

V. A theory of fluid mixtures

The traditional treatment of **mixtures** often relies on rules concerning the additivity of properties; one of the most important ones is the additivity of the energies of the components of a composite system. Most fundamental of all is the postulate of additivity of Lagrangians;

$$\mathcal{L} = \sum_{i=1,2} \mathcal{L}_i = \sum_i \rho_i (\dot{\Phi}_i - \vec{v}_i^2/2) - f - sT, \quad (A)$$

$$f = \sum_i f_i, \quad s = \sum_i s_i;$$

it incorporates the additivity of energies and the additivity of entropies. The algebraic sum of the Lagrangians of two adiabatic systems describes an adiabatic system with two non **interacting components**.

Realistically, coexistent systems are never non interacting and ways have to be found to take the interaction into account. The strategy will be to begin by joining the Lagrangians of components, with the expectation that corrective terms, ‘interactions’, will have to be added. The systematic application of this point of view is not wide spread in thermodynamics. (See for example many studies of critical phenomena in mixtures.) But it is a standard, and successful, strategy in more developed branches of theoretical physics - and it incorporates a general concept that helps us understand mixtures:

In the limit when interactions are weak, each constituent behaves as if the others were absent

An overstatement; it overlooks the fact that the two temperatures are replaced by just one and the important role that is consequently played by the adiabatic condition, about which much more below. ¹

Recall that in unary thermodynamics it is axiomatic that the free energy (or any other fundamental potential expressed in terms of the natural variables) tells us all that we need to know about a substance. It follows that a mixture in which each constituent behaves as if it were alone is described by variables that satisfy the usual equations of motion of a unary system. The natural variables for the mixture is thus the collection of natural variables for the ingredients. And if this mixture is characterized by an action principle, then the action must be a sum of individual actions, in the limit of no interactions.

Although the attitude that has just been expressed is quite traditional, it is decidedly less so when seen in the context of the formula

$$s = \rho_1 S_1 + \rho_2 S_2, \tag{B}$$

for it implies the relation

$$\rho_1 s_1 + \rho_2 s_2 = -\frac{\partial f}{\partial T},$$

which is much more than $s = -\partial f/\partial T$, merely a definition of the entropy.

The principles expressed in Eq. (A) and Eq. (B) are characteristic of the Lagrangian approach; much more consequential than the idea that each gas behaves as if it were alone.

¹Compare the Gibbs-Dalton hypothesis. Section V.4.

The persistent use of a **Lagrangian** does much to distinguish our approach to thermodynamics, the choice of variables is just as important. I confess to being perplexed by the common usage, especially the occasional suppression of degrees of freedom and the preference for molar fractions over partial densities. Here is the addition formula for free energy of a mixture of ideal gases,

$$F = \frac{f_1 + f_2}{\rho} = N_1 F_1 + N_2 F_2 + \mathcal{R}T(N_1 \ln N_1 + N_2 \ln N_2).$$

In terms of ordinary densities this statement takes the form $f = f_1 + f_2$.

Until further notice it will be assumed that no chemical reactions are taking place in the mixtures under consideration, and that the equilibria are uniform. In this case an important idea is the Gibbs-Dalton hypothesis, to be developed in this chapter and used in Chapter VI.

Chemical interactions change the picture materially; they will occupy us for the remainder of this chapter. Immiscible fluids form an other category of mixtures, the subject of Chapter VI.

V.1. Variables and potentials

A description of two non interacting systems requires two sets of variables. In particular, each system has a temperature or a temperature field. This is natural if the two systems occupy different, non overlapping regions of space. Situations exist where two systems occupy the same space and for which it has nevertheless been found useful to maintain a notion of separate temperatures. For example, in plasma physics, and in Cosmology. But in this book the temperature shall always be taken to be a unique field extended over the total vessel. Two components may be present in the same region but we shall try to get by with only one temperature field. If this strategy fails then it shall be abandoned, reluctantly. That has not come to pass, so far.

Taken for granted is the idea that each distinct component has an independent flow vector field. Otherwise, there would be no way to formulate the separate **conservation of masses** and separate equations of continuity, for each component (and no way to visualise the ‘mixing’). More precisely, we say that, if two densities are separately conserved, then one needs two independent velocity fields \vec{v}_1 and \vec{v}_2 in order to be able to assert that

$\dot{\rho}_1 + \text{div}(\rho_1 \vec{v}_1) = 0$ and $\dot{\rho}_2 + \text{div}(\rho_2 \vec{v}_2) = 0$.² But if only the total density is conserved then there can be only one velocity and only one continuity equation. The analysis becomes simpler if one assumes that the mixture behaves as a one component fluid,³ with properties defined by interpolation between those of the components. This drastic assumption, first used by van der Waals, is tempting in the case of mixtures of many components; it is common, for example, in calculations relating to the interior of the Sun. But it ignores physical degrees of freedom and cannot account for all observed phenomena. Others introduce individual densities and velocities without comment, as in Bois and Kubicki (2000). Let us keep an open mind on this question.

By adopting a two-velocity approach to binary mixtures without chemical reactions we depart in an essential way from what is common practice. The most important 2-fluid theory is Landau's theory of superfluidity. But Landau's equations are not derived from an action principle and consequently, even in that case, we shall propose a new direction. See Chapter VIII. For an example of a treatment of mixtures in terms of multiple velocities see Glavatsky (2009).

In the ideal case, when there is (if there were) no interaction between the components, there can be no objection to two separate and independent velocities; they are unaware of each other and they pass freely through each other. But this simple scenario is not realistic, for the insistence on a single temperature amounts to an interaction between the two components. There is only one adiabatic condition; each component in a mixture satisfies an adiabatic condition that depends on the dynamical variables configuration of the other component.

The imperfect transparency of each component with respect to the other will be further affected when we allow for an explicit interaction between the components, the simplest being an addition to the total free energy density,

$$f = f_1 + f_2 + f_{int}, \quad f_{int} = \alpha \rho_1 \rho_2, \quad \alpha \text{ constant.}$$

An interaction of this type was used with some success by van der Waals. With α positive it has the effect of discouraging the overlap of the densities of the two species and the interaction is a repulsion and *mutatis mutandis*.)

²As in Landau's 2-fluid theory of liquid helium with its 2 equations of continuity.

³"Air is a mixture that behaves, under normal conditions, like an ideal gas." Mueller 2009.

From now on it is taken for granted that the dynamical variables of mixtures at rest are the **individual densities** ρ_i , individual specific entropies S_i (next section), and T . The variables chosen by Gibbs, and used almost universally ever since, are the total volume or density and the **molar fractions**, instead of the individual densities. This leads to a definition of the Gibbs function as a function of pressure, temperature, and molar fractions, related to the free energy by a Legendre transformation, $G(P, T, x) = F(V, T, x) + VP$. In our approach, using densities, the **Gibbs potential density** is not related to the free energy density by a Legendre transformation. The **Legendre transformations** of densities are natural generalizations of those listed in Section III.7, including the following,

$$p(T, \mu_1, \mu_2, \dots) = \sum_i \rho_i \mu_i - f, \quad dp = \sum_i \rho_i d\mu_i + s dT, \quad (5.1.1)$$

with

$$\mu_i = \left. \frac{\partial f}{\partial \rho_i} \right|_T = \left. \frac{\partial u}{\partial \rho_i} \right|_s.$$

and

$$dp = s dT + \sum_i \rho_i d\mu_i.$$

The natural variables of the internal energy are s and ρ_1, ρ_2, \dots :

$$u(\rho_1, \rho_2, \dots, s) = f(\rho_1, \rho_2, \dots, T) + sT, \\ du = \sum \mu_i d\rho_i + T ds, \quad df = \sum \mu_i d\rho_i - s dT.$$

All the potentials have $n + 1$ variables (n is the number of components.) There is no potential $p(T, \mu)$. The Clapeyron equation, that oddly is not presented in the literature in differential form, arises from the fixing of the molar fractions. Instead the correct equation is

$$\frac{\partial p}{\partial T} = s.$$

The interpretation of the pressure as a thermodynamical density potential was stressed in Section III.5. The thermodynamic variables are the entropy density s with its conjugate T and each partial density ρ_i with its conjugate μ_i .

For a multi component system, with no interaction between the constituents, we shall make the natural assumption that the free energy is

$$f = \sum_i f_i,$$

where f_1, f_2, \dots are the same expressions for the free energy of the components, in terms of their natural variables, that apply when they are by themselves.

The principal density potentials for multicomponent thermodynamics are

$$p(T, \vec{\mu}) = f(T, \vec{\rho}), \quad u(s, \vec{\rho}), \quad h(s, \vec{\mu}).$$

The introduction, by Gibbs, of molar fractions as principal variables, the associated approach to chemical potentials and the complications that this brings to analysis (Gibbs - Duhem relation, a separate treatment of open systems) will be eschewed; the variables are T , the densities, and the chemical potentials defined above.

Molar fractions and ‘free energy of mixing’

With the introduction of molar fractions and the associated chemical potentials, Gibbs arrives at expressions for the differentials of thermodynamical potentials. When those relations are rewritten in terms of densities all reference to molar fractions drops out and one ends up with the simpler set of differentials given above. We leave the verification of this to the skeptical reader.

We must not neglect to point out that the above formula for pressure can be expressed in the more familiar fashion as

$$p(T, \rho, N_1, \dots) = f - \rho \left. \frac{\partial f}{\partial \rho} \right|_{T, N_1, N_2, \dots}, \quad (5.1.2)$$

where N_1, N_2, \dots are the molar fractions. However, the formula $f = f_1 + f_2$ may seem controversial. The standard approach is to express the free energy for N moles of the liquid as NF , thus F is the free energy of one mole of the pure gas when it is alone. Then the usual formula for the mixture is,

$$F = f/\rho = N_1 F_1 + N_2 F_2 + F_{\text{mix}}.$$

We can compare the two expressions in the case of a mixture of two ideal gases. In terms of molar densities the free energy of an ideal gas is

$$f(\rho_i, T) = \mathcal{R} \rho_i T \ln \frac{\rho_i}{T^{n_i}}.$$

In the mixture, if the molar fraction is $N_1 = \rho_1/\rho$, one writes

$$f_i(\rho_i, T) = \rho_i \mathcal{R} T \ln \frac{\rho_i}{T^{n_i}} = \rho N_i \mathcal{R} T (\ln \frac{\rho}{T^{n_i}} + \ln N_i). \quad (5.1.3)$$

We hold that this separation is wholly unwarranted. It results in the unwieldy expression

$$F = \frac{f_1 + f_2}{\rho} = N_1 F_1 + N_2 F_2 + \mathcal{R}T(N_1 \ln N_1 + N_2 \ln N_2). \quad (5.1.4)$$

The last term is F_{mix} ; it is regarded as a ‘mixing correction’ and in the general case it is replaced by a phenomenological correction.⁴ When the densities are used as fundamental variables all the awkward mixing terms disappear.

For non interacting gases the more natural formula $f = f_1 + f_2$ will be used in this book; there is no mixing term. Interactions will be introduced by adding a term that depends on both sets of variables,

$$f = f_1 + f_2 + f_{\text{int}}.$$

The same remarks apply to entropy; the concept “**entropy of mixing**” does not appear again in this book. The densities f and s are additive in the absence of interaction.

Remark. The **Gibbs-Duhem** relation is the statement that the function f depends on the $n + 1$ variables $\rho_i = \rho N_i$ and T , and not separately on ρ .

V.2. Entropy and equations of motion

The following expression for the Lagrangian density is appropriate when there are no chemical reactions and all the densities are independent variables. Note that each individual kinetic energy term $-\rho_i \vec{v}_i^2/2$ must be accompanied by the term $\dot{\Phi}_i$, for Galilei invariance. See Section III.11. Clearly, this implies a set of canonical pairs of basic variables $(\rho_i, \dot{\Phi}_i)$. It was argued, and postulated in the introduction to this chapter, that the action for an ideal composite system - one without interactions between the constituents - must be additive; consequently, before including an interaction term we have the tentative Lagrangian,

$$\mathcal{L} = \sum_{i=1,2} \mathcal{L}_i = \sum_i \rho_i (\dot{\Phi}_i - \vec{v}_i^2/2) - f - sT. \quad (5.2.1)$$

with

$$f = \sum_i f_i \quad \text{and} \quad s = \sum_i s_i, \quad i = 1, 2.$$

⁴See Lemmon and Jacobsen (1968), where we find $F = N_1 F_1 + N_2 F_2 + F_{\text{mix}} + F_{\text{int}}$.

Variation of the temperature gives the adiabatic condition

$$s = -\frac{\partial f(T, \rho_1, \rho_2)}{\partial T} = \frac{\partial f_1(T, \rho_1)}{\partial T} + \frac{\partial f_2(T, \rho_2)}{\partial T}; \quad (5.2.2)$$

in the absence of interactions it expresses a weak form of the Gibbs-Dalton hypotheses, to be discussed below. This formula is one of the most important consequences of formulating thermodynamics as an **action principle**.

The structure of the kinetic term is appropriate in the absence of chemical reactions. It is strongly motivated by the need to preserve the equations of continuity. We are very reluctant to modify the structure of this term; interactions will be taken into account by modifications of the potential. Changes that are appropriate in the case of chemical reactions will be discussed in Section V.6.

We shall suppose that particles of distinct components are distinguishable; whence the additivity of the entropy. More precisely: for the same reasons that have made us limit attention to the case of uniform specific entropy densities in a one component system, we shall assume that, interactions present or not, the entropy density of a multicomponent system, the density s that appears, multiplied by T , as the last term in the above Lagrangian, is a linear function of the densities, with constant coefficients

$$s = \sum \rho_i S_i. \quad (5.2.3)$$

This assures that the identification of the pressure with the on shell value of the Lagrangian density extends to mixtures. That S_1 and S_2 are uniform in the absence of interactions has been our working assumptions; no exceptions have been encountered so far. Obedience to this command is presumed to have been achieved during mixing, by a non-adiabatic development, but we are concerned only with the final result, and the adiabatic development that may follow. That (5.2.3) remains true when interactions are present is, at the time of writing, a working assumption. It implies the absence of unexpected entropic forces (forces proportional to the gradient of the specific entropies) in the Bernoulli equation, and that all the other fields are also uniform in the absence of external forces.

This is a place to recall what is one of the most important aspects of Gibbs approach, the role of entropy in the formulation of the variation principle. In the case of a simple system the entropy is fixed. In general, it is agreed that an adiabatic system is one with fixed entropy; we have followed the lead of Prigogine in generalizing this :

A unary adiabatic system has a fixed entropy distribution; the entropy density is $s = \rho S$ with a fixed, uniform value of S .

Here we are going further, to postulate, as a working assumption, that

In an adiabatic Lagrangian the entropy density is a fixed linear function of the densities, with constant coefficients.

In the case of a binary mixture, $s = \rho_1 S_1 + \rho_2 S_2$. Note the inevitable appearance of two **entropy parameters**; the allocation of entropy between the two components is now an issue. The explicit modeling of the entropy density is an important feature of our procedure; it is not standard. It aims at an improved **predictive power** and the possibility of doing without the ubiquitous '**reference state**'. A little reflection will show that this approach is new. There may be antecedents, but discussions of the structure of the entropy density are extremely rare. We mean by that the proposal of an expression for the entropy density of mixtures in terms of the mass densities, that goes into the formula for $f + sT$; that is, the formula $s = \rho_1 S_1 + \rho_2 S_2$ and the assumption that S_1, S_2 are uniform. It is not that this assumption is inevitable, but that, if there are exceptions then that would be worthy of notice. It is a working assumption.

The appearance of two entropy parameters, adiabatic invariants, in the expression for the total Lagrangian of a 2-component system, invites a re-examination of the concept of two time scales in thermodynamics. Experience shows that the addition of heat to any system eventually leads to an adiabatic system with well defined entropy; so if the formula $s = \sum_i \rho_i S_i$ is valid, then the ultimate adiabatic system is characterized by a particular partition of the total entropy among the two components; that is, by a one-dimensional subset of the entropy plane, the plane with coordinates S_1, S_2 . This subspace defines a path along which the system moves as the entropy is changed by the addition of heat. But what determines the path, and how does the system reach a point on this path?

Suppose the system is initially in a state of absolute equilibrium, reached after being isolated long enough for dissipation to have run its course. Suppose further that a manipulation of the system leads to a Lagrangian in which $s = \sum \rho_i S_i$, with fixed but randomly chosen values of S_1, S_2 . Mathematically, it appears to be a well defined adiabatic system with adiabatic processes that, by definition, do not modify the entropy parameters. The motion that brings the system back to the point of absolute equilibrium is a

process of another kind; that is, it is not adiabatic and the most economical standpoint is to characterize it as one of dissipation or degradation driven by a search for maximal entropy. But the choice of the actual path may have a different explanation: It may be driven by the search for maximum entropy, but another factor may be the condition of adiabatic stability. We can offer no general insight into this problem as yet; the best we can do is to examine particular processes and the way that the problem has been approached in the past.

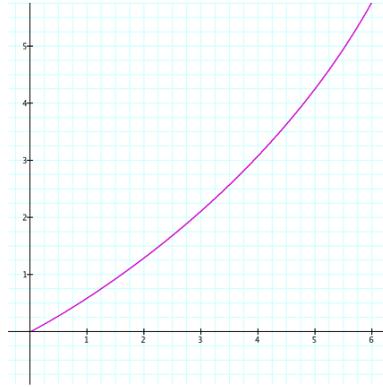


Fig.5.2.1. **Entropy path.** The coordinates are the specific entropies S_1, S_2 . To each adiabatic there corresponds a point in the plane; addition of heat makes it trace out a path.

From now on we shall assume that Eq. (5.2.3) holds and that the coefficients S_i are often uniform. It is proposed as a useful working assumption; to be honored until it is proved wrong.

Variation of the action with respect to the densities gives, when the entropy parameters are uniform, a pair of **Bernoulli equations**

$$\frac{Dv_i}{Dt} = -\mu_i - S_i T \quad \mu_i := \left. \frac{\partial f}{\partial \rho_i} \right|_T, \quad i = 1, 2. \quad (5.2.4)$$

This too is hardly conventional. Landau's two-flow theory recognizes two independent velocities and incorporates similar equations, but instead of individual chemical potentials μ_i on the right hand side, there appears the gradient of the total pressure p in both equations. That is, the two fluids interact with each other by an unusual mechanism that is not found in other physical systems. Certainly, mutual interactions must be included. But we

shall take a suggestion from the field theories of elementary particles, to introduce the interaction in a different way, by means of an interaction term f_{int} , a function of the two densities, in the total Lagrangian density. Landau assumes that each fluid feels the pressure of the other, and that is reasonable; but we shall obtain the same effect by including an interaction (attractive or repulsive) in the Lagrangian.

The concept of the entropy of the mixture as a linear function of the densities leads to a new view of the problem of mixtures and a new way to analyze experiments. A principal problem is to determine, for any mixture, the path that it chooses as it winds its way through the entropy plane.

We may be opening up a new direction of development of thermodynamics. It is based on what we believe to be the most important concept introduced by Gibbs: the concept of “**assigned entropy**”. In global, adiabatic thermodynamics a numerical value is assigned to the entropy; then the energy functional is minimized. In the local theory of mixtures the entropy density has to be given as a linear function of the densities, with assigned values of the coefficients, to define an adiabatic system. Linearity is a working assumption. It is strange that no previous attempt to model the assigned entropy could be found; perhaps a clear statement of the concept was not widely known.

Partial pressures

The (total) pressure was defined in (5.1.1). As in the case of a unary system this is justified by showing that it coincides with the pressure on the walls. “Partial pressures” p_i can be defined by

$$p = \sum_i p_i, \quad p_i := \rho_i \frac{\partial f_i}{\partial \rho_i} - f_i,$$

but their significance is unexpectedly complicated.

In Chapter 3 we derived the Bernoulli equation, Eq.(3.6.1) for a unary system. To express Euler-Lagrange equation, in which a principal term is $\vec{\nabla}(f + sT)$, in terms of the gradient of the pressure, we used the identity

$$\rho \vec{\nabla}(\mu + T \frac{\partial s}{\partial \rho}) = \vec{\nabla} p + (\rho \frac{\partial s}{\partial \rho} + \frac{\partial f}{\partial T}) \vec{\nabla} T + \rho T \vec{\nabla} \frac{\partial s}{\partial \rho} = 0.$$

Then we used the adiabatic relation $\partial f/\partial T = -s$ to simplify, to obtain the familiar Bernoulli equation of motion for a unary system in terms of $\vec{\nabla}p$,

$$\dot{\vec{v}} + \vec{\nabla}(\vec{v}^2/2 - \Phi) = \frac{1}{\rho} \vec{\nabla}p.$$

For a binary system we get the same equation for each component,

$$\rho_i \vec{\nabla}(\mu_i + T \frac{\partial s_i}{\partial \rho_i}) = \vec{\nabla}p_i + (\rho_i \frac{\partial s_i}{\partial \rho_i} + \frac{\partial f_i}{\partial T}) \vec{\nabla}T + \rho_i T \vec{\nabla} \frac{\partial s_i}{\partial \rho_i} = 0. \quad (5.2.5)$$

but now there is an additional difficulty; we have only one adiabatic condition, $\partial f/\partial T = -s$, and no way to reduce the quantities $\partial f_i/\partial T$. The trouble with this approach is that we have no physical interpretation of the ‘partial pressures’ and no formula for $\partial f_i/\partial T$. This development leads nowhere, in general, but the situation changes somewhat in the case that the Gibbs-Dalton hypothesis is valid, as we shall see.

All this just to show that the partial pressure may be a useless concept. The Euler - Lagrange equations have no need to be expressed in terms of partial pressures. They are explicit expressions for the accelerations in terms of the densities and the temperature.

There is, perhaps, one exceptional case: superfluid Helium is a mixture in which the superfluid component S_2 of the specific density is zero. In that case $\partial f_1/\partial T = -S_1$ and $\partial f_2/\partial T = 0$ and this gives rise to an entropic force $\rho_1 S_1 \vec{\nabla}T$. Such a term appears explicitly in Landau’s equations of motion and is used to explain the fountain effect. The problem with the interpretation of the partial pressures is circumvented by the replacement of both by p .

V.3. Mixture of 2 ideal gases

This example will throw some light on the question of allocation of entropy.

Imagine a vessel, divided into two parts by a wall, the two parts filled with an ideal gas of type 1 and an ideal gas of type 2, respectively. Assume that the wall is impenetrable to either gas; but that it admits the transfer of heat. The Lagrangian density for this system is,

$$\mathcal{L} = \sum \mathcal{L}_{i=1,2} = \sum_i \left(\rho_i (\dot{\Phi}_i - \vec{v}_i^2/2) - f_i - s_i T \right),$$

where $s_i = \rho_i S_i$ and S_1, S_2 , are adiabatic invariants. It is postulated that there is a unique, continuous **temperature field**, extending over both vessels, continuous at the wall (See Section III.8.).

This Lagrangian describes two separate systems that interact with each other solely by sharing the boundary condition implied by the continuity of the temperature at the wall. The feasibility of this setup is amply confirmed by experiments.

What happens if the **dividing wall** is removed? The most common observation is that **mixing** takes place, the particles of gas number 1 begin to “diffuse” into the space formerly reserved for the other gas, and vice versa. If no external forces are acting the mixture often becomes uniform. At this stage of our study we shall not inquire into the physical, probably non adiabatic process that causes the mixing, but only try to describe the final states.

The process aside, we need to find the Lagrangian of the system after mixing. One result of mixing is a reassignment of entropies. After mixing, each of the originally separated gases have expanded to a larger volume, with attendant changes in the entropy parameters; what are the final values? A law discovered by Dalton states as follows:

Dalton’s law. At equilibrium, the total pressure of the mixture of two ideal gases (the pressure against the walls) is the sum of the pressures that would have been obtained if each gas would have occupied the total volume in the absence of the other, at the same temperature.

Important as it is, this information is a very small part of what we wish to know: what are the dynamical properties of this mixture, that is, what is the Lagrangian for this new gas? This need to know more led some people to overstate Dalton claims. Dalton was said to have held that each gas in a mixture behaves as if it were alone. He did not. Some of the controversy is discussed in Dalton’s book (Dalton 18).⁵

If indeed it were so, that each gas in the mixture behaves as if it were alone, then we should obtain the Hamiltonian density for the mixture by simply adding the two Hamiltonian densities and integrating over the vessel

⁵Here is a sample statement of the law in a modern textbook: “... the assumption is made that each gaseous component of the mixture behaves as if it existed at the temperature of the mixture and filled the entire volume ...” (Holman1980).

filled by both, assigning a different temperature to each gas. This concept of dual temperatures is unphysical except in certain cases where a method is devised to measure the two separate temperatures. We postulate a single temperature field and we are led to consider the following Lagrangian density for the mixture,

$$\mathcal{L} = \sum_i \left(\rho_i (\dot{\Phi}_i - \vec{v}_i^2/2) - f_i - s_i T \right), \quad (5.3.1)$$

where $f_1(T, \rho_1)$ and $f_2(T, \rho_2)$ are the expressions for the free energy appropriate for each gas when alone. We repeat that this is undertaken merely as a first step towards the eventual construction of a realistic Lagrangian. The adoption of this Lagrangian is in accord with the spirit of Dalton's law. The thermodynamic pressure is

$$p = \sum \rho_i \frac{\partial f}{\partial \rho_i} - f = \sum \mathcal{R}_i \rho_i T \quad (5.3.2)$$

and the entropy density is

$$s = \sum s_i = \sum \rho_i S_i.$$

The formula for the total pressure expresses Dalton's law; the inclusion of interactions will invalidate it, unless it is of total degree one. This suggests that we keep in mind a particularly interesting interaction,

$$f_{int} \propto \sqrt{\rho_1 \rho_2}. \quad (5.3.3)$$

The first question that needs to be discussed arises from the appearance of two entropy parameters when only one was expected. The total entropy density is a linear function of the two densities, depending on two parameters S_1, S_2 . Exploring the merits of any explicit expression for the Lagrangian of

a binary or multi component system is a departure from common practice. Attempts to model the Gibbs function are common, but they involve a 'reference pressure' p_0 (usually one atmosphere) and a 'reference state' with an unspecified Gibbs function $G(T, p_0)$ consecrated in tables. Confrontation with observation would seem to point to a determination of the correct form for the unknown function, but we have seen no attempt to do this. The special, linear form that is being postulated for the **assigned entropy** gives a structure to the modeling that can easily be tested by experiments. The overall plan is to test naive expressions for the Lagrangian, including the entropy, and make improvements as necessary. The most important advantage

of this program is that each attempted application will suggest a refinement of the Lagrangian and, especially, the fact that one Lagrangian has to accommodate a variety of effects and experiments. The search is on for a best possible Lagrangian capable of accounting for all properties of the mixture of the two gases.

Additivity of the Lagrangian for a system of two non interacting components embodies additivity of the Hamiltonians, which is natural, but also additivity of the thermodynamic potentials, even when that is only as a bench mark, subject to modifications as required by observation. Though it seems natural, this attitude is not standard. Consequently, from this point onwards there will be a significant divergence from the usual approach. To defend this deliberate departure from tried and tested methods in the treatment of mixtures it may be said that, certainly, there can be nothing wrong with it in the limit of a very weak interaction between the components. And this can not be said with as much assurance of some other approaches.⁶ Our reward will be a theory with a very much enhanced predictive power. The predictions are, of course, to be tested.

V.4. Gibbs-Dalton hypothesis for ideal gases ...

The additivity of energies that is implied by the addition of Lagrangians is an attractive assumption, and probably a must in the absence of interactions, but what can be done about the two entropy parameters? Addition of heat to the system must change the parameters and if the system is to end up in a well defined configuration then it has to follow a fixed path in the ‘entropy plane’ with coordinates S_1, S_2 . A partial answer to this question is provided by a literal interpretation of the **Gibbs-Dalton hypothesis**, developed by Gibbs from Dalton’s law, namely

Gibbs-Dalton hypothesis. When the mixture of ideal gases reaches a final equilibrium each gas has the entropy that it would have if it were alone.

Discussion. In our context Dalton’s law appears to be expressed by Eq.(5.3.2) and to be a direct consequence of the additivity of Lagrangians. But this is not what Dalton’s law means. Dalton’s law $p = \sum p_i$ has content only

⁶This criticism, if that is what it is, can be countered, to some extent, by making the observation that, realistically, no interaction implies vanishing density. A problem would arise, however, with the discovery of gases that are ideal at a finite density.

after we decide what the symbols “ p_i ” stand for. To Dalton they are the pressures of a pure gas with temperature T and density ρ_i ; in the case of an ideal gas $p_i = \mathcal{R}_i \rho_i T$. But the summands $p_i = \rho_i \partial f_i / \partial \rho_i - f_i$ in Eq.(5.3.2) are expressed in terms of the temperature, the densities and the entropy. To define them we need to eliminate the entropy; hence Dalton’s law follows from (5.3.2) only if the entropy is a sum of partial entropies and each partial entropy is related to density and temperature by the same expression as it is in the case of the components in isolation. This is what leads to the Gibbs-Dalton hypothesis.

One interpretation of the Gibbs-Dalton hypothesis is the adiabatic relation that is one of the Euler-lagrange equations,

$$s = -\frac{\partial f}{\partial T}.$$

We shall call this the weak form of the hypothesis. It is of little use without a prescription for assigning a value to the entropy parameters. We have insisted on maintaining Gibbs’ point of view, that the variational principle minimizes the energy for a fixed value of the entropy. In extended, one component thermodynamics this was interpreted in the sense of the specific entropy density, and the latter has been found to be uniform in a wide context. In the case of a heterogenous system Gibbs does not offer guidance. The last formula serves only to calculate the entropy for a given configuration of the system, which is of little use.

To be useful, the adiabatic relation needs to be supplemented by a rule for assigning entropy. A first step, and a major one, is to demand additivity, in the strong form

$$s = \sum s_i = \sum \rho_i S_i,$$

with uniform values of S_1 and S_2 . That leaves only the problem of tracing the path followed by the system through the entropy plane, a problem for the solution of which we defer to experiment.

A stronger interpretation of the Gibbs - Dalton hypothesis is possible, namely

Strong Gibbs-Dalton hypothesis. When the mixture of ideal gases reaches a final equilibrium each gas has the entropy that it would have if it were alone at the same density and temperature.

When each gas is alone these relations hold:

$$S_i = -\mathcal{R}_i(\ln \frac{\rho_i}{T^{n_i}} - n_i), \quad i = 1, 2 \quad \text{separated gases.}$$

According to the strong version of the hypothesis it holds for a mixture, but only at equilibrium:

$$S_i = -\mathcal{R}_i(\ln \frac{\rho_i}{T^{n_i}} - n_i), \quad i = 1, 2 \quad \text{at equilibrium.}$$

This is what we shall mean by ‘the strong Gibbs-Dalton hypothesis’ (for a mixture of ideal gases). It is expected to hold in the absence of any chemical reactions or external forces.⁷ The virtue of the statement is that, as a statement about the value of the entropy, it applies to the adiabatic system in general, not just to equilibrium states; it removes the ambiguity in the Lagrangian by fixing a relation between the two (or several) entropy parameters defined in (5.2.1).

Consider two ideal gases with

$$f_i + s_i T = \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{T^{n_i}} + \rho_i S_i T, \quad i = 1, 2.$$

If each gas were alone we should have the 2 equations of motion (adiabatic relations),

$$\mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T^{n_i}} - n_i) + \rho_i S_i = 0, \quad i = 1, 2, \quad (5.4.1)$$

from variation of each Lagrangian with respect to the temperature, but variation of the proposed total Lagrangian (5.3.1) with respect to the common temperature yields only one adiabatic equation:⁸

$$\sum_{i=1,2} \left(\mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T^{n_i}} - n_i) + \rho_i S_i \right) = 0. \quad (5.4.2)$$

The strong Gibbs-Dalton hypothesis requires that both of Eq.s (5.4.1) hold for the unified system, but only at equilibrium. If the equilibrium is characterized by uniform densities then this amounts to the required relation between S_1 and S_2 , a relation that provides the required path in the entropy plane. Suppose that there is a value T_0 of T such that both terms vanish, then for all T

$$\mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T^{n_i}} - n_i) - \rho_i S_i = n_i \mathcal{R}_i \rho_i \ln \frac{T_0}{T}$$

⁷Please remember that these relations are restrictions on the values of T and the densities. The numerical values assigned to S_1 and S_2 are **adiabatic invariants**.

⁸This is enough to give the formula for the internal energy density, $u = \sum_i n_i \mathcal{R}_i \rho_i T$.

and the equation of motion Eq.(5.3.2) reduces to

$$\left(\sum n_i R_i \rho_i\right) \ln \frac{T_0}{T} = 0.$$

This can be true only at $T = T_0$. That is, if such a value of T exists when the densities take equilibrium values, then the equation of motion implies that this is the value of T at equilibrium and that both terms vanish separately at equilibrium. The strong Gibbs-Dalton hypothesis can thus be stated within the present context as follow:

Gibbs-Dalton hypothesis, strong version:

For correctly assigned values of the entropy parameters S_1 and S_2 , the equilibrium temperature is uniquely fixed by the requirement that both terms in (5.4.2) vanish separately

Away from equilibrium only (5.4.2) holds and each component gas no longer behaves as if the other component were absent! The two gases at equilibrium may not be ‘aware of each other’, but in configurations other than equilibrium the pair of adiabatic conditions that characterize the pure gases is replaced by the single adiabatic condition (5.4.2).

For a system of ideal gases with fixed total quantities of each component and with uniform equilibrium densities the Gibbs-Dalton hypothesis predicts the following entropy path,

$$\frac{S_1}{n_1 \mathcal{R}_1} - \frac{S_2}{n_2 \mathcal{R}_2} = \ln \frac{\rho_2^{1/n_2}}{\rho_1^{1/n_1}}, \quad (5.4.3)$$

where ρ_1, ρ_2 are the densities at equilibrium. It agrees with Boltzmann’s distribution law if $n_1 = n_2$. See Section V.4.

V.5. ... and what lies behind it

We shall attempt to determine what it is that would drive the mixed gas to satisfy the strong version of the Gibbs-Dalton hypotheses.⁹ Let

$$x = \frac{\rho_1}{k_{01}(eT)^{n_1}}, \quad y = \frac{\rho_2}{k_{02}(eT)^{n_2}}, \quad S_i = -\mathcal{R}_i \ln k_{0i}, \quad i = 1, 2,$$

⁹The answer given by Boltzmann to this question is the foundation of statistical mechanics. Here we are looking for an answer within our chosen context of thermodynamic field theory.

so that the Gibbs-Dalton hypothesis makes $x = y = 1$, and the adiabatic relation (5.4.2) takes the form

$$x \ln x + ay \ln y = 0, \quad a = (\mathcal{R}_2 k_{02} / \mathcal{R}_1 k_{01})(eT)^{n_2 - n_1}. \quad (5.5.1)$$

Let us fix S_1 and S_2 , and consider an equilibrium configuration in which all the fields are uniform. Fig. 5.5.1 shows the locus of points in the x, y plane at which Eq.(5.5.1) holds, for a particular value of T . Since the variables x, y are constant multiples of the densities these variables are in fact scaled densities and we may refer to the plane of the figure as the density plane. There is a family of such curves, one for each value of T . The figure also shows several lines of constant total pressure,

$$p = (\rho_1 \frac{\partial}{\partial \rho_1} + \rho_2 \frac{\partial}{\partial \rho_2} - 1)(f_1 + f_2) = T(\mathcal{R}_1 \rho_1 + \mathcal{R}_2 \rho_2). \quad (5.5.2)$$

The loci of p - the isobars - are straight lines. The isotherm intersects the isobar at 2 points, at one point, or at no point in the ρ -plane. If they intersect at no point then there is no such configuration.

If the curves touch at one point then the densities are uniquely determined. The tangents of the two curves at any point are given by

$$\mathcal{R}_1 d\rho_1 (\ln x + 1) + \mathcal{R}_2 d\rho_2 (\ln y + 1) = 0,$$

and

$$\mathcal{R}_1 d\rho_1 + \mathcal{R}_2 d\rho_2 + (\mathcal{R}_1 \rho_1 + \mathcal{R}_2 \rho_2) \frac{dT}{T} = 0,$$

respectively; they coincide, for a fixed value of T , only if

$$\ln x = \ln y. \quad (5.5.3)$$

By virtue of Eq. (5.4.2) that implies that both logarithms are zero, as required by the Gibbs-Dalton hypothesis.

There remains the possibility of two intersections, at points A and B in the figure. To justify the Gibbs-Dalton hypothesis we have to throw some aspersions on this case. Well, if the gas at equilibrium is homogeneous, then the ratio $r = \rho_1 / \rho_2$ is given in advance by the ratio of total masses. This number need not coincide with the value of either of the ratios $r(A)$ or $r(B)$. If it is intermediate between those values then the gas must separate into two parts, one part in which $r = r(A)$ and another part in which it is $r = r(B)$.

Later we shall see that mixtures exist, where this does indeed happen, but in the case of ideal gases, or at high temperature or low pressure for most gases, we know that it does not; so there is no stationary state available. That is the same as to say that such states are adiabatically unstable to **convection** . Flow will develop and eventually the kinetic energy will degenerate to heat. The final state will be stationary but the values of the entropy parameters must have changed. If an equilibrium is finally reached then it must satisfy the Gibbs-Dalton hypothesis.

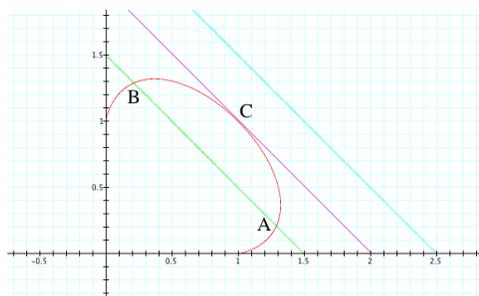


Fig.5.5.1. GibbsDalton. The coordinates are the (scaled) densities x and y . The oval is the locus of (5.4.2) determined by fixing T, S_1 and S_2 . The straight lines are isobars.

The only stable, homogeneous equilibrium available is the point C where the two curves have the same tangent. At that point both terms in (5.4.2) vanish separately, as we have shown.

If the values of the densities and of the temperature are given, then this is a restriction on the values of the two entropy parameters S_1 and S_2 . For a given system with fixed mass and with uniform equilibrium densities, there will be a curve $T \mapsto (S_1(T), S_2(T))$, the image of which is the path followed by the system as the temperature is varied so as to move it through a succession of equilibrium configurations, see Fig 5.5.1.

We seem to be able to conclude that the Gibbs-Dalton hypothesis finds the only stable mixture and that this is what determines how the entropy is apportioned between the two components. An argument based on the maximal entropy principle was expected. Instead we have here an analogue of **free expansion**; the assumed initial point is unstable and goes into an agitated state, out of equilibrium. The final equilibrium is reached by degradation of the kinetic energy, leading to a state of maximal entropy.

Thus it seems that the Gibbs-Dalton distribution of entropy is not reached by a purely dissipative process but because it is the only one that allows for the existence of equilibrium states, or more generally for any stable adiabatic system. (The fact that values of pressure and entropy cannot be assigned at random is easily proved by more elementary examples. See Section III.5 and Fig. 3.5.2.) If this conclusion is correct it shows that some important questions about equilibrium thermodynamics are answered only by the extension to hydro-thermo-dynamics.

It seems that the entropy chosen by the Gibbs-Dalton hypothesis is a kind of **critical point**. Recall that, in general, a critical point in thermodynamics is one in which a Legendre transformation is singular (Tisza 1970). For example, consider the Legendre transformation

$$p(T, q_1, q_2) = \sum \rho_i \mu_i - f, \quad \mu_i = \frac{\partial f}{\partial \rho_i}, \quad i = 1, 2.$$

An example of a critical point is a point where

$$\det(\partial^2 p / \partial \rho_i \partial \rho_j) = 0.$$

The critical point at hand is defined by the vanishing of the Jacobean of the transformation $T, p \rightarrow \rho_1, \rho_2$,

$$J = \left| \frac{\partial T \partial p}{\partial \rho_i \partial \rho_j} \right|;$$

that is, a point where the two gradients in the density plane

$$\left(\frac{\partial T}{\partial \rho_1}, \frac{\partial T}{\partial \rho_2} \right), \quad \left(\frac{\partial p}{\partial \rho_1}, \frac{\partial p}{\partial \rho_2} \right)$$

are parallel. The derivations are to be taken with S_1, S_2 fixed.

With this interpretation we can ask for a generalization of the hypothesis to the case of a mixture of real, interacting gases. This question will be taken up again in Section VI.1.

The suggested form of the Lagrangian for a mixture, with the concept of an entropy space and the need to find the path through this space chosen by the system, is a central feature of the treatment proposed in this book.

In the case of a mixture of real gases we do not expect the original Gibbs-Dalton hypothesis to apply; this includes van der Waals gases fluids as well as

ideal fluids with other types of mutual interaction. Both of these cases will be studied below. It also does not apply to the case of two ideal gases in the case when dissociation and recombination take place. This case shall be studied in Section V.7. The condition for equilibrium, Eq. (5.7.3), is not compatible with the strong Gibbs-Dalton condition, unless $R_2(n_2 + 1) = R_1(n_1 + 1)$.

V.6. Gibbs-Dalton hypothesis for some real gases

In the case of two fluids of very different nature the Dalton law of partial pressures is not expected to be valid, and the Gibbs-Dalton hypothesis even less. The Gibbs-Dalton hypothesis applies to ideal gases, and real gases are not ideal gases. Can anything be said about the distribution of entropy in a mixture of real gases? We shall answer this question in the affirmative.

One expects that there is an **interaction** between two dissimilar atoms. As was first shown by van der Waals (1890), this interaction can sometimes be simulated by adding an interaction term to the free energy. Because we are interested in the equilibrium states the density gradients will be small and it is enough to consider an interaction energy that is an algebraic function of the densities, not involving their gradients. As a preliminary test of this idea we merely add the following term to the free energy density,

$$f_{\text{int}} = \alpha(\rho_1\rho_2)^k, \quad (5.6.1)$$

with α and k constant. There is direct experimental evidence in favor of this expression, since the measured “excess free energy” (Rowlinson 1969 page 138) sometimes has exactly this shape, with k in the region of .5 to 1 or higher. See Fig. 5.6.1. The forces are often repulsive, which makes α positive. The total free energy is $f_1 + f_2 + f_{\text{int}}$. For f_1 and f_2 we shall use, in a first instance, the expressions that pertain to the one-component ideal gases. Thus, at equilibrium, the Hamiltonian density is

$$\rho_1 \vec{v}_1^2/2 + \rho_2 \vec{v}_2^2/2 + f + sT, \quad f = f_1 + f_2 + \alpha(\rho_1\rho_2)^k, \quad s = \sum \rho_i S_i. \quad (5.6.2)$$

$$f_1 = \mathcal{R}_1 T \rho_1 \ln \frac{\rho_1}{T^{n_1}}, \quad f_2 = \mathcal{R}_2 T \rho_2 \ln \frac{\rho_2}{T^{n_2}}.$$

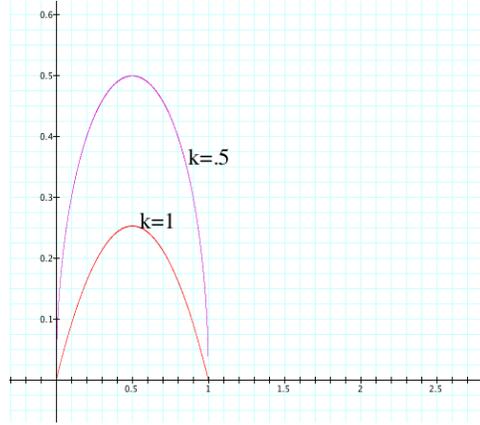


Fig.5.6.1.Int. Illustration of the dependence of the excess free energy of a mixture on the concentration, for a fixed value of the total density. It is not always positive.

The Gibbs-Dalton hypothesis specifies a relation between S_1 and S_2 by focusing on the unique equilibrium configuration. We are not admitting external forces, so the densities are uniform and determined by the total volume and the masses; the temperature is also uniform. The statement of the strong Gibbs-Dalton hypothesis is a relation between the entropy parameters that is related to the equilibrium values of the densities.

Now we ask in what way this rule is expected to be modified by the interaction. A simple and possibly universal hypothesis is available: that the stability interpretation discovered in Section V.2 applies, namely

$$\det \frac{\partial(p, T)}{\partial(\rho_i, \rho_j)} = 0. \quad (5.6.3)$$

The partial derivatives are adiabatic; that is, the entropy parameters are kept fixed. We have

$$dp = [\mathcal{R}_1 T + k(2k - 1)\alpha(\rho_1 \rho_2)^k / \rho_1] d\rho_1 + [\mathcal{R}_2 T + k(2k - 1)\alpha(\rho_2 \rho_2)^k / \rho_2] d\rho_2$$

and the adiabatic condition

$$\mathcal{R}_1 \rho_1 \ln x + \mathcal{R}_2 \rho_2 \ln y = 0,$$

where

$$x = \frac{\rho_1}{k_{01}(eT)^{n_1}}, \quad y = \frac{\rho_2}{k_{02}(eT)^{n_2}}$$

gives

$$dT \propto [\mathcal{R}_1(\ln x + 1)]d\rho_1 + [\mathcal{R}_2(\ln y + 1)]d\rho_2.$$

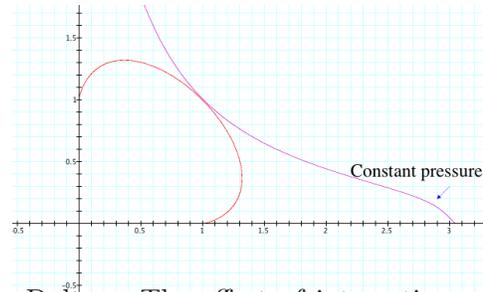


Fig.5.6.2. Gibbs-Dalton. The effect of interaction on the Gibbs-Dalton critical point. The oval is the locus of solutions of the adiabatic condition for fixed values of T, S_1, S_2 , the coordinates x, y are the densities, scaled: $x \ln x + y \ln y = 0$. The other curve is a locus of constant pressure, $x + y + (xy)^{4.2} = 3.05$.

The condition for tangency takes the form

$$\frac{1 + \ln x}{1 + \ln y} = \frac{1 + \alpha'(\rho_1\rho_2)^k/R_1\rho_1T}{1 + \alpha'(\rho_1\rho_2)^k/R_2\rho_2T}, \quad \alpha' := k(2k - 1)\alpha.$$

The Gibbs-Dalton relation $x = y = 1$ is thus modified, unless the molar density is the same for both gases. This is illustrated in Fig. 5.6.2, for $k = 1/2, \alpha' > 0$.

There remains an interesting possibility that α' may in special cases be negative. Then the situation illustrated in Fig.5.6.3 may be realized. Here the generalized Gibbs-Dalton hypothesis is satisfied at two points, with different concentrations. Before we conclude that two different concentrations may coexist we have to investigate the condition of equilibrium.

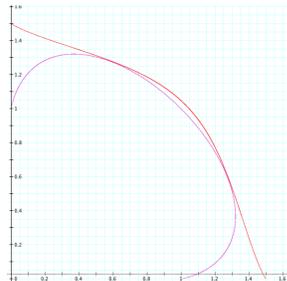


Fig.5.6.3. Gibbs-Dalton. An interesting possibility. Same as the preceding equation but the pressure is $x + y - .37(2k - 1)(xy)^k$, $k = 1.2$ or $x + y + 2.6(2k - 1)$ with $k = .4$.

V.7. The simplest mixtures. Boltzmann theory

Consider a gas with a ground state with free energy $f = 0$, consisting of molecules with two quantum levels. More precisely, consider a molecule that converts freely between two energy levels, a lowest level 1 with vanishing free energy $f_1 = 0$ and an “excited” level 2 with internal energy density $f_2 = \epsilon\rho_2$. Suppose that

$$\epsilon = (S_2 - S_1)T. \quad (5.7.1)$$

This is analogous to what we found to be an expression of Maxwell’s rule.

Now let us take a route that may be risky: irrespective of the properties that we have imputed to the gas, assume (with Gibbs-Dalton, strong version) that the familiar expression for the entropy of an ideal gas applies to each component of the mixture,:

$$S_i = -\mathcal{R} \ln \frac{\rho_i}{(eT)^{n_i}}, \quad i = 1, 2. \quad (5.7.2)$$

Thus

$$\frac{\rho_2}{\rho_1} = (eT)^{n_2 - n_1} e^{-\epsilon/\mathcal{R}T}. \quad (5.7.3)$$

This is Boltzmann’s distribution law for the population of the two levels. Both equations (5.7.1) and (5.7.3) are standard lore and not to be tampered with, this in spite of any doubts that may arise concerning the actual direct, experimental verification of Eq.(5.7.3).

Consider now the Lagrangian density

$$\dot{\Phi}\rho - f - sT = \dot{\Phi}\rho - \sum (\mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + \rho_i S_i T).$$

Note that only the total density is conserved; therefore there is only one velocity potential and there is no way to include the binding energy directly, though it is accounted for via Eq.(5.7.1). The new equations of motion are, the adiabatic relation (variation of T)

$$\sum \rho_i (\mathcal{R}_i \ln \frac{\rho_i}{(eT)^{n_i}} + S_i) = 0,$$

the equation of continuity (variation of Φ) and the hydrostatic condition (variation with $d\rho_1 = -d\rho_2$)

$$\ln \frac{\rho_2^{1/n_2}}{\rho_1^{1/n_1}} = -(S_2 - S_1), \quad (*)$$

where, as before, S_i is the entropy per mol of the i 'th component. I have followed the same method as for saturation. The two cases are very different, for in one case the two components are separated and in the other case they are mixed, so that we cannot be sure that this is right.

V.8. Chemical reactions: Dissociation

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



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

$$m_1 = 2, \quad n_1 = 5/2.$$

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

$$\rho_1 = \rho = M/V, \quad \ln \frac{\rho}{T^{n_1}} - n_1 = -s_1/R_1.$$

At sufficiently high temperatures the gas is almost purely atomic, with $m_2 = 1$, $n_2 = 3/2$. At equilibrium,

$$\rho_2 = \rho = M/V, \quad \ln \frac{\rho}{T^{n_2}} - n_2 = -s_2/R_2.$$

Consider a mixture of two gases, similar in all respects to H and H_2 , except that the reaction analogous to $H_2 \leftrightarrow 2H_1$ does not take place. The Lagrangian density would be

$$\mathcal{L}' = \sum \left(\rho_i \dot{\Phi}_i - \vec{v}_i^2/2 - \phi \right) - \sum \left(\mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + T \rho_i S_i \right),$$

A hypothesis that can be tried is that this expression retain some validity for the real hydrogen problem. But it must be changed in essential ways. In \mathcal{L}' there are two independent velocity fields and therefore two independent

potentials Φ_1 and Φ_2 . Variation leads to independent conservation laws, atoms and molecules are independently conserved. The difference between this hypothetical system and real Hydrogen is that in the real system only the total density (grams/cm³) is preserved, so we have only one conservation law and we can admit only one variation, hence only one independent potential velocity field,¹⁰

$$\vec{v}_1 = \vec{v}_2 = \vec{v}, \quad \dot{\Phi}_1 - \dot{\Phi}_2 = \epsilon = \text{constant}. \quad (5.8.1)$$

The **Lagrangian** density becomes

$$\mathcal{L} = \rho_1 \dot{\Phi}_1 + \rho_2 \dot{\Phi}_2 - \rho(\vec{v}^2/2 + \phi) - \sum (\mathcal{R}_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + T \rho_i S_i), \quad (5.8.2)$$

with $\rho = \rho_1 + \rho_2$. The distinction between one molecule and two atoms is not entirely lost, for we are able to maintain two independent densities; indeed this must be so for otherwise the problem of two kinds of gases, atomic and molecular, would not exist. The densities are separately observable and we shall derive a formula for the concentrations in the mixture. Generalisations, to the case of more than two component fluids with chemical interactions, will be considered in the next section. Some formal considerations are being relegated to the end of this section.

Let us study the equations of motion in the case that the fluid is at rest, $\vec{v} = 0$ everywhere. The effect of gravity will be neglected. Variation with respect to T yields the adiabatic relation

$$\sum \left(\mathcal{R}_i \rho_i \left(\ln \frac{\rho_i}{T^{n_i}} - n_i \right) + \rho_i S_i \right) = 0. \quad (5.8.3)$$

Independent, local variation of the two densities tells us that all the fields are uniform. The actual values of ρ_1 and ρ_2 are not obtained, for the variational equations each get a contribution from a $\rho \dot{\Phi}_i$ -term. But in variation of the densities with ρ fixed, $\delta \rho_1 = -\delta \rho_2$, the contributions of these terms cancel out because $\Phi_1 - \Phi_2$ is fixed and we obtain an additional relation,

$$R_1 T \left(\ln \frac{\rho_1}{T^{n_1}} + 1 \right) + S_1 T - R_2 T \left(\ln \frac{\rho_2}{T^{n_2}} + 1 \right) - S_2 T = 0,$$

Now it is at once clear that the question that has occupied us in the first 4 Sections of this chapter has a different dimension for this, very different, type

¹⁰In this section the densities are in grams, not mols

of mixture. In the condition of equilibrium we have an additional relation, for fixed temperature, between densities and entropies. Eq,s (5.8.1) and (5.8.3), together, define a mapping,

$$(\rho_1, \rho_2) \leftrightarrow (S_1, S_2).$$

If this mapping is one - one, is more information needed? Certainly it is locally one-to-one almost everywhere. We may ask if the Gibbs-Dalton hypothesis is valid, if it is compatible with the equation of motion. Contrary to the case of the unary fluid the answer is that it is most likely not, and that if it happens to be then this circumstance gives no useful information.

Gibbs' phase rule

For a mixture of C components and P phases, this famous rule says that the number of degrees of freedom is $C + 2 - P$, a non-negative number. It is based on counting the number of relations at equilibrium and comparing with the number of independent field variables. In other words, $C + 2$ is the number of *a priori* field variables and P is the number of conditions for equilibrium. In the case of a single component this rule predicts that there is a unique equilibrium for any pair of values of p and T . Binary mixture with a single phase we have only one condition for equilibrium and one more condition is needed to reach the same result, either the (1) Gibbs-Dalton hypothesis or else (2) the second condition for equilibrium that comes with a second phase. In the second case the Gibbs-Dalton hypothesis is not satisfied.

Solving the equations

The densities are the normal kind, in grams/cm³. The particular linear combination that appears here reflects the fact that it is mass that is preserved by the reaction, and not (for example) the number of particles. Since for hydrogen $\mathcal{R}_2 = 2\mathcal{R}_1$, Eq.(5.5.2) reads

$$\ln \frac{\rho_1}{\rho_2} - (n_1 - 2n_2) \ln T - 1 = \frac{S_2 - S_1}{\mathcal{R}_1}.$$

In general, with $\mathcal{R}_i = \mathcal{R}/m_i$, where m_1, m_2 are the atomic molecular weights,

$$\ln \frac{\rho_1^{\frac{m_2}{m_1}}}{\rho_2} - (n_1 m_2 - n_2 m_1)(\ln T + 1) = \frac{m_1 m_2}{\mathcal{R}}(S_2 - S_1). \quad (5.8.4)$$

The right hand side is usually expressed in terms of the binding energy, by means of Boltzmann's formula

$$\epsilon = (S_1 - S_2)T. \quad (5.8.5)$$

We shall try to derive this formula.

Minimal energy

As in the case of condensation, we need to understand what is meant by ‘energy’ in this context. The boundary conditions are the same, the Hamiltonian is still the free energy; we only need to include the binding energy in the Hamiltonian, thus

$$h = \epsilon\rho_1 + f_1 + f_2.$$

Probably, this cannot be strictly justified, but it is in fact standard, see for example Landau and Lifshitz (1965). To do this without affecting the action - we already have the correct equations of motion - all that is needed is a slight change of vocabulary. The Lagrangian density is

$$\dot{\Phi}\rho + \epsilon\rho_1 - sT - h, \quad h = \epsilon\rho_1 + f_1 + f_2,$$

the Euler-Lagrange equations are the same as before and, at equilibrium, minimization of the Hamiltonian implies the Boltzmann relation (5.8.5)

What we have gained is the proper definition of ‘energy’ as understood by Boltzmann, and Boltzmann’s formula (5.8.5). This result confirms the validity of our entropy postulate for the mixture, namely

$$s = \rho_1 S_1 + \rho_2 S_2;$$

compare the discussion that follows Eq. (4.4.1). To sum up, the thermodynamical action principle, knowing nothing about binding energies, gives (5.8.4); at equilibrium the principle of minimum energy, without invoking the concept of entropy, gives the same result but with $(S_2 - S_1)T$ replaced by ϵ . Together, they yield **Boltzmann’s formula**

$$T(S_2 - S_1) = \epsilon, \tag{5.8.5}$$

This relation is usually taken for granted; see for example Prigogine (1955), page 41. Thus finally

$$\ln \frac{\rho_1}{\rho_2} - (n_1 - 2n_2) \ln T - 1 = \epsilon/R_1 T. \tag{5.8.6}$$

To compare this with the result of Eckert (1920) that was famously applied by Saha (1921) to stellar atmospheres, we replace the partial densities by the partial pressures, defined here by $p_i = \mathcal{R}_i \rho_i T$, to get

$$\ln \frac{p_1}{p_2} \frac{\mathcal{R}_2^2}{\mathcal{R}_1} - \left((n_1 + 1) - 2(n_2 + 1) \right) \ln T - 1 = \frac{\epsilon}{\mathcal{R}_1 T}$$

or, finally

$$\ln \frac{p_1}{p_2} = \frac{C_{P1} - 2C_{P2}}{\mathcal{R}} \ln T + \frac{\epsilon}{\mathcal{R}_1 T} + 1 - \ln 2\mathcal{R}, \quad (5.8.7)$$

where $C_{P_i} = (n_i + 1)\mathcal{R}_i$.

This is the result contained by Saha from kinetic theory.

Remark. The **Euler-Lagrange equations** (5.8.2-3) allow us to determine how the total entropy is distributed among the two species. Both approaches agree that the total entropy density before mixing is

$$- \sum \mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T^{n_i}} - n_i),$$

and there may be an expectation that the two summands represent the share of entropy allocated to each species as predicted by the Gibbs-Dalton hypothesis. Instead, from the condition of equilibrium and the adiabatic condition we obtain

$$S_1 = -R_1 (\ln \frac{\rho_1}{T^{n_1}} - n_1) - \frac{\rho_2}{\rho} [\mathcal{R}_1 (1 + n_1) - \mathcal{R}_2 (1 + n_2)].$$

This is not in contradiction with classical theory, since that theory does not deal with the question; it can be understood as follows. ‘**Entropy production**’ refers to the difference between the entropies in two hypothetical, equilibrium situations, at the beginning and at the completion of a process. During the process the traditional position is that entropy is undefined. Our understanding is that, at equilibrium, the total entropy is determined (in terms of the temperature) by the adiabatic condition and that the allocation of entropies at equilibrium (the difference $S_1 - S_2$) was calculated with the same result as in the classical theory. ‘Entropy production’ can be calculated by comparing the total entropy at final equilibrium with the total equilibrium before mixing, provided that we are given the temperatures. (In the case that no chemical reaction takes place we know that the temperature does not change. We do not try to determine whether this entropy production is due to mixing, to the progress of the chemical reaction or to the removal of the wall of separation. The classical theory does not say, nor does it ask.

De Groot and Mazur have proposed that, once mixing is complete, entropy production can be understood in terms of the progress of the chemical reaction. In that theory $\dot{\Phi}$ is the rate of specific heat flow.

Numerical calculations produce Fig.5.8.1 and Fig.5.8.2 and Fig.5.7.3. 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.5.7.1 shows r versus T , for $n_1 = 5/2$, $n_2 = 3/2$ with $1/\epsilon\rho = 1000$.

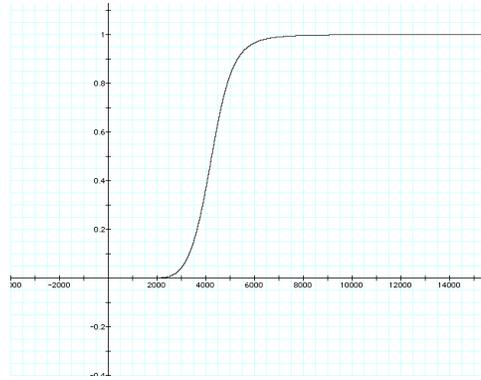


Fig.5.7.1. The ratio r against T , Eq.(5.5.4).

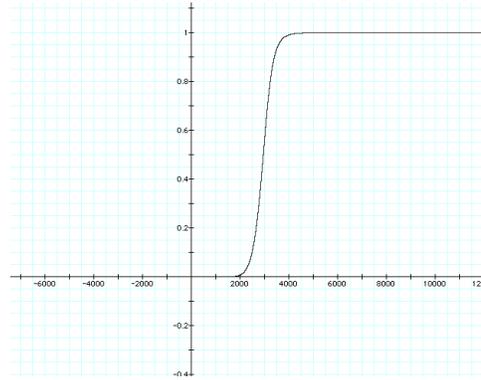


Fig.5.7.2. The ratio r against T , Eq.(5.5.5).

The measurements are usually performed under conditions of constant pressure. Setting $\rho_1/2 + \rho_2 = p/\mathcal{R}T$ we get, when $n_1 = 5/2$ and $n_2 = 3/2$,

$$\frac{\rho_2^2}{\rho\rho_1} = \frac{r^2}{1-r^2} = \frac{\mathcal{R}}{2\epsilon\rho} T^{3/2} e^{-\epsilon/\mathcal{R}_1 T}; \quad r = \rho_2/\rho. \quad (5.8.8)$$

This relationship is plotted in Fig.5.7.2. for $\mathcal{R}\epsilon\rho = 1000$.

We must return to the beginning to answer a reasonable question. If we have only one velocity then we have only one velocity potential, but two distinct densities. The system is no longer Hamiltonian. The best reply that we can make is to describe the procedure in slightly different terms. We conserve the full set of variables, retain the Hamiltonian structure, and work out all the Euler-Lagrange equations. Then we impose the constraint (5.8.1). The only thing that can go wrong is that the constraint is inconsistent with the equations of motion. The result is exactly the same. Below, we shall propose a generalization of of this constraint and it will then be shown that it responds favorably to some tests. In the meantime we are encouraged by the results obtained here.

V.9. Other **chemical reactions**

More complicated reactions raise new questions. Consider the choice of variables, in the slightly more complicated case of a reaction of the type



where ν_A molecules of type A changes into ν_B molecules of type B and ν_C molecules of type C . Let ϵ be the excess energy produced. The densities (in mols) of components A, B, C are ρ_A, ρ_B, ρ_C . We shall convey these data more concisely as follows. Define

$$\nu_A A - \nu_B B - \nu_C C =: \vec{v} \cdot \vec{A}, \quad \vec{v} := (\nu_A, -\nu_B, -\nu_C), \quad \vec{A} := (A, B, C)$$

and combine the formula (5.9.1) with the information about the energy in this form

$$\vec{v} \cdot \vec{A} = \epsilon.$$

Two densities are independently conserved, for example

$$\nu_A \rho_A + \nu_B \rho_B, \quad \text{and} \quad \nu_B \rho_B - \nu_C \rho_C.$$

We therefore need two Lagrange multipliers and two velocities. The space of conserved densities is a 2-dimensional linear vector space and any two independent densities form a basis for it. A sum of squared velocities is not linear, so what is the correct expression for the kinetic energy? Any attempt to eliminate one of the velocities leads to disorderly formulas; it is better to impose a constraint.

We take the complete Lagrangian density, regardless of interactions, to be, as in the case that there are no chemical reactions,

$$\mathcal{L} = \rho_A(\dot{\Phi}_A - \vec{v}_A^2/2) + \rho_B(\dot{\Phi}_B - \vec{v}_B^2/2) + \rho_C(\dot{\Phi}_C - \vec{v}_C^2/2) - f_A - f_B - f_C - sT, \quad (5.9.2)$$

with

$$s = \rho_A S_A + \rho_B S_B + \rho_C S_C \quad (5.9.3)$$

and with uniform coefficients S_A, S_B, S_C . The densities are in grams per cm^3 and the kinetic energies are in common, cgs units.

Conjecture. The effect of the reaction is to impose the **linear constraint**

$$\nu_A \dot{\Phi}_A = \nu_B \dot{\Phi}_B + \nu_C \dot{\Phi}_C = \epsilon; \quad (5.9.4)$$

thus

$$\vec{\nu} \cdot \dot{\vec{\Phi}} = 0.$$

Immediate support for this idea comes from the equations of motion. Variation with respect to the constrained potentials,

$$\vec{\nu} \cdot \delta \dot{\vec{\Phi}} = 0, \quad (5.9.5)$$

gives the two conservation laws,

$$\delta \mathcal{L} = \sum_i \left(\dot{\rho}_i + \vec{\nabla} \cdot (\rho_i \vec{v}_i) \right) \delta \Phi_i = 0$$

or

$$\dot{\rho}_i + \vec{\nabla} \cdot (\rho_i \vec{v}_i) = \nu_i Z(x), \quad i = A, B, C. \quad (5.9.6)$$

This is a succinct, and I think beautiful expression for the equations of continuity that hold during a chemical reaction.

This account of the independent variables and the conservation laws is an alternative to the treatment by Prigogine (1949) and his school.

The conjecture (5.9.4) is based on the significance of the velocity potential, more precisely the time derivative $\dot{\Phi}$, as an energy parameter. We have already remarked, in the simpler case of dissociation, as well as in the case of saturation, that it includes the latent heat. See Section IV.3, "Interpretation of the velocity potential".

At equilibrium all the fields are uniform and the remaining information that comes from the Euler-Lagrange equations includes the adiabatic relation

$$\frac{\partial}{\partial T}(f_A + f_B + f_C + sT) = 0 \quad (5.9.7)$$

and stationarity of (5.8.2) with respect to the local variations of the densities. A principal result is that, at equilibrium, in the absence of external forces, the densities are uniform. We shall assume that each component is an ideal gas, then (5.9.7) takes the familiar form

$$\sum_{i=A,B,C} \left(R_i \rho_i \left(\ln \frac{\rho_i}{T^{n_i}} - n_i \right) + s_i \rho_i \right) = 0.$$

Additional information comes from an independent global variations of the densities that leave invariant the constraint (5.9.4), namely

$$\delta \vec{\rho} \propto \vec{\nu} := (\nu_A, -\nu_B, -\nu_C).$$

Thus

$$\vec{\nu} \cdot \vec{\mu} = T \vec{\nu} \cdot \vec{S}, \quad \vec{\mu} = (\mu_A, \mu_B, \mu_C)$$

In the case of 3 ideal gases the full expression for this is

$$\frac{(\rho^{\nu/m})_A}{(\rho^{\nu/m})_B (\rho^{\nu/m})_C} (eT)^{-(n/m)_A + (n/m)_B + (n/m)_C} = e^{-\vec{\nu} \cdot \vec{S} / \mathcal{R}T}. \quad (5.9.8)$$

Here m_A is the molecular weight of fluid A and $(n/m)_A := n_A/m_A$. The affinity to the Saha equation is evident. For other fluids the right hand side depends on the interaction between the components. It is a function of the densities alone, independent of the temperature. The chemists resort to accumulated tables.

As in the case of dissociation, we claim that maximization of the entropy makes the Hamiltonian stationary or equivalently that

$$T \vec{\nu} \cdot \vec{S} = \epsilon, \quad (5.9.9)$$

and here it is becoming manifest that the constraint (5.9.1) is pertinent. The last equation determines the partitioning of the entropy. At equilibrium the condition that the Hamiltonian is stationary is equivalent to the condition

$$\vec{\nu} \cdot (\vec{\Phi} - T \vec{S}) = 0. \quad (5.9.10)$$

In other words, when the entropy is distributed according to Eq.(5.9.9) then the constraint (5.9.4) is a property of the equilibrium state.

Eq.(5.9.9) leads to the alternative statement

$$\frac{(\rho^{\nu/m})_A}{(\rho^{\nu/m})_B(\rho^{\nu/m})_C} = (eT)^{(n/m)_A - (n/m)_B - (n/m)_C} e^{-\epsilon/\mathcal{R}} \quad (5.9.bis)$$

Either form gives a value for the “**reaction constant**”

$$K_c = \frac{(\rho^{\nu/m})_A}{(\rho^{\nu/m})_B(\rho^{\nu/m})_C},$$

as a function of the temperature. While the specialization to ideal gases limits the practical value of this result it is nevertheless a little strange that this function is always taken from experiment and that no attempt is made to predict it, with the exception of the work of Saha, *op cit*.

V.10. Taking stock.

The approach to binary mixtures through the addition of Lagrangians furnishes a two parameter family of model Lagrangian densities. The two parameters are interpreted in terms of the entropies assigned to each type of molecule. As heat is added to the system the entropy must change and a decision has to be made about the allotment of additional entropy to each gas; this gives us the concept of a 2-dimensional entropy space and the path in this space that is chosen by the system. We had expected that the key to the determination of the path is entropy maximization, but this expectation has not been confirmed.

We have studied some mixtures of gases that are free to transmogrify, and we have seen two examples of a rule that would have the physical path through entropy space reduce to relations of the type $\epsilon = (S_2 - S_1)T$. In the case of ideal gases that do not make chemical reactions the stronger statement furnished by the strong Gibbs-Dalton hypothesis may apply.

When we begin to consider mixtures of van der Waal’s gases in the next chapter we shall find that condensation is a major part of it, so that both items of insight summarized here will be put to severe tests.

So far, there was no attempt to predict **rates** of chemical reactions. In the case that the reactions are driven by input of energy the rates will be determined by the rate of input of heat or other forms of energy, as in electrolysis. In the case of spontaneous reactions that produce heat, the difficulty lies in the almost impossible task of preparing suitable initial conditions. A few very special circumstances may offer some hope for fruitful analysis.

1. Many systems have metastable configurations that can be reached with care, such as is the case with supercooled vapors or superheated liquids. Then an initial state can be prepared that is characterized by simple properties, such as uniformity. Possibly, the decay of such states may take place without convection setting in, or with convection with a high degree of symmetry.

2. Solids may offer possibilities for analysis, because of the simplification that is the absence of convection. The simplest instance is offered by the slab, when an initial uniform configuration is disturbed by suddenly bringing one of the bounding plates to a higher temperature. There may be an opportunity of deriving Fourier's heat transfer law from thermodynamics.

Project 1. Study speed of sound in a mixture over a wide range of densities and temperatures. Collect data and test models. Then use the same models to study critical phenomena.

Project 2. Adapt the Gibbs-Dalton hypothesis to real gases.

Project 3. Use the entropy model to study chemical reactions. Holman gives several examples that may be useful.

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