

Uniqueness of chemical equilibria in ideal mixtures of ideal gases

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We prove the uniqueness of chemical equilibrium for an ideal mixture of ideal gases in a closed, spatially homogeneous volume. Uniqueness, a fundamental issue of chemical physics, is incompletely justified in textbooks and much of the scientific literature. We first reproduce a little known proof by Zel'dovich and show in a more direct fashion than originally presented that a unique equilibrium exists for isothermal reactions. Zel'dovich's approach is then extended to the adiabatic case, and a more complete exposition than that of Aris is provided. The example of an isothermal, isochoric O-O₂-O₃ system provides an illustration of uniqueness. The discussion should be useful for students and instructors of graduate level thermal physics, as well as for researchers in macroscale reaction dynamics. © 2008 American Association of Physics Teachers.
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I. INTRODUCTION

The identification of pressure, temperature, and molecular species concentrations at chemical equilibrium is of fundamental importance in reaction dynamics as well as all of chemical physics. Such an exercise is common in high school and beginning college curricula. However, it is unusual in such courses to show that the equilibrium which is identified is unique. The practical understanding of a variety of physical devices and phenomena, ranging from internal combustion engines to atmospheric chemical dynamics, relies on the knowledge of whether or not the equilibrium state exists and is unique. Thus, this problem is of fundamental importance.

There are cases where the equilibrium is nonunique.¹ It has long been realized that the possibility of multiple physical equilibria exists in open systems,² that is, systems for which mass exchanges with the surroundings are permitted. Such systems will not be considered here. Multiple physical equilibria are also admitted in closed systems for nonideal mixtures.^{3,4} Such mixtures are common in liquid solutions in which the adhesive forces between molecules of different type are different than the cohesive forces between molecules of the same type. Ideal mixtures, which include gases which obey Dalton's law of partial pressures, have a symmetry of such forces. Third, when the entire pressure, temperature, and molecular species concentration space including physically nonrealizable portions is considered, multiple equilibria also exist in ideal mixtures in closed systems. It seems, though, that all but one appear in physically unrealizable regions. Nevertheless, finding these nonphysical equilibria has value in constructing slow invariant manifolds associated with the long time dynamics of the system.^{5,6} In short, their identification enables use of dynamic system theory to efficiently construct heteroclinic orbits which describe the time evolution of the species concentrations. These important orbits commence in nonphysical regions, pierce into the physical domain, and proceed to a physical equilibrium. On such orbits the fast time scale events have been equilibrated, and the system's time dependency is strictly confined to slow time scales. To construct such orbits, it is crucial to know whether or not the physical equilibrium condition is unique.

If we restrict ourselves to closed systems of ideal mix-

tures, a physically realizable chemical equilibrium is nearly always associated with a point in the pressure, temperature, species composition space at which an appropriate thermodynamic variable acquires an extremum value. A counter example is discussed by Alberty⁷ in which the consideration of reaction kinetics, if the number of reactions is small, can render the physical equilibrium inaccessible; such a condition is rarely met for realistic systems with a large number of reactions. It is typically assumed that if such a minimum is found, it is unique, though the rigorous justification of such an assumption is generally absent.

In special cases, a rigorous, but little known, uniqueness proof exists. Zel'dovich⁸ showed this uniqueness for isothermal-isochoric systems consisting of spatially homogeneous ideal mixtures of ideal gases. Many years later Aris, who was likely unaware of Zel'dovich's proof, provided a terse exposition of uniqueness for isobaric systems under isothermal⁹ and adiabatic¹⁰ conditions. Shortly thereafter, and again apparently unfamiliar with Refs. 8–10, Shear¹¹ gave an independent uniqueness proof based on Lyapunov theory. Other discussions on the uniqueness of equilibria are given in Refs. 12–15.

In this paper we illustrate and expand on the approach of Zel'dovich, which we believe gives the most transparent explanation. The present work clarifies the analysis and reveals important nuances not readily evident in earlier studies. We first reproduce Zel'dovich's proof for an isothermal-isochoric system using a more direct procedure based on a differential form of the second law. We subsequently extend the analysis to the isothermal-isobaric, adiabatic-isochoric, and adiabatic-isobaric cases.

II. PRELIMINARY ANALYSIS

Before commencing with the uniqueness proof, it is necessary to give a brief but complete exposition of the fundamental mass, energy, and entropy constraints, as well as definitions of the various thermodynamic variables and assumptions.

We consider a system consisting of a mixture of N molecular species, with each species composed from L atomic elements. We take $N > L$, N finite; the proof is easily adjusted for the less common case of $N \leq L$. The system is assumed to be closed to mass exchanges with its surroundings, open to

mass exchanges among species within it, and open to work and heat exchanges with the surroundings. We consider only work and heat exchanges that are reversible; irreversible exchanges could be considered, but are extraneous to the uniqueness proof.

A. Mass/mole constraints

In the absence of nuclear reactions the number of moles of each element is conserved, and the total mass is conserved. Mathematically, this conservation can be expressed as a system of linear algebraic equations, and standard notions from linear algebra¹⁶ can be exploited. A mass balance for each atomic element requires the linear constraint:

$$\sum_{i=1}^N \phi_{li} n_i = \sum_{i=1}^N \phi_{li} n_i^*, \quad (1)$$

where n_i and n_i^* are, respectively, the instantaneous and initial number of moles of species i , with n_i^* assumed positive semidefinite and finite, and ϕ_{li} is the number of atoms of element l in species i . The term ϕ_{li} is described by an $(L \times N)$ matrix which generally is nonsquare and full rank. Recall that a full rank matrix may be rectangular and has a rank which is the smaller of the matrix dimensions. For our analysis ϕ_{li} will be assumed to be nonsquare and of full rank L . Unless otherwise stated, we will let $i=1, \dots, N$, and $l=1, \dots, L$.

Equation (1) is generally underconstrained for the unknown n_i s; we can find solutions of the form

$$n_i = n_i^* + \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k. \quad (2)$$

Equation (2) allows the N values of n_i to be expressed in terms of $N-L$ values of the reduced composition variables ξ_k . It will be seen that because the n_i s are linearly dependent, they are not the most convenient set of thermodynamic variables. In contrast, the linearly independent ξ_k s are of greater value. A detailed example, given later, will illustrate the construction of Eq. (2) for a realistic chemical system. Here and elsewhere, we take $k=1, \dots, N-L$. The constant matrix \mathcal{D}_{ik} is of dimension $N \times (N-L)$ and has full rank $N-L$. Each of the $(N-L)$ column vectors of \mathcal{D}_{ik} has length N and is linearly independent of the remaining column vectors. This set is composed of all the vectors that lie in the right null space of the matrix ϕ_{li} :

$$\sum_{i=1}^N \phi_{li} \mathcal{D}_{ik} = 0. \quad (3)$$

The matrix \mathcal{D}_{ik} is not unique, which is of no consequence for the analysis. We can differentiate Eq. (2) to obtain

$$\left. \frac{\partial n_i}{\partial \xi_p} \right|_{\xi_j \neq p} = \mathcal{D}_{ip} \quad (p = 1, \dots, N-L). \quad (4)$$

We require that $n_i \geq 0$ for all N species. The hyperplanes given by $n_i = 0$ define a closed physical boundary in reduced composition space. We next require that changes in n_i which originate from the surface $n_i = 0$ be positive. For such curves we thus require that near $n_i = 0$, perturbations $d\xi_k$ be such that

$$dn_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k > 0. \quad (5)$$

B. Thermodynamic constraints

The Gibbs equation for a multicomponent material^{17,18} is

$$dU = -PdV + TdS + \sum_{i=1}^N \mu_i dn_i. \quad (6)$$

Here $U = U(V, S, n_i)$ is the internal energy, and the independent canonical variables are volume V , entropy S , and n_i . The associated conjugate variables are pressure P , temperature T , and the chemical potentials μ_i .

The first law for a closed system is

$$dU = \delta Q + \delta W, \quad (7)$$

where δQ and δW are the inexact differentials of heat and work transfer into the system, respectively. The notation δ is used to distinguish an inexact differential from an exact one, which is denoted by d . We will restrict attention to reversible work transfers arising from pressure forces:

$$\delta W = -PdV. \quad (8)$$

The second law of thermodynamics for such a system is given by

$$dS \geq \frac{\delta Q}{T}. \quad (9)$$

Equation (7) with Eq. (8) allows Eq. (9) to be rewritten as

$$TdS \geq dU + PdV. \quad (10)$$

We use Eqs. (5) and (6) to reduce Eq. (10) to

$$\sum_{i=1}^N \mu_i \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k \leq 0. \quad (11)$$

Thus, for a system that is confined to only reversible work and heat transfer, the only source of irreversibility is chemical reactions.

C. Ideal mixtures of ideal gases

We further restrict attention to ideal mixtures of calorically imperfect ideal gases obeying Dalton's law of partial pressures. For such a material^{17,18} we have

$$P_i = \frac{n_i RT}{V}, \quad (12)$$

$$h_i(T) = h_i^o(T) = h_i^o(T_o) + \int_{T_o}^T c_{P_i}(\hat{T}) d\hat{T}, \quad (13)$$

$$u_i(T) = u_i^o(T) = h_i^o(T) - RT, \quad (14)$$

$$s_i^o(T) = s_i^o(T_o) + \int_{T_o}^T \frac{c_{P_i}(\hat{T})}{\hat{T}} d\hat{T}, \quad (15)$$

$$s_i(T, P, n_i) = s_i^o(T) - R \ln \left(\frac{P_i}{P_o} \right), \quad (16)$$

$$g_i(T, P, n_i) = \mu_i(T, P, n_i) = h_i - Ts_i, \quad (17)$$

$$\mu_i(T, P, n_i) = \mu_i^o(T) + RT \ln\left(\frac{P_i}{P_o}\right), \quad (18)$$

$$f_i(T, P, n_i) = u_i - Ts_i, \quad (19)$$

$$c_{P_i}(T) = \frac{dh_i}{dT}, \quad (20)$$

$$c_{V_i}(T) = \frac{du_i}{dT} = c_{P_i}(T) - R. \quad (21)$$

The superscript o denotes evaluation at a reference pressure P_o . For species i , P_i is the partial pressure, h_i is the partial molar enthalpy, c_{P_i} and c_{V_i} are the molar specific heats at constant pressure and volume, respectively, u_i is the partial molar internal energy, s_i is the partial molar entropy, g_i is the partial molar Gibbs free energy, and f_i is the partial molar Helmholtz free energy. The reference state temperature is T_o , and the universal gas constant is R .

The mixture pressure, internal energy, Helmholtz free energy, number of moles, and molar specific heats at constant volume and pressure are P , U , F , n , c_v , and c_p , respectively, and are given by

$$P = \sum_{i=1}^N P_i, \quad (22)$$

$$U = \sum_{i=1}^N n_i u_i, \quad (23)$$

$$F = \sum_{i=1}^N n_i f_i, \quad (24)$$

$$n = \sum_{i=1}^N n_i, \quad (25)$$

$$c_v = \frac{1}{n} \sum_{i=1}^N n_i c_{V_i}, \quad (26)$$

$$c_p = \frac{1}{n} \sum_{i=1}^N n_i c_{P_i}. \quad (27)$$

We also have the mixture enthalpy, $H = \sum_{i=1}^N n_i h_i$, mixture entropy, $S = \sum_{i=1}^N n_i s_i$, and mixture Gibbs free energy, $G = \sum_{i=1}^N n_i g_i$.

We note that n_o , the total number of moles at the reference pressure, is

$$n_o \equiv \frac{P_o V}{RT}. \quad (28)$$

With Eqs. (12), (22), and (28), it is easy to see that

$$\frac{P_i}{P_o} = \frac{n_i}{n_o}. \quad (29)$$

In general, n_o is constant only for isothermal-isochoric systems. Similarly, it is straightforward to show, using Eq. (25), that

$$\frac{P_i}{P_o} = \frac{n_i P}{n P_o}. \quad (30)$$

Equation (30) is useful for isobaric systems.

To obtain a necessary expression for $d\mu_i^o/dT$, we substitute Eqs. (13) and (15) in Eq. (17) at the reference pressure to get

$$\mu_i^o = h_i^o(T_o) + \int_{T_o}^T c_{P_i}(\hat{T}) d\hat{T} - T \left(s_i^o(T_o) + \int_{T_o}^T \frac{c_{P_i}(\hat{T})}{\hat{T}} d\hat{T} \right). \quad (31)$$

We differentiate μ_i^o with respect to T to obtain

$$\frac{d\mu_i^o}{dT} = -s_i^o(T). \quad (32)$$

III. UNIQUENESS PROOFS

A. Isothermal-isochoric case

We consider the case discussed by Zel'dovich.⁸ For an isothermal-isochoric system it is useful to employ the Legendre transformation $F = U - TS$. We have $dF = dU - TdS - SdT$, and Eq. (6) becomes

$$dF = -SdT - PdV + \sum_{i=1}^N \mu_i dn_i. \quad (33)$$

The canonical representation of the Helmholtz free energy is of the form $F(T, V, n_i)$, and the second law (10) becomes $dF \leq -SdT - PdV$. For this case the second law reduces to

$$dF|_{T,V} \leq 0. \quad (34)$$

Thus, F must always decrease until it reaches a minimum, at which

$$dF|_{T,V} = 0. \quad (35)$$

If we consider Eq. (33) in the isothermal-isochoric limit, we find $dF|_{T,V} = \sum_{i=1}^N \mu_i dn_i$, so that at equilibrium, we have

$$dF|_{T,V} = \sum_{i=1}^N \mu_i dn_i = 0. \quad (36)$$

Not all of the dn_i s are linearly independent in Eq. (36), and so there is concern about how Eq. (36) can be enforced. This concern is removed by considering how F varies with the independent reduced composition variables ξ_p . We determine this variation using Eq. (5) and the relation $dF|_{T,V} = \sum_{p=1}^{N-L} (\partial F / \partial \xi_p|_{T,V,\xi_{j \neq p}}) d\xi_p$, and cast Eq. (36) as

$$dF \Big|_{T,V} = \sum_{i=1}^N \mu_i \sum_{p=1}^{N-L} \mathcal{D}_{ip} d\xi_p = \sum_{p=1}^{N-L} \frac{\partial F}{\partial \xi_p} \Big|_{T,V,\xi_{j \neq p}} d\xi_p = 0. \quad (37)$$

Because the $d\xi_p$ s are linearly independent, Eq. (37) requires

$\partial F / \partial \xi_p|_{T,V,\xi_{j \neq p}} = 0$ at equilibrium. Regrouping the middle terms of Eq. (37), we also find

$$\sum_{p=1}^{N-L} \left(\frac{\partial F}{\partial \xi_p} \Big|_{T,V,\xi_{j \neq p}} - \sum_{i=1}^N \mu_i \mathcal{D}_{ip} \right) d\xi_p = 0. \quad (38)$$

Again, because the $d\xi_p$ s are linearly independent, the only way to guarantee satisfaction of Eq. (38) is to require that the term multiplying $d\xi_p$ be zero for all p , $(\partial F / \partial \xi_p|_{T,V,\xi_{j \neq p}}) = \sum_{i=1}^N \mu_i \mathcal{D}_{ip}$. Thus at equilibrium, we have

$$\nabla F = \frac{\partial F}{\partial \xi_p} \Big|_{T,V,\xi_{j \neq p}} = \sum_{i=1}^N \mu_i \mathcal{D}_{ip} = 0. \quad (39)$$

We have adopted the Gibbs notation for the gradient of F , where the ∇ operator is the gradient in ξ_p space. Equation (39) is valid for a general equation of state. For the isothermal-isochoric system, the chemical potential is a function of the $(N-L)$ independent reduced composition variables ξ_k , in which case, Eq. (39) forms $(N-L)$ nonlinear equations in the $(N-L)$ unknowns.

We use Eqs. (18) and (29) and write Eq. (39) for an ideal gas mixture as

$$\nabla F = \frac{\partial F}{\partial \xi_p} \Big|_{T,V,\xi_{j \neq p}} = \sum_{i=1}^N \left[\mu_i^o + RT \ln \left(\frac{n_i}{n_o} \right) \right] \mathcal{D}_{ip} = 0. \quad (40)$$

Following Zel'dovich,⁸ we rearrange Eq. (40) in the form:

$$\ln \prod_{i=1}^N \left(\frac{n_i}{n_o} \right)^{\mathcal{D}_{ip}} = - \sum_{i=1}^N \frac{\mathcal{D}_{ip} \mu_i^o}{RT}. \quad (41)$$

We use Eq. (2) to eliminate n_i and obtain

$$\ln \prod_{i=1}^N \left[\left(n_i^* + \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k \right) \frac{1}{n_o} \right]^{\mathcal{D}_{ip}} = - \sum_{i=1}^N \frac{\mathcal{D}_{ip} \mu_i^o}{RT}. \quad (42)$$

For isothermal-isochoric systems, every term in Eq. (42), except for ξ_k , is constant. Equation (42) forms an $(N-L)$ -dimensional nonlinear system of algebraic equations in the $(N-L)$ unknown values of ξ_k which can be solved numerically by an iterative procedure. Note that as of yet, no proof exists that the solution of this system is unique. Nor is it certain whether or not F is minimized for such a solution.

We can determine if the solution is a minimum by examining the second derivative, obtained by differentiating Eq. (40). We find the Hessian, \mathbf{H} , to be

$$\mathbf{H} = \frac{\partial^2 F}{\partial \xi_j \partial \xi_p} = RT \sum_{i=1}^N \frac{\mathcal{D}_{ip} \mathcal{D}_{ij}}{n_i}. \quad (43)$$

Here $j=1, \dots, N-L$. Scaling each of the rows of \mathcal{D}_{ip} by a constant does not affect the rank. So we can say that the $N \times (N-L)$ matrix whose entries are $\mathcal{D}_{ip} / \sqrt{n_i}$ has rank $N-L$, and consequently the Hessian \mathbf{H} , of dimension $(N-L) \times (N-L)$, has full rank $N-L$, and is symmetric. It is easy to show by means of singular value decomposition, or other methods, that the eigenvalues of a full rank symmetric square matrix are all real and nonzero.

Now, consider whether $\partial^2 F / \partial \xi_j \partial \xi_p$ is positive definite. By definition, it is positive definite for an arbitrary vector z_j of length $(N-L)$ with nonzero norm if Y_{TV} is positive:

$$Y_{TV} = \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \frac{\partial^2 F}{\partial \xi_j \partial \xi_p} z_j z_p > 0. \quad (44)$$

Here, and in the remainder of the text, we take Y to denote an appropriate positive definite scalar. The subscripts denote the variables which are constant for the particular case, here T and V for isothermal-isochoric. We define a vector y_i of length N , also with nonzero norm, as

$$y_i \equiv \sum_{j=1}^{N-L} \mathcal{D}_{ij} z_j, \quad (45)$$

and substitute Eqs. (43) and (45) into Eq. (44) to show that

$$Y_{TV} = RT \sum_{i=1}^N \frac{y_i^2}{n_i}. \quad (46)$$

If we restrict the domain to the physically accessible space, $n_i \geq 0$, $T > 0$, for arbitrary \mathcal{D}_{ij} and arbitrary y_i (with $\|y\| > 0$), we find that $Y_{TV} > 0$. Hence, we conclude that the Hessian matrix of F is positive definite globally.

We next consider the behavior of F near a generic point in the physical space $\hat{\xi}$ where $F = \hat{F}$. If we let $d\xi$ represent $\xi - \hat{\xi}$, we can represent the Helmholtz free energy by the Taylor series

$$F(\xi) = \hat{F} + d\xi^T \cdot \nabla F + \frac{1}{2} d\xi^T \cdot \mathbf{H} \cdot d\xi + \dots, \quad (47)$$

where ∇F and \mathbf{H} are evaluated at $\hat{\xi}$. Now if $\hat{\xi} = \xi^{\text{eq}}$, where eq denotes an equilibrium point, $\nabla F = 0$, $\hat{F} = F^{\text{eq}}$, and

$$F(\xi) - F^{\text{eq}} = \frac{1}{2} d\xi^T \cdot \mathbf{H} \cdot d\xi + \dots. \quad (48)$$

Because \mathbf{H} is positive definite in the entire physical domain, any isolated critical point will be a minimum. Note that if more than one isolated minimum point of F were to exist in the domain interior, a maximum would also have to exist in the interior, but maxima are not allowed by the global positive definite nature of \mathbf{H} . Subsequently, any extremum which exists away from the boundary of the physical region must be a minimum, and the minimum is global.

Global positive definiteness of \mathbf{H} alone does not rule out the possibility of nonisolated multiple equilibria, as seen by the following analysis. Because it is symmetric, \mathbf{H} can be orthogonally decomposed into $\mathbf{H} = \mathbf{Q}^T \cdot \mathbf{\Lambda} \cdot \mathbf{Q}$, where \mathbf{Q} is an orthogonal matrix whose columns are the normalized eigenvectors of \mathbf{H} . Note that $\mathbf{Q}^T = \mathbf{Q}^{-1}$. Also $\mathbf{\Lambda}$ is a diagonal matrix with real eigenvalues on its diagonal. We can effect a volume-preserving rotation of axes by taking the transformation $d\mathbf{w} = \mathbf{Q} \cdot d\xi$; thus, $d\xi = \mathbf{Q}^T \cdot d\mathbf{w}$. Hence,

$$\begin{aligned} F - F^{\text{eq}} &= \frac{1}{2} (\mathbf{Q}^T \cdot d\mathbf{w})^T \cdot \mathbf{H} \cdot \mathbf{Q}^T \cdot d\mathbf{w} + \dots \\ &= \frac{1}{2} d\mathbf{w}^T \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot \mathbf{\Lambda} \cdot \mathbf{Q} \cdot \mathbf{Q}^T \cdot d\mathbf{w} + \dots \\ &= \frac{1}{2} d\mathbf{w}^T \cdot \mathbf{\Lambda} \cdot d\mathbf{w} + \dots. \end{aligned} \quad (49)$$

The application of these transformations gives in the neighborhood of equilibrium the quadratic form

$$F - F^{\text{eq}} = \frac{1}{2} \sum_{p=1}^{N-L} \lambda_p (dw_p)^2 + \dots \quad (50)$$

For F to be a unique minimum, $\lambda_p > 0$. If one or more of the $\lambda_p = 0$, then the minimum could be realized on a line or higher dimensional plane, depending on how many zeros are present. The full rank of \mathbf{H} guarantees that $\lambda_p > 0$. For our problem the unique global minimum which exists in the interior will exist at a unique point.

Finally, we need to verify that a local minimum does not exist on the boundary of the physical region. We combine Eqs. (16), (18), (19), (24), and (29) to obtain

$$F = RT \sum_{i=1}^N n_i \left[-1 + \frac{\mu_i^o}{RT} + \ln \left(\frac{n_i}{n_o} \right) \right]. \quad (51)$$

On the physical boundary given by $n_q = 0$, we must be careful when $i = q$ in Eq. (51) because of a potential logarithmic singularity. However, because $\lim_{n_q \rightarrow 0} n_q \ln n_q = 0$, F has no singularity on the boundary and takes on finite values.

We next examine changes in F in the vicinity of boundaries given by $n_q = 0$. We will restrict our attention to changes which give rise to $dn_q > 0$. We employ Eq. (40) and find that

$$\begin{aligned} dF &= \sum_{p=1}^{N-L} d\xi_p \left. \frac{\partial F}{\partial \xi_p} \right|_{T,V,\xi_{j \neq p}} \\ &= \sum_{i=1}^N \left[\mu_i^o + RT \ln \left(\frac{n_i}{n_o} \right) \right] \sum_{p=1}^{N-L} \mathcal{D}_{ip} d\xi_p. \end{aligned} \quad (52)$$

On the boundary given by $n_q = 0$, the dominant term in the sum is for $i = q$, and so on this boundary

$$\lim_{n_q \rightarrow 0} dF = RT \ln \left(\frac{n_q}{n_o} \right) \underbrace{\sum_{p=1}^{N-L} \mathcal{D}_{qp} d\xi_p}_{>0} \rightarrow -\infty. \quad (53)$$

The term identified by the brace is positive because of Eq. (5). Because R and $T > 0$, we see that as n_q moves away from zero into the physical region, changes in F are large and negative. So the physical boundary can be a local maximum, but never a local minimum in F . Hence, the only admissible equilibrium is the unique minimum of F found from Eq. (42); this equilibrium is found at a unique point in reduced composition space.

B. Isothermal-isobaric case

For a system in which T and P are constant the appropriate Legendre transformation is $G = U + PV - TS$, where G is the Gibbs free energy. We have $dG = dU + PdV + VdP - TdS - SdT$, and after substitution into Eq. (6) we obtain

$$dG = VdP - SdT + \sum_{i=1}^N \mu_i dn_i. \quad (54)$$

Hence, the canonical representation is of the form $G(P, T, n_i)$, and the second law (10) becomes $dG \leq VdP - SdT$. For the isothermal-isobaric case this condition reduces to

$$dG|_{T,P} \leq 0, \quad (55)$$

and G must decrease until it reaches a minimum. If we eliminate dU in Eq. (6) in favor of dG and consider isothermal-isobaric conditions, we have $dG|_{T,P} = \sum_{i=1}^N \mu_i dn_i$, so that at equilibrium

$$dG|_{T,P} = \sum_{i=1}^N \mu_i dn_i = 0. \quad (56)$$

As before, we consider the variation of G with the independent variables ξ_p and find

$$\left. \frac{\partial G}{\partial \xi_p} \right|_{\xi_{j \neq p}} = \sum_{i=1}^N \mu_i \mathcal{D}_{ip} = 0. \quad (57)$$

We use Eqs. (18) and (30) and cast Eq. (57) in the form

$$\sum_{i=1}^N \mathcal{D}_{ip} \left(\mu_i^o + RT \ln \left(\frac{n_i P}{n P_o} \right) \right) = 0, \quad (58)$$

or

$$\ln \prod_{i=1}^N \left(\frac{n_i P}{n P_o} \right)^{\mathcal{D}_{ip}} = - \sum_{i=1}^N \mathcal{D}_{ip} \frac{\mu_i^o}{RT}. \quad (59)$$

Again we use Eq. (2) to eliminate n_i and n to get

$$\begin{aligned} \ln \prod_{i=1}^N \left(\frac{(n_i^* + \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k) P}{\left(\sum_{q=1}^N (n_q^* + \sum_{k=1}^{N-L} \mathcal{D}_{qk} \xi_k) \right) P_o} \right)^{\mathcal{D}_{ip}} \\ = - \sum_{i=1}^N \mathcal{D}_{ip} \frac{\mu_i^o}{RT}. \end{aligned} \quad (60)$$

Every term in Eq. (60) is constant except for the $(N-L)$ values of ξ_k . These $(N-L)$ nonlinear algebraic equations can be solved for the $(N-L)$ unknown ξ_k s via iteration.

We can repeat our previous analysis to show that this equilibrium is unique in the physically accessible region of composition space. By differentiating Eq. (57) it is seen that

$$\frac{\partial^2 G}{\partial \xi_j \partial \xi_p} = RT \sum_{i=1}^N \mathcal{D}_{ip} \frac{\partial}{\partial \xi_j} \ln \left(\frac{n_i}{n} \right), \quad (61)$$

$$= RT \left(\sum_{i=1}^N \frac{\mathcal{D}_{ip} \mathcal{D}_{ij}}{n_i} - \frac{1}{n} \sum_{i=1}^N \sum_{q=1}^N \mathcal{D}_{ip} \mathcal{D}_{qj} \right). \quad (62)$$

Next consider the sum

$$\begin{aligned} Y_{TP} &= \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \frac{\partial^2 G}{\partial \xi_j \partial \xi_p} z_j z_p = RT \sum_{j=1}^{N-L} \sum_{p=1}^{N-L} \left(\sum_{i=1}^N \frac{\mathcal{D}_{ip} \mathcal{D}_{ij}}{n_i} \right. \\ &\quad \left. - \frac{1}{n} \sum_{i=1}^N \sum_{q=1}^N \mathcal{D}_{ip} \mathcal{D}_{qj} \right) z_j z_p. \end{aligned} \quad (63)$$

We use Eq. (45) and reduce Eq. (63) to the positive definite form

$$Y_{TP} = \frac{RT}{n} \sum_{i=1}^N \sum_{j=i+1}^N \left(\sqrt{\frac{n_j}{n_i}} y_i - \sqrt{\frac{n_i}{n_j}} y_j \right)^2 > 0. \quad (64)$$

On the boundary $n_i=0$, and as for the isothermal-isochoric case, it can be shown that $dG \rightarrow -\infty$ for changes with $dn_i > 0$. Thus, the boundary has no local minimum, and we can conclude that G is minimized in the interior and the minimum is unique.

C. Adiabatic-isochoric case

For the isochoric and adiabatic case the Gibbs Eq. (6) is already in terms of the canonical variables. The conditions correspond to a chemical reaction in a fixed volume ($dV=0$) which is thermally insulated ($\delta Q=0$). For this system the work vanishes, $\delta W=-PdV=0$. The first law, Eq. (7), reduces to $dU=0$. The second law, Eq. (10), reduces to

$$dS|_{U,V} \geq 0, \quad (65)$$

and S must monotonically increase until it reaches a maximum where

$$dS|_{U,V} = 0. \quad (66)$$

Next, we consider Eq. (6) for $dU=0$, $dV=0$, $dS|_{U,V} = -(1/T)\sum_{i=1}^N \mu_i dn_i$, so that at equilibrium

$$dS|_{U,V} = -\frac{1}{T} \sum_{i=1}^N \mu_i dn_i = 0. \quad (67)$$

We use Eq. (5) to eliminate dn_i :

$$dS = -\frac{1}{T} \sum_{i=1}^N \sum_{k=1}^{N-L} \mu_i \mathcal{D}_{ik} d\xi_k. \quad (68)$$

We then employ Eq. (18) and consider the variation of S near equilibrium

$$\left. \frac{\partial S}{\partial \xi_j} \right|_{U,V,\xi_{p \neq j}} = -\frac{1}{T} \sum_{i=1}^N \left[\mu_i^o + RT \ln \left(\frac{P_i}{P_o} \right) \right] \mathcal{D}_{ij} = 0, \quad (69)$$

$$\begin{aligned} &= -\sum_{i=1}^N \left[\frac{\mu_i^o}{T} + R \ln \left(\frac{T}{T_o} \right) \right. \\ &\quad \left. + R \ln \left(\frac{n_i RT_o}{P_o V} \right) \right] \mathcal{D}_{ij} = 0. \end{aligned} \quad (70)$$

For convenience we define the temperature-dependent function $\psi_i(T)$ as

$$\psi_i(T) \equiv \frac{\mu_i^o}{T} + R \ln \left(\frac{T}{T_o} \right). \quad (71)$$

We can rewrite Eq. (70) as

$$\left. \frac{\partial S}{\partial \xi_j} \right|_{U,V,\xi_{p \neq j}} = -\sum_{i=1}^N \left[\psi_i(T) + R \ln \left(\frac{n_i RT_o}{P_o V} \right) \right] \mathcal{D}_{ij} = 0, \quad (72)$$

and rearrange Eq. (72) in the familiar form

$$\ln \prod_{i=1}^N \left[\frac{\left(n_i^* + \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k \right) RT}{P_o V} \right]^{\mathcal{D}_{ij}} = -\sum_{i=1}^N \mathcal{D}_{ij} \frac{\mu_i^o}{RT}. \quad (73)$$

We see that Eq. (73) is a function of the $(N-L)$ values of ξ_k as well as the unknown T , and hence the $(N-L)$ equations require an additional equation. The necessary equation is

provided by the caloric equation of state (23), in which the energy is held constant at U^* :

$$U^* = \sum_{i=1}^N n_i u_i(T). \quad (74)$$

To determine if the equilibrium solution obtained from solution of Eqs. (73) and (74) is a maximum, consider the Hessian matrix of S found by differentiating Eq. (72):

$$\frac{\partial^2 S}{\partial \xi_k \partial \xi_j} = -\sum_{i=1}^N \left(\frac{d\psi_i(T)}{dT} \frac{\partial T}{\partial \xi_k} + \frac{R}{n_i} \mathcal{D}_{ik} \right) \mathcal{D}_{ij}. \quad (75)$$

Equation (75) requires an expression for $\partial T / \partial \xi_k$. We differentiate Eq. (74)

$$0 = \sum_{q=1}^N \left(n_q \frac{du_q}{dT} dT + u_q dn_q \right), \quad (76)$$

employ the definitions Eqs. (21) and (26), and use Eq. (5) to obtain

$$dT = -\frac{1}{nc_v} \sum_{q=1}^N \sum_{p=1}^{N-L} u_q \mathcal{D}_{qp} d\xi_p. \quad (77)$$

Hence,

$$\left. \frac{\partial T}{\partial \xi_k} \right|_{U,V,\xi_{r \neq k}} = -\frac{1}{nc_v} \sum_{q=1}^N u_q \mathcal{D}_{qk}. \quad (78)$$

Now consider the temperature derivative of Eq. (71):

$$\frac{d\psi_i}{dT} = -\frac{\mu_i^o}{T^2} + \frac{1}{T} \frac{d\mu_i^o}{dT} + \frac{R}{T}. \quad (79)$$

If we use Eqs. (32), (14), and (17), we find that Eq. (79) reduces to

$$\frac{d\psi_i}{dT} = -\frac{1}{T^2} u_i. \quad (80)$$

We substitute Eqs. (78) and (80) into Eq. (75) and find

$$\frac{\partial^2 S}{\partial \xi_k \partial \xi_j} = -\frac{1}{nc_v T^2} \sum_{i=1}^N \sum_{q=1}^N u_i u_q \mathcal{D}_{qk} \mathcal{D}_{ij} - R \sum_{i=1}^N \frac{\mathcal{D}_{ik} \mathcal{D}_{ij}}{n_i}. \quad (81)$$

As before, we can use Eq. (45) and straightforward algebra to show that

$$\begin{aligned} Y_{UV} &= \sum_{k=1}^{N-L} \sum_{j=1}^{N-L} \frac{\partial^2 S}{\partial \xi_k \partial \xi_j} z_{kj} = -\frac{1}{nc_v T^2} \left(\sum_{i=1}^N u_i v_i \right)^2 \\ &\quad - R \sum_{i=1}^N \frac{v_i^2}{n_i}. \end{aligned} \quad (82)$$

Because $c_v > 0$ and $n_i \geq 0$, and all other terms involve perfect squares, it is obvious that $Y_{UV} < 0$, and the Hessian matrix is negative definite. Consequently, the extremum point of S represents a maximum. Because $\lim_{n_i \rightarrow 0} dS \rightarrow \infty$ for changes with $dn_i > 0$, there is no local maximum on the boundary, and any maximum of S in the interior is unique.

D. Adiabatic-isobaric case

A similar proof holds for the adiabatic-isobaric case. Here the appropriate Legendre transformation is $H=U+PV$, where

H is the enthalpy. We omit the details, which are similar to those of previous sections, and find a term which must be negative semidefinite, Y_{HP} :

$$Y_{HP} = \sum_{k=1}^{N-L} \sum_{j=1}^{N-L} \frac{\partial^2 S}{\partial \xi_k \partial \xi_j} z_k z_j \quad (83)$$

$$= -\frac{1}{nc_p T^2} \left(\sum_{i=1}^N h_i y_i \right)^2 - \frac{R}{n} \sum_{i=1}^N \sum_{j=i+1}^N \left(\sqrt{\frac{n_j}{n_i}} y_i - \sqrt{\frac{n_i}{n_j}} y_j \right)^2. \quad (84)$$

Because $c_p > 0$ [see Eq. (27)] and $n_i \geq 0$, the term involving $h_i y_i$ is a perfect square, and the term multiplying R is positive definite for the same reasons as discussed before. Hence, $Y_{HP} < 0$, and the Hessian matrix is negative definite.

IV. EXAMPLE

To illustrate the concepts that we have introduced we consider a mixture of O, O₂ and O₃ for which $N=3$ and $L=1$. We take $i=1,2,3$ to correspond to O, O₂, and O₃, respectively. We will find the equilibrium state of an isothermal ($T=4000$ K), isochoric ($V=1$ m³) mixture which has initial molar compositions of $n_1^*=0$ mole, $n_2^*=0$ mole, and $n_3^*=1$ mole with $n^*=n_1^*+n_2^*+n_3^*=1$ mole. With $R=8.314$ J/mole/K, Eqs. (12) and (22) give the initial mixture pressure as 3.326×10^4 Pa.

For such a mixture $\phi_{li}=(1,2,3)$. Equation (1) gives L linear equations, which for this $L=1$ system reduce to

$$n_1 + 2n_2 + 3n_3 = \underbrace{n_1^*}_{=0} + \underbrace{2n_2^*}_{=0} + \underbrace{3n_3^*}_{=1} = 3 \text{ mole}. \quad (85)$$

The right-hand side is the number of atoms of element O. The physical boundaries given by $n_i=0$ are formed by the surfaces

$$n_1 = 0, \quad n_2 = 0, \quad n_3 = 1 - \frac{1}{3}n_1 - \frac{2}{3}n_2 = 0. \quad (86)$$

The boundaries form a triangle in (n_1, n_2) space, whose interior represents the physically realizable region. The underconstrained Eq. (85) has three unknowns. We introduce the reduced composition space variables ξ_1 and ξ_2 and write a solution in the form of Eq. (2):

$$\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} = \underbrace{\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}}_{=n_i^*} + \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{3} & -\frac{2}{3} \end{pmatrix}}_{=D_{ik}} \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix}. \quad (87)$$

Because $n_1 = \xi_1$, $n_2 = \xi_2$, the (n_1, n_2) plane is coincident with the reduced composition space. The differentials dn_i are thus given by

$$\begin{pmatrix} dn_1 \\ dn_2 \\ dn_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{3} & -\frac{2}{3} \end{pmatrix} \begin{pmatrix} d\xi_1 \\ d\xi_2 \end{pmatrix}. \quad (88)$$

For this system the chemical potentials at the standard state pressure and $T=4000$ K are given by¹⁹ $\mu_1^o = -5.357 \times 10^5$ J/mole, $\mu_2^o = -1.045 \times 10^6$ J/mole, and $\mu_3^o = -1.155 \times 10^6$ J/mole. The mixture Helmholtz free energy can be evaluated from Eqs. (51) and (87) as

$$\begin{aligned} F = & -5.690 \times 10^5 \xi_1 - 1.078 \times 10^6 \xi_2 \\ & - 1.188 \times 10^6 \left(1 - \frac{1}{3}\xi_1 - \frac{2}{3}\xi_2 \right) \\ & + 3.326 \times 10^4 \left[\xi_1 \ln \xi_1 + \xi_2 \ln \xi_2 \right. \\ & \left. + \left(1 - \frac{1}{3}\xi_1 - \frac{2}{3}\xi_2 \right) \ln \left(1 - \frac{1}{3}\xi_1 - \frac{2}{3}\xi_2 \right) \right]. \quad (89) \end{aligned}$$

The constants are such that when ξ_1 and ξ_2 have the units of mole, F has units of J . We can find the extremum of F by setting its partial derivatives with respect to ξ_1 and ξ_2 equal to zero and solving the resulting nonlinear algebraic equations via Newton–Raphson iteration. The solution is

$$\xi_1^{\text{eq}} = n_1^{\text{eq}} = 1.351 \text{ mole}, \quad (90)$$

$$\xi_2^{\text{eq}} = n_2^{\text{eq}} = 0.8247 \text{ mole}, \quad (91)$$

$$1 - \frac{1}{3}\xi_1^{\text{eq}} - \frac{2}{3}\xi_2^{\text{eq}} = n_3^{\text{eq}} = 3.073 \times 10^{-6} \text{ mole}, \quad (92)$$

$$F^{\text{eq}} = -1.649 \times 10^6 \text{ J}. \quad (93)$$

It is no surprise that O₃ has a relatively small value at equilibrium, and that at the elevated temperature, O and O₂ have similar values. At $T=4000$ K molecular collisions are sufficiently energetic to induce breakup of di- and especially triatomic molecules; thus, O₂, which is preferred at lower temperatures, is no longer dominant. Note the number of moles increased from $n^*=1$ mole to $n^{\text{eq}}=n_1^{\text{eq}}+n_2^{\text{eq}}+n_3^{\text{eq}}=2.175$ mole. The ideal gas law gives the equilibrium pressure as $P^{\text{eq}}=7.234 \times 10^4$ Pa. For the isothermal, isochoric equilibration the pressure increase is due to the increase in number of moles.

We can study the local behavior of F in the neighborhood of equilibrium by considering its Taylor series. In matrix form we have

$$\begin{aligned} F = F^{\text{eq}} + (d\xi_1 \quad d\xi_2) & \underbrace{\begin{pmatrix} \frac{\partial F}{\partial \xi_1} \\ \frac{\partial F}{\partial \xi_2} \end{pmatrix}}_{\xi_1^{\text{eq}}, \xi_2^{\text{eq}} = 0} + \frac{1}{2} (d\xi_1 \quad d\xi_2) \\ & \times \begin{pmatrix} \frac{\partial^2 F}{\partial \xi_1^2} & \frac{\partial^2 F}{\partial \xi_1 \partial \xi_2} \\ \frac{\partial^2 F}{\partial \xi_1 \partial \xi_2} & \frac{\partial^2 F}{\partial \xi_2^2} \end{pmatrix}_{\xi_1^{\text{eq}}, \xi_2^{\text{eq}}} \begin{pmatrix} d\xi_1 \\ d\xi_2 \end{pmatrix} + \dots \quad (94) \end{aligned}$$

Here $d\xi_i \equiv \xi_i - \xi_i^{\text{eq}}$ is the deviation of ξ_i from its value at equilibrium. By the nature of the equilibrium, the gradient of F must be zero. For our example, Eq. (94) reduces to the quadratic form

$$F - F^{\text{eq}} = \frac{1}{2} \begin{pmatrix} d\xi^1 & d\xi^2 \end{pmatrix} \begin{pmatrix} 1.203 \times 10^9 & 2.405 \times 10^9 \\ 2.405 \times 10^9 & 4.810 \times 10^9 \end{pmatrix} \begin{pmatrix} d\xi^1 \\ d\xi^2 \end{pmatrix} + \dots \quad (95)$$

The units of the numbers in the matrix are J/mole². Equation (95) is of the form of Eq. (48). After implementing the transformations we have presented in the discussion preceding Eq. (50), we find

$$F - F^{\text{eq}} = \frac{1}{2} (\lambda_1 (dw_1)^2 + \lambda_2 (dw_2)^2) + \dots, \quad (96)$$

where λ_1 and λ_2 are the eigenvalues of \mathbf{H} . In our example we find $\lambda_1 = 6.012 \times 10^9$ and $\lambda_2 = 2.776 \times 10^4$, where the units are J/mole². The eigenvalues are both positive, which shows that in the neighborhood of equilibrium, F is minimized, which is consistent with our proof that F is a global minimum in the physical region. Also note that the eigenvalues are widely disparate, which indicates that contours of F in the neighborhood of equilibrium are ellipses with a large eccentricity.

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