configuration is the same as that of the initial configuration, then since both are equilibria of the same ideal gas we have $U = nRTM =$
\[ U' = nRT'M, \] the prime referring to the asymptotic state. Hence \( T = T' \), and since \( \rho' = \alpha \rho, k'_0 = \alpha k_0 \) and the change in the function \( S \) is \( \delta S = -RM \ln \alpha \), which represents an increase since the fraction \( \alpha \) is less than 1. In general, if some heat is lost or supplied, we shall have

\[ \delta S := -RM \delta \ln k_0 = RM \ln \frac{k_0}{k'_0}. \]

and on shell,

\[ \delta S = RM \left( \ln \frac{\rho}{\rho'} + n \ln \frac{T'}{T} \right). \tag{2.20} \]

II.6. Work

We consider changes of volume, and begin with the case of a cylinder with a piston. The cross section is \( A \) and the longitudinal variable is \( z \), with \( 0 < z < z_1 \). Conjugate to \( z_1 \) is the external pressure \( P \) exerted by the piston.

A change \( dV = Adz_1 \) of the volume requires that the gas supply energy in the form of work, \( dE = PdV = PAz_1 \). The total, conserved energy of the gas is thus modified by a term \( +PV \) (an additive constant has no significance) and the lagrangian is modified by the inclusion of a term \( -PV = -PAz_1 \),

\[
\int d^3x \mathcal{L} \to \int d^3x \left( \rho \left( \dot{\Phi} - \vec{v}^2 / 2 + \lambda \right) - RT \rho \left( \ln \frac{\rho}{Tn k_0} + 1 \right) - PAz_1 \right). 
\]

The action is to be extremized, in particular, by variations that vanish at \( \partial \Sigma \). The earlier equations of motion therefore continue to hold. In addition, we must consider the one parameter family of mass preserving variations of the form \( \delta \rho / \rho = -\delta z_1 / z_1, \delta \Phi = \delta T = 0 \). This gives an additional equation of motion,

\[
\int d^2x \mathcal{L} - \frac{1}{z_1} \int \Sigma d^3x \left( \rho \left( \dot{\Phi} - \vec{v}^2 / 2 + \lambda \right) - RT \rho \left( \ln \frac{\rho}{Tn k_0} + 1 \right) \right) = 0. \tag{2.21} 
\]

The first term comes from changing the boundary, the second from variation of \( \rho \) and the third from the new term that was added to the lagrangian. With \( p = RT \rho \) from the equations of motion; after multiplication by \( z_1 \) it is

\[
z_1 \int d^2\Sigma x \mathcal{L} - \int \Sigma d^3x (\mathcal{L} - p) - PV = 0. 
\]

By the equations of motion, \( \mathcal{L} = p \). The conclusion is that the external pressure \( P \) is equal to the average of the gas pressure over the face of the piston.

The hamiltonian associated with the expanded lagrangian,

\[
H = \int \partial \Sigma d^3x \left( \rho \vec{v}^2 / 2 + RT \rho \left( \ln \frac{\rho}{Tn k_0} \right) \right) + PV
\]
is identified, in the case of an equilibrium configuration, with the Helmholtz free energy $U + PV$. In general, the extra term that is needed in the case of a variable boundary can be expressed as
\[ \int_{\Sigma} d^3 x P, \]
where $P$ is a field that coincides with the external pressure at the boundary $\partial \Sigma$.

In open atmospheres $P = 0$ at the upper end; it implies that $T = 0$ there.

**Remark.** In Einstein’s theory of gravitation the cosmological constant can be interpreted as an external pressure on space time at infinity.
III. Mixtures

III.1. Basic postulates

The adiabatic action for a system of two parts, occupying distinct portions of a total domain $\Sigma$, with no interaction or mutual constraint between them, is the sum of the adiabatic actions of each,

$$\int_{\Sigma} \mathcal{L} = \int_{\Sigma_1} \mathcal{L}_1 d^3z + \int_{\Sigma_2} \mathcal{L}_2 d^3z, \quad \Sigma_1 \cup \Sigma_2 = \Sigma.$$ 

In the case of two ideal gases,

$$\int_{\Sigma} \mathcal{L} = \sum \int_{\Sigma_i} d^3x \left( \rho_i (\dot{\Phi}_i - \vec{v}_i^2/2 - \phi + \lambda_i) - V_i \right),$$

with

$$V_i = R_i T_i \rho_i \ln \frac{k_i}{k_0i}, \quad k_i = \frac{\rho_i}{T_i n_i}, \quad i = 1, 2.$$ 

The temperature field is defined over $\Sigma$; we may write $T_i = T_i |_{\Sigma_i}, \quad i = 1, 2.$

We restrict ourselves, temporarily, to the approximation in which the gravitational field is ignored. In this case there is a unique, static solution of the equations of motion with uniform densities $\hat{\rho}_1, \hat{\rho}_2$ and temperatures $\hat{T}_1, \hat{T}_2$ given by $\hat{\rho}_i = M_i / V_i$ and $(e^{\hat{T}_1})^n = \hat{\rho}_i / k_0i, \quad i = 1, 2.$

We want to know what happens to the system if at $t = 0$ the barriers that have confined the two gases to their respective domains are removed. Each gas will expand (diffuse) into the region originally occupied by the other. This implies motion and kinetic energy. Since energy is conserved, the adiabatic equations of motion do not lead to a state of equilibrium. But a real physical system can be depended upon to find its way to rest, it is therefore necessary to postulate some non adiabatic process, with a longer time scale. As in the case of simpler situations examined in Section II, and for the same reason, we may suppose that this slow process takes the system through a sequence of lagrangians indexed by $k_{01}$ and $k_{02}$, the only parameters that are available. The changes can be interpreted in terms of a changing (increasing) entropy.

We expect, then, that the mixture will eventually be governed by the same lagrangian (but both densities will extend to the whole domain), with a new set $k_{01}', k_{02}'$ of parameters. Can we predict these new values? More precisely, the problem is to determine a relation between the two parameters. As heat is added to or withdrawn from the mixtures the entropy changes, tracing a path through the $k_01, k_02$ plane. We need to fix this path.
Fig 1. Example of a path followed by a two component system in entropy space. The coordinates are the entropy parameters $k_{01}$ and $k_{02}$ and the shown shape conforms to the case of disassociation of atomic hydrogen.

The Gibbs-Dalton hypothesis (Gibbs 1876, Dalton 1808), justified within the kinetic interpretation of the ideal gas as an ensemble of non interacting particles, predicts that each gas undergoes the same change of specific entropy as would be the case if the other gas were absent. It is assumed that no chemical reaction is taking place.

The mathematical statement of the Gibbs-Dalton hypothesis is, in view of Eq. (2.20)

$$\ln \frac{k'_{0i}}{k_{0i}} = \ln \frac{\rho'_{i}}{\rho_{i}} + n_{i} \ln \frac{T_{i}}{T'},$$

where $\hat{\rho}_{i}$ and $\hat{T}_{i}$ are the densities and temperatures before mixing, $\rho'_{i}$ and $T'$ are the densities and the common temperature of the final equilibrium configuration.

The pre-mix parameters satisfy the relations

$$\ln \frac{\hat{\rho}_{i}}{T_{i}k_{0i}} = n_{i}, \quad i = 1, 2.$$ 

It may happen that $\hat{T}_{1} = \hat{T}_{2}$, and we may wish to equalize the temperatures before mixing. But in any case the Gibbs-Dalton hypothesis is the condition that the two equations

$$\ln \frac{\rho'_{i}}{T'k'_{0i}} = n_{i}, \quad i = 1, 2,$$

(3.1)

with equilibrium values of the densities, are solved by the same value of $T'$. A possible interpretation is that the difference between the two temperatures defined by (3.1), dissipates with adjustment of the entropies.

The extension of this constraint to non uniform configurations is problematic, as will be seen.
This Gibbs-Dalton constraint imposes a relation between \( k'_{01} \) and \( k'_{02} \),

\[
(k'_{01}/M_1)^{n_2} = (k'_{02}/M_2)^{n_1}.
\] (3.2)

To the extent that the Gibbs-Dalton hypothesis is verified experimentally we can regard
this constraint, and the lagrangian determined by it, as being dictated by experiments.
The lagrangian of the mixture is now determined by a single, real parameter that serves
as a record of heat that is lost or supplied.

A natural choice for the lagrangian is

\[
\mathcal{L} = \sum \left( \rho_i (\dot{\Phi}_i - \bar{v}_i^2/2 - \phi + \lambda_i) - \mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^2 k_{0i}} \right),
\] (3.3)

with \( \rho_1, \rho_2 \) defined over \( \Sigma \), the masses \( M_i = \int_{\Sigma} d^3x \rho_i \) fixed, and constants \( k_{0i} \) satisfying

\[
(k_{01}/M_1)^{n_2} = (k_{02}/M_2)^{n_1}.
\] (3.4)

We have dropped the primes on these parameters.

The equations of motion are the equations of continuity, the Bernoulli equation, namely

\[
\dot{\Phi}_i - \bar{v}_i^2/2 - \phi + \lambda_i = \mathcal{R}_i T (\ln k_i/k_{0i} + 1), \quad k_i := \frac{\rho_i}{T^2 n_i}, \quad i = 1, 2,
\]

and from variation of \( T \) the adiabatic condition

\[
\sum \mathcal{R}_i \rho_i (\ln k_i/k_{0i} - n_i) = 0.
\] (3.5)

Consider the uniform distribution, for which \( \rho_i = M_i/V \). In that case, because of (3.4),
both expressions \( \ln k_i/k_{0i} - n_i, \ i = 1, 2 \), vanish for one and the same value \( T' \) of \( T \). We have
\( \ln k_i/k_{0i} - n_i = n_i \ln (T'/T) \) so that the third equation reduces to \( \sum \mathcal{R}_i \rho_i n_i \ln (T'/T) = 0 \),
with the unique solution \( T = T' \). Hence \( \ln k_i/k_{0i} - n_i = 0, \ i = 1, 2 \), at equilibrium and
both gases are polytropic.

Before mixing, both terms in (3.5) vanish separately on shell. The constraint (3.4)
ensures that there is a solution for which this is true for the mixture as well.

The total pressure; that is, the pressure on the walls, is

\[
P = \mathcal{L} - \sum \rho_i \frac{\partial \mathcal{L}}{\partial \rho_i} = T \sum \mathcal{R}_i \rho_i.
\] (3.6)

Individual pressures are suggested by inspection of the “Bernoulli equations” of motion,

\[
\text{grad } (\bar{v}_i^2/2 + \phi + \frac{\partial V}{\partial \rho_i}) =: \text{grad } (\bar{v}_i^2/2 + \phi) + \frac{1}{\rho_i} \text{grad } p_i = 0.
\]

This yields \( p_i = \mathcal{R}_i \rho_i T \) for equilibrium configurations, but nothing that is useful in general.
Additivity of pressures is valid in the sense of (3.6), where each term is the pressure of a
single gas occupying the total volume. It is also valid, but only at equilibrium, in terms
of the pressures that are identified through their role in the Bernoulli equations.
III.2. About the Gibbs-Dalton hypothesis

The constraint (3.4) is an expression of the Gibbs-Dalton hypothesis. This hypothesis is widely used in the context of equilibrium thermodynamics. It is, however, nonlocal. Consider a long tube filled with a mixture of two ideal gases. One can wait until mixing is complete and the temperature has become uniform over long distances. But if something should perturb the system locally, even if the disturbance is uniform over a moderate interval, then one is at a loss to understand how the constraint, depending as it does on the total masses, is to be implemented locally. We feel that a localized version of the Gibbs-Dalton hypothesis may be appropriate in such cases.

A local version of the constraint would replace the masses by the local densities; requiring that, at equilibrium, both terms in Eq. (3.5) vanish separately. But this would be inconsistent with the other equations of motion whenever external forces, such as gravity, are present.

The strongest version of the Gibbs-Dalton hypothesis would relate the two densities to each other under all conditions, not just in equilibrium configurations, thereby reducing the number of degrees of freedom. It seems that this is done routinely in some applications, which explains the fact that dynamical processes have been described in terms of a single, uniformly mixed density distribution. (Exception: superfluid helium.)

The truth may lie somewhere between these extreme interpretations of Gibbs-Dalton; between a local version that admits only one independent density degree of freedom, and the global version with two densities that are locally independent while only the masses are involved in the constraint. Implications for equilibrium configurations are identical in all versions, in the absence of external forces.

One way to think about this problem may be to postulate a slow, non adiabatic process that is observed as a tendency of the mixture to anull the difference $\rho_1/k_{01} - \rho_2/k_{02}$. It is an irreversible process that calls for a role to be played by entropy. A Lagrange multiplier may be interpreted as the limiting case of a force that implements this tendency instantaneously. But it is characteristic of all irreversible processes that they are slow, and they can be taken into account in dynamical processes only under that condition. The local version, with its strong identification of densities, is difficult to justify. Only global versions will be studied in this section.

III.3. Dissociation

We consider the simplest example of a chemical reaction involving ideal gases, the transformation between atomic and molecular hydrogen,

$H_2 \leftrightarrow 2H$.

We fix, once and for all, the domain $\Sigma$ with volume $\mathcal{V}$ and the total mass $M$.

At sufficiently low temperatures the gas is almost purely molecular, with molecular weight and adiabatic index

$\mu_1 = 2, \quad n_1 = 5/2$.

At equilibrium we shall have $\bar{v} = 0$ and

$\rho_1 = \rho = M/\mathcal{V}, \quad \ln \frac{\rho}{T^{n_1} k_{01}} = n_1$. 

15
At sufficiently high temperatures the gas is almost purely atomic, with $\mu_2 = 1, \ n_2 = 3/2$. At equilibrium, 
\[ \rho_2 = \rho = M/V, \ \ln \frac{\rho}{T^{n_2 k_{02}}} = n_2. \]

Consider a mixture of two gases, similar in all respects to $H$ and $H_2$, except that the reaction analogous to $H_2 \leftrightarrow 2H$ does not take place. If we assume the Gibbs-Dalton law for this mixture then we are led to the lagrangian density 
\[ L = \sum \left( \rho_i (\dot{\Phi}_i - \vec{v}^2/2 - \phi + \lambda_i) - \mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^{n_i k_{0i}}} \right), \]
with values of the parameters $k_{01}$ and $k_{02}$ that ensure the compatibility of the on shell conditions $\ln(\rho_i/T^{n_i k_{0i}}) = n_i, \ i = 1, 2$ that must hold at equilibrium. A hypothesis that can be tried is that this Gibbs-Dalton lagrangian retain some validity for the real hydrogen problem. But it must be changed in essential ways.

In the case of real hydrogen the individual masses are not conserved; there is only one equation of continuity and only one velocity field. Consider therefore 
\[ \int \mathcal{L} = \int_{\Sigma} d^3x \left( \rho (\dot{\Phi} - \vec{v}^2/2 - \phi + \lambda) + \epsilon \rho_1 - \sum \mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^{n_i k_{0i}}} \right), \]
with $\rho = \rho_1 + \rho_2$ and $\epsilon > 0$ constant. This expression, with constant parameters $k_{0i}$, is a reasonable candidate for hydrogen, but the Gibbs-Dalton constraint on the parameters is no longer applicable.

The term $\epsilon \rho_1$ is the binding energy of molecular hydrogen. Variation with respect to $T$ yields the relation 
\[ \sum \mathcal{R}_i \rho_i \left( \ln \frac{\rho_i}{T^{n_i k_{0i}}} - n_i \right) = 0, \quad (3.8) \]
a relation that we shall put aside for now.

Variation of the densities with $\rho = \rho_1 + \rho_2$ fixed, in the case of equilibrium, gives
\[ d \left( \sum \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{T^{n_i k_{0i}}} - \epsilon \rho_1 \right) = 0, \]
or explicitly
\[ \mathcal{R}_1 T \left( \ln \frac{\rho_1}{T^{n_1 k_{01}}} + 1 \right) - \mathcal{R}_2 T \left( \ln \frac{\rho_2}{T^{n_2 k_{02}}} + 1 \right) = \epsilon. \quad (3.9) \]
This relation appears in textbooks on thermodynamics, except that, in some of the books consulted (Holman 1974, DeHoff 1993), the binding energy is not taken into account. And the unknown entropy of a reference configuration used in these books is here represented by the term $\sum \mathcal{R}_i T \rho_i \ln k_{0i}$ in the lagrangian, parameterized by $k_{01}, k_{02}$. These parameters, and thus the entropy of the reference state not unknowable; but determined by the experiment.

Relations (3.8) and (3.9) are the equations of motion that determine the configurations of adiabatic equilibrium, for each choice of the parameters $k_{01}$ and $k_{02}$, unique equilibrium values of $T$ and for the ratio $\rho_1/\rho_2$. (The total density $\rho = \rho_1 + \rho_2$ and the volume are both fixed.)
Addition or withdrawal of heat, or a change in energy by other means, produces a non-adiabatic path through the 2-dimensional space of lagrangians with coordinates $k_{01}, k_{02}$. To discover the relation between $T$ and $\rho_1/\rho_2$ we must know this path. See Fig. 1.

Since $\mathcal{R}_2 = 2\mathcal{R}_1$, Eq.(3.9) reads

$$\ln\left(\frac{\rho_1}{\rho_2}\right) - (n_1 - 2n_2) \ln T = \epsilon/\mathcal{R}_1 T + 1, \quad q := \frac{k_{02}^2}{k_{01}}.$$  

or

$$\frac{\rho_2^2}{\rho \rho_1} = \frac{r^2}{1 - r} = \frac{q}{e\rho} T^{1/2} e^{-\epsilon/\mathcal{R}_1 T}; \quad r := \rho_2/\rho. \quad (3.10)$$

If the parameter $q$ is constant, then this is a special case of the famous Saha formula (Eggert 1919, Saha 1920). That $q$ is constant is thus another property of ideal gases that is suggested by statistical mechanics. It is also supported by observation. The molecular binding energy is about 4.5 ev, or in relation to the rest energy, in energy units $\epsilon = (4.5/1876 \times 10^6)c^2 \approx 2.15 \times 10^{12}$. Thus

$$\epsilon/\mathcal{R}_1 = 4.3 \times 10^{12}/.83214 \times 10^8 = 51674.$$  

Fig. 2 shows $r$ versus $T$, for $n_1 = 5/2, n_2 = 3/2$ with $q = 1$. This result shows that a reasonable lagrangian for hydrogen across the dissociation region is obtained by assigning a constant fixed value to $q$.

![Fig.2. The ratio $r$ against $T$, Eq.(3.10).](image)

The measurements are usually performed under conditions of constant pressure. Setting $\rho_1/2 + \rho_2 = p/\mathcal{R}T$ we get, when $n_2 = 5/2$ and $n_2 = 3/2$,

$$\frac{\rho_2^2}{\rho \rho_1} p = \frac{r^2}{1 - r^2} p = \frac{\mathcal{R}q}{2e} T^{3/2} e^{-\epsilon/\mathcal{R}_1 T}; \quad r = \rho_2/\rho. \quad (3.11)$$
This relationship is plotted in Fig. 3 for $qR/p = 1$.

![Graph showing the ratio $r$ against $T$, Eq. (3.11).](image)

Eq. (3.10) applies to laboratory conditions of constant volume. Eq. (3.11) applies under similar conditions when the gas is kept under constant atmospheric pressure. Both equations can be used for atmospheres if the dependence of temperature and density (resp. temperature and pressure) on altitude are known.

Eq. (3.8) gives us other kinds of information. This equation allows to calculate both $k_{01}$ and $k_{02}$ in terms of the equilibrium values of $\rho_1$, $\rho_2$ and $T$. With (3.10) it allows to calculate all the thermodynamic potentials as functions of the same variables. For example, the expression for the on shell internal energy is the same as for the case of a mixture, corrected only by the addition of $-\epsilon \rho_1$.

**III.4. Other reactions**

We consider, briefly, a chemical reaction involving 4 gases, by which a uniform mixture of gases of types 1 and 2 are transformed into gases of types 3 and 4, according to the chemical equation

\[
\sum_{i=1,2} \nu_i A_i \leftrightarrow \sum_{i=3,4} \nu_i A_i
\]
The coefficients are the ratios of reagents, in grams. Three masses are conserved, \( \nu_2 M_1 - \nu_1 M_2, \nu_3 M_2 + \nu_2 M_3, \nu_4 M_3 - \nu_3 M_4 \), and the three corresponding densities satisfy conservation laws. The kinetic part of the lagrangian density therefore must take the form

\[
L_{\text{kin}} = (\nu_2 \rho_1 - \nu_1 \rho_2) (\dot{\Phi}_1 - \vec{v}_1 \dot{2}/2 + \lambda_1)
+ (\nu_3 \rho_2 + \nu_2 \rho_3) (\dot{\Phi}_2 - \vec{v}_2 \dot{2}/2 + \lambda_2)
+ (\nu_4 \rho_3 - \nu_3 \rho_4) (\dot{\Phi}_3 - \vec{v}_3 \dot{2}/2 + \lambda_3)
\]

and

\[
L = L_{\text{kin}} + \rho \phi + \epsilon \rho_1 - \sum_{1 \leq i \leq 4} R_i \rho_i T \ln \frac{\rho_i}{T^{n_i} k_{0i}},
\]

where \( \rho = \sum \rho_i \) and the term \( \epsilon \rho_1 \) represents the energy needed to make the reaction go.

At equilibrium the densities are fixed by the volume and the masses, up to a variation of the form

\[
(d \rho_1, \ldots, d \rho_4) \propto (\nu_1, \nu_2, -\nu_3, -\nu_4).
\]

This, and the variation of \( T \), gives the two equations of motion

\[
\sum R_i \rho_i (\ln \frac{\rho_i}{T^{n_i} k_{0i}} + 1) = 0,
\]

and

\[
\sum_{1 \leq i \leq 4} d \rho_i R_i (\ln \frac{\rho_i}{T^{n_i} k_{0i}} + 1) = d \rho_1 \epsilon / R_1 T.
\]

The latter can be expressed as

\[
\ln \frac{\rho_1^{\nu_1/\mu_1} \rho_2^{\nu_2/\mu_2}}{\rho_3^{\nu_3/\mu_3} \rho_4^{\nu_4/\mu_4}} = \ln q + (n_1 + n_2 - n_3 - n_4) \ln T - \epsilon / R_1 T,
\]

one recognizes the law of mass action (Guldberg and Waage 1864, Gibbs 1875, Holman 1974, page 489), except that here the right hand side is not an unknown function, but a function that is known explicitly in terms of the 4 entropy parameters \( k_{01}, \ldots, k_{04} \). This formula is formally the same as one that one derives from kinetic theory, it provides us with a hint that the parameter \( q \) may be an invariant.

It is tempting to speculate that \( q \) is a constant, in that case there remain 3 independent entropy parameters. It seems likely that they are subject to constraints of the Gibbs-Dalton type. Thus

\[
(k_{01}/M_1)^{n_2} = (k_{02}/M_2)^{n_1}, \quad (k_{03}/M_3)^{n_4} = (k_{04}/M_4)^{n_3}.
\]

In that case the index of entropy is just one free parameter, as it should be for a complete determination of the entropy.
IV. The propagation of sound

IV.1. The ideal gas

The dynamical equations that govern the adiabatic excitations of an ideal gas along a fixed direction are (Section II.3 and Laplace 1816)

\[ \dot{\rho} + (\rho v)' = 0, \quad \dot{\Phi} - \ddot{\Phi} = \mathcal{R}T(\ln \frac{\rho}{T^n k_0} + 1) \]  

(4.1)

and

\[ \ln \frac{k}{k_0} = n, \quad k := \frac{\rho}{T^n}. \]  

(4.2)

For perturbations around static equilibrium, to first order, we have

\[ d\dot{\rho} = -v' \rho, \quad dk = 0, \quad \dot{v} = -\mathcal{R}(\ln \frac{k}{k_0} + 1)dT'; \]  

(4.3)

Thus

\[ \frac{d\ddot{\rho}}{\rho} = -\ddot{v} = \mathcal{R}(n + 1)dT'', \quad \frac{dT'}{T} = nd\rho'/\rho, \]  

and finally

\[ \frac{d\ddot{\rho}}{\rho} = \mathcal{R}T(1 + \frac{1}{n})d\rho''/\rho. \]  

The speed of sound is thus \( \sqrt{\mathcal{R}T\gamma}, \) \( \gamma := 1 + 1/n. \) Only one degree of freedom is excited.

Consider next the implications of the global version of the Gibbs-Dalton constraint. In a mixture of two ideal gases two degrees of freedom are excited and two normal modes of propagation will appear.

IV.2. Propagation of sound in Gibbs-Dalton mixtures

The linearized equations for a perturbation of a Gibbs-Dalton equilibrium configuration are

\[ d\ddot{\rho}_i = -\ddot{v}_i = \frac{\partial^2 V}{\partial \rho_i} \bigg|_T, \]  

(4.4)

\[ \frac{dT''}{T} = \frac{R_1 d\rho'_1 + R_2 d\rho'_2}{n_1 R_1 \rho_1 + n_2 R_2 \rho_2}. \]  

(4.5)

The second equation, - from Eq.(3.5) - defines an adiabatic change. It is assumed that the unperturbed densities and the unperturbed temperature are uniform and that the perturbations depend on only one of the spatial coordinates; the prime denotes the spatial derivative.

Let

\[ \kappa = \frac{R_2}{R_1} = \mu_1/\mu_2; \quad \tau = \rho_1/\rho_2. \]  

20
then
\[
\frac{dT''}{T} = \frac{d\rho_2}{\rho_1} \alpha + \frac{d\rho_1'}{\rho_2} \gamma, \quad A := n_1 \tau + n_2 \kappa,
\] (4.6)

Next
\[
\frac{d\dot{\rho}_1}{\rho_1} = \frac{RT \tau}{\mu_1} \frac{d\rho_1''}{\rho_1} + \frac{RT \kappa}{\mu_1} \frac{d\rho_2''}{\rho_2} + \frac{RT d\rho_1''}{\mu_1},
\] (4.7)
\[
\frac{d\dot{\rho}_2}{\rho_2} = \frac{RT \kappa}{\mu_2} \frac{d\rho_1''}{\rho_1} + \frac{RT \tau}{\mu_2} \frac{d\rho_1''}{\rho_2} + \frac{RT d\rho_2''}{\mu_2}.
\] (4.8)

The matrix of squared velocity is
\[
\frac{RT}{\mu_1} \begin{pmatrix} 1 + \frac{\tau}{A} & \frac{\kappa}{A} \\ \frac{\kappa \tau}{A} & \kappa + \frac{\kappa^2}{A} \end{pmatrix}, \quad A = n_1 \tau + n_2 \kappa.
\]

For mixtures we define the reduced speed \(c\) in terms of the cgs speed \(v = c\sqrt{\frac{R_1 T}{P}}\). This reduced speed is a zero of the determinant of the matrix
\[
\begin{pmatrix} 1 + \frac{\tau}{A} - c^2 & \frac{\kappa}{A} \\ \frac{\kappa \tau}{A} & \kappa + \frac{\kappa^2}{A} - c^2 \end{pmatrix}
\] (4.9)

The theory predicts two modes, with speeds that vary with the concentrations. Experimenters report a single mode. We shall see that this discrepancy can be overcome, but it is of some interest to begin by describing the predictions of the naive, Gibbs-Dalton model in some detail.

Two different types of binary mixtures must be described separately.

**Type 1 mixture, “similar” gases**

This is the case when \(\kappa \gamma_2 > 1\), for example:

Nitrogen/Argon: \(\kappa = 28/40, \; n_1 = 5/2, n_2 = 3/2,\) with \(\kappa \gamma_2 = 35/24\). There is a Laplace mode, with speed intermediate between the adiabatic speeds of the two pure gases. The two amplitudes are in phase. The dominant gas carries most of the energy but the amplitudes are comparable. A second mode has a speed that interpolates between the Newton (isothermal) speeds of the two pure gases. The two amplitudes are in opposite phase. The amplitude of the dominant gas tends to zero in the limit when this gas is alone.

All this tends to be confirmed by experiment. The second mode seems to be anti intuitive and there are several reasons why it may be expected to be unobservable, or at least to justify the fact that it has escaped detection. The prediction of the Gibbs-Dalton model needs only a minor correction to agree with experiment. See Fig.4.
Fig 4. Speed of the two modes of sound in Ni/Ar, plotted against $\ln \frac{\rho_1}{\rho_2}$. The curve just below the data points is the speed given by Eq.(4.10).

Type 2 mixture, “disparate” gases

It is the case when $\kappa \gamma_2 < 1$, for example,

Helium/Argon, $\kappa = 4/40, n_1 = n_2 = 3/2$.

There is a mode, with speed that approaches the adiabatic speed of sound in the lighter gas in the limit when this gas is alone (NE corner), but in the opposite limit it approaches the Newton value of the heavy gas (NW). The amplitudes are in phase.

A second mode has a speed that approaches the adiabatic speed of sound in the heavier gas in the limit when this gas is alone (SW). Surprisingly, the amplitudes are in opposite phase; the two gases are moving in opposite directions. See Fig.5a.

Fig.5a. The speed of sound in He/Xe, a type 2 (disparate) mixture. Coordinates as in Fig.4. The interpolating curve is from Eq.(4.10). Data points from dela Mora (1986) and Bowler (1982).
The physical interpretation is more difficult for this type of mixture. Experiment yields a single mode with a speed that varies with concentration and that approaches the expected values in the limits of either pure gas. It appears that a cross over takes place; in fact, there is evidence of a “critical” concentration.

Experimenters report a single mode in all cases, with a speed that varies smoothly with the concentration. There are frequent hints, however, that there are other, less prominent modes, about which no information is given.

The reason for this disagreement was at first attributed to the fact that no account had been taken of any kind of damping, and for high frequencies this has been confirmed. But at low frequencies the loss of energy to absorption is not thought to be important. Indeed, the measured rates of absorption are extremely low. (Holmes 1960)

The formula that fits the observations, and much better than could be expected, is

$$c^2 = \frac{1}{\gamma_1 \tau + \frac{\tau + \kappa}{n_1 \tau + n_2 \kappa}}.$$  \hfill (4.10)

The origin of this prediction is not thermodynamics but calculations of particle dynamics and the Boltzmann scattering equations. For a brief account of the calculation see de la Mora and Puri (1986). It is predicted to hold in the limit when the effect of diffusion is so strong as to force the two velocities to be nearly equal. That is the key to the success of the formula, and that must be the basic fact that is responsible for its success: apparently something forces the two velocities to be nearly equal. But the conclusion that it is due to strong diffusive damping is not compelling.

The equations that have been proposed to explain the success of (4.10) are equations for the two velocities and, sometimes, two temperatures. We have noted that the introduction of two temperatures may be interpreted in terms of a deviation from Gibbs-Dalton equilibrium conditions. But we are strongly constrained by the need to retain the standard
equations, continuity and Bernoulli. Indeed, any modification of the kinetic part of the lagrangian will cause a lack of conservation of masses: that is, of particle numbers. It is therefore of interest to explore alternatives.

The data quoted are from experiments at frequencies around 1 MHz, except for that of Smorenburg (...), the single, isolated point at a high speed in Fig. 5b, where the frequency was of the order of $10^9$ Hz. More data is needed, over a wide range of frequency and temperature.

**IV.3. A simple model of interactions**

Let us add the following “interaction term” to the potential; that is, to the hamiltonian,

$$\alpha \sqrt{\rho_1 \rho_2}, \quad (4.11)$$

with $\alpha$ constant. The reason for this choice will become clear almost immediately. Such a term will affect the formula for the internal energy, but it does not change the formula for the entropy. The hypothesis of Gibbs and Dalton can be maintained, and we shall assume values of the constants $k_{0i}$ accordingly. The formula (3.6) remains valid; it is the Dalton rule of additivity of pressures.

The equations of motion that would be recognized as Bernoulli equations,

$$\text{grad} \left( \frac{\vec{v}_i^2}{2} + \phi + \mathcal{R}_i T \left( \ln \frac{T^a k_{0i}}{\rho_i} + 1 \right) + \frac{\alpha}{2} \sqrt{\frac{\rho_i}{\rho_j}} \right) = 0,$$

no longer suggest a useful definition of individual pressures. The acceleration of the molecules of each gas is strongly dependent on the configuration of the other.

Again we consider first order perturbations of the equilibrium configuration. The linearized equations (4.4) are modified:

$$d\ddot{\rho}_i = -\dot{v}_i' = \partial^2_x \left( \frac{\partial V}{\partial \rho_i} \right) T + \frac{\alpha}{2} \sqrt{\frac{\rho_j}{\rho_i}}, \quad j \neq i.$$

Eq.s (4.7) and (4.8) gain additional terms,

$$\frac{\alpha}{4} \sqrt{\frac{\rho_2}{\rho_1}} \left( \frac{d\rho''_2}{\rho_1} - \frac{d\rho''_1}{\rho_2} \right) \text{ and } \frac{\alpha}{4} \sqrt{\frac{\rho_1}{\rho_2}} \left( \frac{d\rho''_1}{\rho_2} - \frac{d\rho''_2}{\rho_1} \right).$$

What makes the choice (4.11) special is the fact that, for a monocromatic wave, these additions are proportional to the difference $v_1 - v_2$ of the velocities. Comparison with the standard theory shows that this is what is needed.

The reduced speed of propagation is now obtained by setting to zero the determinant

$$\left( 1 + \frac{\tau}{\kappa} - \beta \tau^{-\frac{1}{2}} - c^2 \quad \kappa + \frac{\kappa}{\tau} - \beta \tau^{\frac{1}{2}} - c^2 \right), \quad \beta := \frac{\alpha}{4\mathcal{R}_1 T}, \quad (4.12)$$

24
In the limit of large $\beta$ the only eigenvector has $d\rho_1/\rho_1 = d\rho_2/\rho_2$ and the eigenvalue $c^2$ is precisely as in (4.10).

Numerical results for a type 1 mixture are in Fig.6. It may be seen that a value $\beta = .5$ is sufficient to bring the theory into substantial agreement with the experiment. Higher values of $\beta$ improves the agreement for low frequencies but tends to spoil it when compared with the few data that are available for the highest frequencies.

![Fig.6. The effect of the interaction (4.11) on sound speed in $N_2/Ar$. The middle curve is from (4.12) with for $\beta = .5$.](image)

Fig.6. The effect of the interaction (4.11) on sound speed in $N_2/Ar$. The middle curve is from (4.12) with for $\beta = .5$.

This modification of the lagrangian will be successful if the observation of a single, dominant mode is limited to low and moderate temperatures. If instead it extends to high temperatures an alternative may become more attractive (see below). The theory predicts no dispersion.

The case of type 2 mixtures (Fig.7.) is more dramatic. very small values of $\beta$ are enough to eliminate the isothermal modes in the SE and NW corners of the figure. The former disappears and the latter drops down to join the Laplace branch at the lower left. Agreement with experiment requires a value of $\beta$ at least equal to 1, near perfect agreement is gotten with $\beta = 5$, and larger values of $\beta$ only improve the fit, except for the data at the highest frequencies.
Fig. 7. Effects of the simple interaction term on the speed of sound in He/Xe, Eq. (4.12). From top to bottom: $\beta = 0, \beta = .01, \beta = .1, \beta = 1$.

### IV.4. A variant

One may try to replace $\alpha$ by $\alpha T$. The potential is then

$$ V = \sum R_i \rho_i T \ln \frac{\rho_i}{T^{n_i} k_{0i}} + \alpha T \sqrt{\rho_1 \rho_2}. $$

The new term may be considered as an addition to the free energy, and the expression for the entropy density is affected; it is possible to retain the homogenous entropy predicted by Gibbs-Dalton theory. Thus we retain the former values of the parameters $k_{0i}$.

Variation of the temperature gives

$$ \sum R_i \rho_i \ln \frac{\rho_i}{(eT)^{n_i} k_{0i}} + \alpha \sqrt{\rho_1 \rho_2} = 0. $$

The individual gases are no longer polytropic, even at equilibrium. The expression for the internal energy is independent of $\alpha$ and the sum formula (2.6) for the total pressure also remains valid.

Adiabatic changes obey

$$ \frac{dT}{T} \sum R_i \rho_i n_i = \sum R_i d\rho_i \left( \ln \frac{\rho_i}{(eT)^{n_i} k_{0i}} + 1 \right) + \frac{\alpha}{2} \sqrt{\rho_1 \rho_2} \sum \frac{d\rho_i}{\rho_i}. $$

Define

$$ N_i = R_i \rho_i \ln \frac{\rho_i}{(eT)^{n_i} k_{0i}}, \quad N = \frac{N_1 - N_2}{2}, $$
then
\[ \frac{dT}{T} \sum R_i \rho_i n_i = \sum R_i d \rho_i + N \left( \frac{d \rho_1}{\rho_1} - \frac{d \rho_2}{\rho_2} \right). \]

The linearized equation of motion is
\[ \frac{d \dot{\rho}_1}{\rho_1} = -\dot{\rho}_1' = \partial_x^2 \partial V, \]
with
\[ \frac{\partial V}{\partial \rho_1} = T R_1 (\ln \frac{\rho_1}{T n_1 k_0} + 1) + \frac{\alpha}{2} \sqrt{\frac{\rho_2}{\rho_1}}. \]

The adiabatic variation is
\[ \frac{d}{d \rho_1} \frac{\partial V}{\partial \rho_1} = \frac{dT}{T} \left( R_1 + \frac{N}{\rho_1} \right) + R_1 T \frac{d \rho_1}{\rho_1} + \frac{\alpha}{4} T \sqrt{\frac{\rho_2}{\rho_1}} \left( \frac{d \rho_2}{\rho_2} - \frac{d \rho_1}{\rho_1} \right) \]
\[ = \sum \frac{R_i \rho_i n_i}{R_i \rho_i n_i} \left( R_1 + \frac{N}{\rho_1} \right) \left( \sum R_i d \rho_i + N \left( \frac{d \rho_1}{\rho_1} - \frac{d \rho_2}{\rho_2} \right) \right) \]
\[ + R_1 T \frac{d \rho_1}{\rho_1} + \frac{\alpha}{4} T \sqrt{\frac{\rho_2}{\rho_1}} \left( \frac{d \rho_2}{\rho_2} - \frac{d \rho_1}{\rho_1} \right) \]

This time, \( c^2 \) is an eigenvalue of the matrix
\[ \begin{pmatrix} 1 + A_1 (\rho_1 + N/R_1) - \beta \tau^{-1/2} & \kappa (\rho_2 - N/R_2) + \beta \tau^{1/2} \\ A_2 (\rho_1 + N/R_1) + \beta \tau^{1/2} & \kappa + A_2 \kappa (\rho_2 - N/R_2) - \beta \tau^{1/2} \end{pmatrix}, \]
where
\[ A_1 = \frac{1}{\sum R_i \rho_i n_i} \left( R_1 + \frac{N}{\rho_1} \right) \]
and \( \beta = (\alpha/4 R_1) \). For large \( \alpha \) the eigen vector has \( d \rho_1/\rho_1 = d \rho_2/\rho_2 \) and \( \alpha \) is eliminated by adding \( \rho_1 \) times the sum of the elements in the first row and \( \rho_2 \) times the sum of the elements in the second row, with the result
\[ A_1 R_1 \rho_1^2 + R_1 T \rho_1 + A_2 R_2 \rho_2^2 + R_2 T \rho_2 - \nu^2 (\rho_1 + \rho_2) = 0, \]
which again agrees with (3.10).

Both models can account for the experiments within a range of temperatures and frequencies. The only observation at a temperature other that room temperature that is known to us is that of Smorenburg et al (Smorenburg 1995). At a molar concentration of 3:1 in He/Ar (Type 2), \( \rho_1/\rho_2 = .3 \), at 160K and 370 bar, they observe the same sound speed as in pure helium. This may indicate that, of our two models, our second one is closer to observation.
V. Application to atmospheres

V.1. Introducing gravitation

Gravitation enters as a component of most, if not all applications of physics. There is a set and tested procedure for introducing the gravitational field into any dynamical context. In classical, non-relativistic physics it consists of adding the gravitational potential energy to the Hamiltonian. For an ideal gas one adds

$$\int \Sigma d^3 x \rho \phi,$$

where $\rho$ is the mass density and $\phi$ is the Newtonian potential. The adiabatic Lagrangian becomes

$$\mathcal{L} = \int \Sigma d^3 x \left( \rho (\dot{\Phi} - \vec{v}^2/2 - \phi + \lambda) - \mathcal{R} T \rho \ln \frac{k}{k_0} \right).$$

The gravitational field appears in the equation of motion,

$$\dot{\Phi} - \vec{v}^2/2 - \phi + \lambda = \mathcal{R} T (\ln \frac{k}{k_0} + 1), \quad k = \rho/T^n.$$

When the effect of gravity is taken into account in the dynamics we get a theory of atmospheres. In the case of terrestrial gravity $\phi = g z$, where $g$ is a constant and $z$ is the elevation. At equilibrium $k$ is constant and the equation

$$\lambda - gz = \mathcal{R} T (n + 1)$$

predicts a constant temperature gradient (lapse rate). The effect has never, to our knowledge, been tested in the laboratory (but see Graeff 2009), but the constant lapse rate is a feature that is observed in the earth’s atmosphere and in the internal structure of stars (Lane 1870, Ritter 1880, Eddington 1926). For the earthly troposphere this formula actually gives a value of the temperature gradient that is closed to observation.

We have noted that this successful application of a theory originally constructed to account for laboratory experiments where gravitational effects are insignificant, modified in standard fashion to include gravity, does not attribute the observed temperature gradient to the radiation from the sun or to any external source other than gravity (Fronsdal 2010).

And yet it is evident that, in the absence of the sun, the present state of the earthly atmosphere could not endure. The extinction of the sun would lead to a general cooling of the atmosphere. This cooling is not described by any process encompassed by the adiabatic Lagrangian dynamics. Instead, an external agent enters the picture, the spontaneous emission of infrared radiation. As this is a slow effect we can regard the cooling as a sequence of equilibria of adiabatic dynamics, a slow loss of entropy and an increase in the value of $k_0$. (Section II.4.) The reverse effect is also possible and if the terrestrial atmosphere is stable over long times then we must conclude that spontaneous cooling by emission is balanced by heating provided by the sun.
V.2. Mixed atmospheres

At one time it was believed that, in an atmosphere consisting of several components with different molecular weights, the lighter gas would float on top. This was surely based on observation, since cooking gas, entered at ground level, tends to remain there; however, it does so only for a short time. Dalton made the radical proposal that each gas behaves as if the other were absent. This was an overstatement and led to much misunderstanding and debate, some of it recorded in Dalton’s book (Dalton 1806). In the case of non evanescent gases that have had time to settle, Dalton’s prediction is fairly close to the truth, but he did not go far enough, for actually it is observed that the concentrations tend to be independent of elevation. In order to account for this, one needs to invoke the intervention of a mechanism, called convection for short, or “mixing due to fluid motions”, or diffusion. This takes us back, once more, to consideration of a dissipative process, which can be interesting, but if the problem that concerns us is the density and temperature profiles of the mixed atmosphere then it begs the question. If, as is often observed, an equilibrium is ultimately reached, then we are mainly interested in the end result, and less in describing the process that leads to it. The process is dissipative and entropy producing; its principal feature is that it is slow. It can be ignored in the study of the final equilibrium configuration, and the adiabatic perturbations of it.

We have embraced the Gibbs-Dalton hypothesis and we have incorporated it into our lagrangian for the mixtures that are not under the influence of gravity. But in the presence of gravity there is an ambiguity. We shall describe an attempt to adopt the global version of the hypothesis to atmospheres. It is only moderately successful. Then we shall determine the lagrangian by direct appeal to experience, to get a perfect fit.

V.3. The Gibbs-Dalton model

Consider at first a vertical column of air consisting of nitrogen and oxygen and confined to the range $0 < z < z_1$ of elevation. Because the Lagrange multipliers are freely adjustable we can fix $z = 0$ at ground level. If gravity were not present we should have an equilibrium configuration with uniform densities and temperature and the equations of motion would give us

$$\rho_i = k_{0i}(eT)^{n_i}, \quad \lambda_i = R_iT(n_i + 1), \quad i = 1, 2,$$

implying the Gibbs-Dalton constraint, at equilibrium

$$(\rho_1/k_{01})^{1/n_1} = (\rho_2/k_{02})^{1/n_2}$$

and thus

$$(M_1/k_{01})^{1/n_1} = (M_2/k_{02})^{1/n_2}$$

Having chosen the domain and the parameters (except the Lagrange multipliers), we add the gravitational field. The masses, presumed unchanged, are now related to the partial pressures at ground level, *

$$gM_i = R_i\rho_i(0)T(0). \quad i = 1, 2.$$
(ρ₁(0) = 3.26ρ₂(0)) and μ₁ = 28, μ₂ = 32, ρ₁(0) = .9184 × 10⁻³, ρ₂(0) = .2816 × 10⁻³, n₁ = n₂ = 2.5.

The constraint (3.4) gives, for the masses implied by these parameter values,

\[ k_{02}/k_{01} = (μ₁/μ₂)(1/4) = .26825. \] (5.1)

The equations that determine the equilibrium configurations are

\[ λ₁ - φ = R₁T(\ln x + 1 + n₁), \quad x := ρ₁/(eT)^{n₁}k_{01}, \] (5.2)

\[ λ₂ - φ = R₂T(\ln y + 1 + n₂), \quad y := ρ₂/(eT)^{n₂}k_{02}, \] (5.3)

\[ R₁ρ₁\ln x + R₂ρ₂\ln y = 0. \] (5.4)

It is useful to note that y(0)/x(0) = μ₂/μ₁. The third equation can be rearranged to give, since n₁ = n₂,

\[ \ln x(0) = \frac{1}{1 + ρ₂/ρ₁} \ln \frac{μ₁}{μ₂}, \quad \ln y(0) = \frac{1}{1 + ρ₂/ρ₁} \ln \frac{μ₁}{μ₂}. \]

Thus ln x(0) = -.02824, x = .9722, ln y = .1053, y = 1.111 and

\[ k_{01} = ρ₁(0)/(eT)^{n₁} = 4.975 \times 10⁻¹¹, \quad k_{02} = ρ₂(0)/(eT)^{n₂} = 1.339 \times 10⁻¹¹ \] (5.5)

and finally λ₁ = 3.09645 × 10⁹, λ₂ = 2.81343 × 10⁹.

The atmosphere ends where the pressure vanishes; that is, where T = 0. Since λ₁ > λ₂, this happens at the point where

\[ φ = λ₁, \quad x = 1, \quad y = 0, \quad z = λ₁/g ≈ 31.6 \times 10⁵ \text{ (32 km)}. \]

Just below this point we find that dT ∝ dz, ρ₁ ∝ Tⁿ₁, ρ₂ ∝ Tⁿ₂e⁻α/T, with dz = λ₁/g – z and α = (λ₁ – λ₂)/R₂ = 121.885. The first gas is dominant and adiabatic as if it alone constituted the atmosphere; the second gas has a different profile in this region.

More interesting are the temperature and density profiles near the ground; we have

\[ -\frac{T'}{T}(0) = 3.2303 \times 10⁻⁷ = 3.23 \%/\text{km}. \] (5.6)

In a nitrogen (oxygen) atmosphere the numbers are 3.14% (resp 3.59 %). The density profiles are

\[ \frac{ρ₁'}{ρ₁}(0) = -7.852 \times 10⁻⁶, \quad \frac{ρ₂'}{ρ₂}(0) = -9.038 \times 10⁻⁶. \] (5.7)

The last two ratios are found by observation to be very much closer. The concentrations are reported with four significant digits (no error bars) at all levels where the theory can be applied with any confidence (up to 10 km).
The slopes were calculated as follows. From (5.2-3),

\[-g\mu_1 = \mathcal{R}T \frac{\rho_1'}{\rho_1} + \mathcal{R}T' (\ln x + 1), \quad -g\mu_2 = \mathcal{R}T \frac{\rho_2'}{\rho_2} + \mathcal{R}T' (\ln y + 1)\]

From (5.4) and some reduction,

\[
\frac{T'}{T} = -\frac{g\mu_1 \mu_2}{\mathcal{R}T} \frac{\rho_1 (\ln x + 1) + \rho_2 (\ln y + 1)}{\mu_1 \rho_2 [(\ln y + 1)^2 + n_2] + \mu_2 \rho_1 [(\ln x + 1)^2 + n_1]}.
\]

The prediction (5.7), of two different rates of decrease of density, is not very far off. It may be correct when the rate of diffusion, that tends to reduce the difference, is small, and for young mixtures, when diffusion did not yet have enough time to act. The difference is only 1 percent per km, but it is much too large to be reconciled with measurements in our atmosphere.

V.4. Entropy from experiment

Let us take it as a result of observation that the concentration of the principal gases in our atmosphere are very nearly constant at low altitudes, and use this datum to find the values of the entropy parameters \(k_{01}, k_{02}\).

The 3 equations of motion are

\[
\sum R_i \rho_i \ln x_i = 0, \quad x_i := \frac{\rho_i}{k_{0i}(eT)^{n_i}}, \quad (5.8)
\]

\[
\lambda_i - gz = \mathcal{R}_i T (\ln x_i + 1 + n_i), \quad i = 1, 2. \quad (5.9)
\]

We eliminate the Lagrange multipliers by differentiation, to get

\[-g = \mathcal{R}_i T' (\ln x_i + 1) + \mathcal{R}_i T \rho_i'/\rho_i, \quad i = 1, 2, \quad (5.10)\]

and introduce the experimental evidence in the form \(\rho_1'/\rho_1 = \rho_2'/\rho_2\).

We begin the reduction of these equations by deriving 2 relations without logarithms. The first is obtained by differentiation of Eq. (5.8),

\[
\frac{\rho_1'}{\rho_1} = \frac{\rho_2'}{\rho_2} = n \frac{T'}{T}, \quad n := \frac{\sum \mathcal{R}_i \rho_i n_i}{\sum \mathcal{R}_i \rho_i}. \quad (5.11)
\]

The second relation is obtained by multiplying (5.10) by \(\rho_i\), summing, and combining with (5.8), and using the last result,

\[-g(\rho_1 + \rho_2) = T' \sum \mathcal{R}_i \rho_i (n + 1),\]

or

\[
T' = \frac{-g\mu}{\mathcal{R}(n + 1)}, \quad \frac{1}{\mu} := \frac{\sum \rho_i/\mu_i}{\sum \rho_i} = 1/28.7179.
\]
Since the two densities are proportional, the quantities \( n \) and \( \mu \) are uniform, and so is the temperature lapse rate.

We are now in position to evaluate the entropy. Eq.s (5.10) give us

\[
\ln x_i = (n + 1)\left(\frac{\mu_i}{\mu} - 1\right) \quad i = 1, 2;
\]

also uniform. (values -.1026 and .3827, \( x = .9024, y = 1.466 \).) Finally,

\[
k_{0i} = \frac{\rho_i}{x_i} (eT)^{-n_i}.
\]

with values \( 5.359 \times 10^{-11} \) and \( 1.011 \times 10^{-11} \), compare (5.5) and \( k_{02}/k_{01} = .1887 \), see (5.1).

The entropies that are determined this way, using the observed constancy of concentrations, are not very different from those calculated on the basis of the Gibbs-Dalton hypothesis.

When heat is supplied or withdrawn, without loss or gain in total mass, we note that

\[
k_{0i} = \frac{p_i}{x_i R_i} (eT)^{-n_i - 1},
\]

where \( p_i \) is the partial pressure. Evaluated at ground level, the first factor remains constant, so that the system moves on a path

\[
q := \frac{k_{01}^{n_2+1}}{k_{02}^{n_1+1}} = \text{constant}.
\]

The entropy density, given by the on shell condition (4.8) as

\[
s = \sum R_i \rho_i \ln k_{0i} = \sum R_i \rho_i (\ln \rho_i - n_i \ln eT),
\]

is a function of the densities, the parameters and the temperature. The temperature lapse rate (uniform) is 9.67 K per km and the proportional rate at ground level \(-T'/T(0)\) is \(3.23 \times 10^{-7}\) or 3.2 % per km. The fractional density gradient is \(\rho'(0)/\rho(0) = 8.075\%\) per km.

\section*{V.5. Interaction model}

It is common to all models that failure of the Gibbs-Dalton hypothesis (about equilibrium entropies) to account for the observation of (a single) sound speed in mixtures is attributed to the effect of interactions between the atoms of the two species. But the properties of mixtures at equilibrium do seem to be accounted for by this hypothesis. It is therefore of interest to discover whether the observed atmospheric concentrations can be accounted for without affecting the entropies. A model of sound propagation examined in Section IV.3 does have this property.

This first model has the appealing property of preserving the simplicity of the Gibbs-Dalton equilibrium; the equation of motion that comes from variation of \( T \) has a unique
solution such that the two terms in Eq.(4.4) vanish individually; thus $x = y = 1$. The interaction term (4.11) affects the density-variation equations. Instead of (5.2-3),

$$\lambda_1 - \phi = R_1 T (1 + n_1) + \frac{\alpha}{2} \sqrt{\frac{\rho_2}{\rho_1}},$$

$$\lambda_2 - \phi = R_2 T (1 + n_2) + \frac{\alpha}{2} \sqrt{\frac{\rho_1}{\rho_2}},$$

This is incompatible with constant concentration if $\mu_1 \neq \mu_2$. This model cannot, by itself, do the job, but of course it may work in conjunction with an adjustment of the entropy.

The second model leads to

$$\lambda_1 - \phi = R_1 T (1 + n_1) + \frac{\alpha T}{2} \sqrt{\frac{\rho_2}{\rho_1}},$$

$$\lambda_2 - \phi = R_2 T (1 + n_2) + \frac{\alpha T}{2} \sqrt{\frac{\rho_1}{\rho_2}},$$

and this is compatible with constant concentration for one value of $\alpha$, namely $\beta = \alpha / 4 R_1 \approx .004$.

5.6. The hydrogen atmosphere

Saha (1821) used his formula in studies of dissociation in stellar atmosphere, with pressure and temperature data obtained from other sources, with results that agreed well enough with observation. But there was no study of these profiles within the context of the theory. Here, with the advantage of a complete formulation of the dynamics, we can calculate the profiles directly.

To describe a hydrogen atmosphere we include the gravitational potential in the lagrangian. An isolated atmosphere is characterized by fixed entropy. The equilibrium relations (3.10-11) remain valid; they are the two equations that remain when the gravitational potential is eliminated from the equations of motion. If instead we eliminate the logarithms we get the simple result given on Eq.(5.11) below.

What is needed in addition is a relationship between $r$ and $T$ for constant entropy; that is, for constant values of the parameters $k_{01}$ and $k_{02}$. The other equation of motion, Eq. (3.8), is the fundamental relation of the gas, for which there is no counterpart in Saha’s approach. From it we can extract a formula for the density. But the most revealing result is obtained by eliminating the density $\rho = \rho_1 + \rho_2$ from the three equations of motion. The result is the following two simple equations of motion,

$$\lambda - gz + \epsilon r = T < R(n + 1) >,$$  \hspace{1cm} (5.11)

and

$$(n_1 - n_2) \ln T = \frac{< R(n + 1) >}{R} + (1 + r) \frac{\epsilon}{RT} + \text{constant}. \hspace{1cm} (5.12)$$
where

\[ < R(n+1) > := \sum R_i (n_i + 1) \frac{\rho_i}{\rho} \, \rho . \]

Eq. (3.10) - resp. (3.11) - is a relation between \( r \) and \( T \) that holds through a sequence of equilibrium configurations with different energies (assuming that \( q \) is constant), at constant volume - resp. at constant pressure. Eq. (5.11-12), on the other hand, hold throughout the atmosphere, with fixed entropy.

Eq. (5.11) is a smooth interpolation between the atmosphere of molecular hydrogen at low temperatures and the atomic atmosphere of high temperatures. There is an important change in the lapse rate across the transition region.

The Lagrange multiplier \( \lambda \) controls the total mass and the constant in the second equation is the entropy; both are free parameters.

From (5.11) and (5.12) on easily obtains profiles of temperature and densities. Further work in this direction is deferred.
VI. Conclusions

Let us assess what has been done and, especially, what has not been done here.

(a) It was, of course, well known that irrotational hydrodynamics can be formulated as an eulerian field theory with an action principl. Conservation of energy is a cornerstone of thermodynamics and all adjacent sciences. What appears to be new is including the temperature in the set of independent dynamical variables, with respect to which the action is an extremum. By this means all required information about a system is stored, once and for all, in the lagrangian. Traditional thermodynamics is an on shell projection; more precisely, a partial projection on the solutions of one or more of the variational equations.

(b) Given the gas law and the expression for the internal energy of an ideal gas it is commonplace to calculate the entropy as a function of, say, density and temperature. This is a fundamental relation of the ideal gas, from which all its properties can be deduced (Callen 1960). What may be new is that there is an off shell level of theory at which $S, T$ and $\rho$ are independent variables, and that the fundamental relation is the on shell condition obtained by variation of the temperature; it is one of the equations of motion.

(c) The equations that constitute the Euler Lagrange equations do not contain anything new, as far as the one component ideal gas is concerned. What may be new is the total reliance on the chosen lagrangian for all subsequent applications. Any expansion or generalization of the system or of the context must be done (so we say) by making whatever changes that are necessary in the lagrangian, in a manner so as not to upset any of the applications that have already been successful. This last is a very strong restraint on invention. It is the main reason for pursuing this line of inquiry.

(d) Mixtures are usually studied by means of the Gibbs function, but such studies are always, as far as we know, hampered by the fact that this function is known only relatively to that of a reference configuration. It seems that the lagrangian gives more information than what has been extracted from the Gibbs function. We have taken literally, perhaps more so than is traditional, the additivity of lagrangians for composed systems. We have been led to a suggestion for the lagrangians for mixtures that are precise except for the values of a small set of parameters, in number equal to the number of components. This has greatly facilitated the task of using experimental information to pin down the entropy of mixtures, something that we have found to be unexpectedly easy. This is our best result.

(e) The suggestion of “second sound” in a gaseous mixture is not confirmed by observation. We have suggested that this signals a limitation of the Gibbs-Dalton hypothesis to serve as a guide for dynamics. It was shown that some of the observations can be explained in terms of an interaction of densities, without the assistance of kinetic theory. Further exploration of this model must wait for more data, over a wider range of frequencies and temperatures.

(f) There are seeds of a controversy in all this. There is no doubt that all the results can be obtained without using an action principle. But, as was stressed already, the action principle is a powerful guide to further applications. Indeed, the action principle, combined with what is known about gravitation, may be at variance with the common conception of an isothermal equilibrium of an isolated gas in the presence of a gravitational field. For this reason we have continued the investigation, begun in the first paper of this series, of the classical arguments that seem to have convinced all our thermodynamicists.
Results have been relegated to the Appendix, to avoid giving the impression that this is all we are trying to say in this paper. We suggest that measurements of the temperature gradient in a supercentrifuge should be carried out. Such measurements should relatively simple; it would settle once and for all (via the principle of equivalence) the question of the isolated atmosphere. A profound reassessment would be required, whatever the result, for an isolated, isothermal atmosphere does not have a natural place in thermodynamics (Fronsdal 2010), while the existence of a temperature gradient is widely believed to be a violation of the second law of thermodynamics.

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Appendix. The controversial “isolated” atmosphere

If a vertical column of an ideal gas is isolated from radiation, both emitted and absorbed, then it may be reasonable to believe that both may be left out of consideration. That is, an isolated column of gas in the gravitational field would obey the equations of motion and exhibit a temperature gradient. This conclusion was reached long ago by Loschmidt (1876) and others. It was refuted by Maxwell (1868) and Boltzmann (1909), as follows.

If we would grant that an isolated, vertical column of air in equilibrium were colder at the top and warmer at the bottom, then a paradox would arise. Consider this arrangement: A heat bath with the lowest point at \( z = 0 \) is maintained with temperature \( T = T_0 \) (at \( z = 0 \) if not everywhere). Below it is suspended a vertical cylinder filled with an ideal gas, in thermal contact at \( z = 0 \) with the heat bath, but otherwise isolated. The theory predicts that, while the gas at the top of the cylinder has temperature \( T_0 \), the bottom will be warmer, with temperature \( T_1 > T_0 \). It is proposed to utilize this temperature difference to run an engine, taking heat from the bottom of the cylinder and returning it to the bath. The argument is circular, for a complete analysis would require a theory of heat engines operating between different levels of the gravitational field. Maxwell circumvented this objection by replacing the heat engine by a second cylinder, filled by another ideal gas, with different characteristics (molecular weight, density, adiabatic index). This second cylinder, at equilibrium, would have the same temperature \( T_0 \) at the top, but a different temperature \( T_2 \neq T_1 \) at the bottom. Now provide thermal contact between the bottoms of the two cylinders and suppose that \( T_0 < T_1 < T_2 \) at \( t = 0 \). Then both \( T_1 \) and \( T_2 \) will begin to change, in the direction of equalization. If “heat flow” is defined in terms of the gradient of the temperature then, according to Maxwell, a permanent, closed heat flow will be established; apparently, a perpetuum mobile of the second kind.

We believe that the force of the conclusion is strongly affected if it is shown that no energy flows.

The perpetuum mobile of Maxwell is one in which no work is being accomplished, “nothing really happens”, since the energy flow of the final, asymptotic configuration can be assumed to vanish without contradiction. But what is this final state? Does it in fact exist? We believe that, at late times, a stationary state will be reached, and we try to calculate it.

To remove a slight complication, let us take away the heat bath but retain the thermal contact between the two cylinders at both ends, isolating the system. The original, adiabatic equations of motion cannot apply as they stand, since they require two different lapse rates. Another process is needed, similar to “cooling”, in which there is a change in entropy. To account for this additional process we use the model lagrangian

\[
\mathcal{L}_{\text{tot}} = \mathcal{L}[\Phi, \rho, T, ...] + \mathcal{L}[k, \sigma],
\]

with the gravitational potential included as before in the adiabatic part. The field \( \sigma \) is canonically conjugate to \( T \). The domain is the union of the two cylinders. The equations of motion include the equation of continuity, unchanged, and, at equilibrium,

\[
-\phi + \lambda_i = \mathcal{R}_i T (\ln \frac{k_i}{k_0} + 1), \quad k_i := \rho_i / T^{n_i}, \quad i = 1, 2,
\]
\[
\mathcal{R}\rho_i (\ln \frac{k_i}{k_0} - n_i) = c \Delta \sigma_i, \\
c\Delta T = 0.
\]

It is important to emphasize that the entropy is not driven directly by gravity—that would imply an unorthodox gravitational interaction and probably a violation of the equivalence principle. When the thermal contact is made, between the lower ends of the two tubes, the temperature at that point will eventually settle at a value \(\hat{T}\) intermediary between \(T_1\) and \(T_2\), resulting in a temperature gradient different from that induced by gravity in either of the two separated tubes. Let

\[
\delta T'_i = (\hat{T} - T_i)/\ell, \quad i = 1, 2,
\]

where \(\ell\) is the length of the tubes, or more precisely the difference in elevation between the upper and lower ends. This increment drives the entropy, thus

\[
c\sigma''''_i = -\frac{\mathcal{R}_i (n_i + 1) \rho_i}{T} \delta T'_i.
\]

Because the process is reversible, \(\sigma''''_1 + \sigma''''_2\) must be zero, which leads to

\[
T' \approx -g \frac{\rho_1 + \rho_2}{\mathcal{R}_1 \rho_1 (n_1 + 1) + \mathcal{R}_2 \rho_2 (n_2 + 1)},
\]

where, to this order, one should interpret the densities as averages. This represents a reasonable interpolation between the two extreme cases in which one or the other cylinder is absent.

There is no energy flow within the tubes and, since the temperature is continuous, no energy passes the boundary.

If instead one would justify the belief that a heat engine can be made to run on the temperature difference between the lower ends of the two cylinders (Graeff 2007), then a similar analysis involving entropy needs to be made.

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