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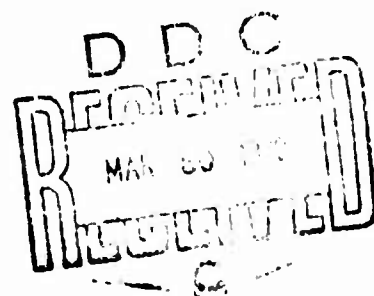
MEMORANDUM

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FEBRUARY 1970

CHEMICAL EQUILIBRIUM PROBLEMS WITH UNBOUNDED CONSTRAINT SETS

James H. Bigelow, James C. DeHaven and Norman Z. Shapiro



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10. ABSTRACT <p>An investigation of the use of mathematical models to explore the chemical aspects of physiological systems; this deals with the theoretical and computational aspects of understanding the chemistry of human physiological function. The question of existence of solutions to problems having unbounded constraint sets is investigated by relating their existence (or nonexistence) to a property of a solution to an auxiliary chemical equilibrium problem with a bounded constraint set. An example system is selected consisting of gases in contact with an aqueous buffer solution at a uniform total hydrostatic pressure and temperature. The numerical problem of determining the amount of CO₂ to be added to achieve a specified partial pressure of CO₂ in the gas phase, and its effects on the composition of the total system, is solved by using a procedure suggested by the concept of unbounded constraint sets, requiring 2.8 seconds on an IBM 7044 using a FORTRAN IV program. Findings may apply to design of artificial life-support systems needed in extraterrestrial environments related to Air Force missions.</p>		11. KEY WORDS Mathematics Biochemistry Biology Physics Physiology Mathematical programming	

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PREFACE

This study is a part of a continuing Project RAND effort exploring the use of mathematical models to investigate the chemical aspects of physiological systems. Such synthesis of the chemistry of human physiological function is expected to aid in the design of artificial life-support systems and assist in monitoring the state of man in extra-terrestrial and other stressful, antagonistic environments related to Air Force missions. Additionally, these models have been applied to the solution of associated problems of rocket propulsion systems, planetary atmospheres, re-entry body design, etc.

The present Memorandum deals with theoretical and computational questions which have arisen in connection with this RAND research. In particular, the work described here enhances the application of electronic computer techniques for the solution of complex chemical problems which, until recently, were far too complicated for any quantitative analysis--e.g. models of complex physiological systems. As the capability to use computers in such applications becomes better understood, certain hitherto unresolved questions of mathematics and chemistry become apparent. This Memorandum considers the resolution of several of these problems, and should be of interest to both mathematicians and chemists.

SUMMARY

A chemical equilibrium problem may be thought of as the problem of minimizing a certain function of composition, subject to linear constraints. When the problem is that of finding a solution to what the chemist classically denotes as a chemical equilibrium problem the constraint set (the set of compositions satisfying the linear constraints) is always bounded. In this case, of course, there is always a solution.

It has been discovered, however, that problems of exactly the same mathematical form arise in some nonchemical situations, as in geometric programming problems. Geometric programming is a recent technique whose main application seems to be in the field of engineering design. There is no reason why such problems must have bounded constraint sets. In addition, the steady-state behavior of certain "open" chemical systems--systems which mass may enter or leave--can most economically be determined by solving a chemical "equilibrium" problem whose constraint set is unbounded.

We relate the existence of solutions of a chemical equilibrium problem whose constraint set is unbounded to an auxiliary chemical equilibrium problem with a bounded constraint set. A solution to the auxiliary problem will yield a value of the objective function which is greater than, equal to, or less than, zero. Based on this trichotomy,

we show whether the solution set of the original problem is bounded and nonempty, either empty or unbounded, or certainly empty.

Finally, we demonstrate with an example that problems with unbounded constraint sets are useful in chemical applications. The example system consists of a liquid phase and a gaseous phase, in which the partial pressure of CO_2 in the gaseous phase is maintained at a constant value from an outside source. We find the steady-state composition of this system by solving a chemical equilibrium problem whose constraint set is unbounded.

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The authors are indebted to Mordecai Avriel for calling their attention to the possible importance of chemical equilibrium problems whose constraint sets are unbounded, and they also appreciate the processing of the illustrative unbounded problem by Leola Cutler.

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CHEMICAL EQUILIBRIUM PROBLEMS
WITH UNBOUNDED CONSTRAINT SETS

1. Introduction. A single- or multi-phase chemical equilibrium* problem may be thought of as the problem of minimizing a certain function (the free energy) of composition subject to the constraints that the composition vector have all its components nonnegative and satisfy a system of linear equations (the mass balance laws). The free energy is continuous. It is therefore obvious that a chemical equilibrium problem has a solution if its constraint set (the set of composition vectors whose components are nonnegative and which satisfy the mass balance laws) is bounded and nonempty. In a previous article one of us stated that chemical equilibrium problems in which the constraint set is unbounded are of no practical interest ([1], page 371). Since then we have discovered that chemical equilibrium problems with unbounded constraint sets do arise in practical situations (although not in the solution of problems which are classically denoted as chemical equilibrium problems by the chemist).

*We use the phrase "chemical equilibrium problem" to denote the kind of mathematical problem discussed in [1] and elsewhere in the mathematical literature, without intending to confine ourselves to the narrower but included class of problems subsumed under that title in the chemical literature. See [5] for a partial bibliography of work on theoretical and computational aspects of chemical equilibrium problems.

First, one technique for solving "geometric programming" problems involves the solution of derived chemical equilibrium problems in which the constraint set may be unbounded (see [2, 3, 4]). Second, we have recently observed that the steady-state behavior of certain "open" chemical systems can be determined by solving chemical equilibrium problems in which the constraint set is unbounded. An open chemical system is one which mass may enter or leave. A chemist would not say that such a system is in equilibrium even when it is in a steady (stationary) state. We give a simple example in Section 3 below of the determination of the steady state composition of an open chemical system by the solution of a chemical equilibrium problem with an unbounded constraint set.

It was noted (p. 371, [1]) that all the results of [1], except Theorem 9.9* on page 371, were applicable to chemical equilibrium problems with unbounded constraint sets. We are thus left with the question of the existence of solutions to problems having unbounded constraint sets. Such problems need not have solutions.

In Section 2 we study the existence of solutions to chemical equilibrium problems whose constraint sets are unbounded. We relate the existence (or nonexistence) of a solution to such a problem to an auxiliary chemical

*Theorem 9.9 as stated in [1] is incorrect. It should read "If $H \cap Q$ is bounded and nonempty then D is nonempty." (The word "nonempty" was inadvertently omitted in [1].) That is, chemical equilibrium problems in which the constraint set is bounded and nonempty, possess solutions.

equilibrium problem whose constraint set is bounded. We incidentally obtain some information about the boundedness of the set of solutions to a problem whose constraint set is unbounded.

Historical note. Before his death E. Eisenberg told us of his plans to publish conditions for the existence of solutions to one-phase chemical equilibrium problems whose constraint sets are unbounded. We have never seen these results and Eisenberg's work has not affected ours. However we posthumously acknowledge his priority for the one-phase case.

2. Existence of solutions to a chemical equilibrium problem whose constraint set is unbounded. Let Q be the nonnegative orthant of E^n , Euclidean n -space. Let F be a continuous, convex, real valued function on Q . We will assume that F is homogeneous of degree 1 (that is, $F(tx) = tF(x)$ for all $x \in Q$ and $t \geq 0$). F will be the free energy.

Remark. For the class of functions considered in [1], namely, the free energy of "ideal systems," the continuity of F is Theorem 8.3, page 365 [1]; the convexity of F is Theorem 8.13, page 368, [1]; the homogeneity of F is contained in Lemma 8.14, page 368, [1]. For more general (non-ideal) free energies, the homogeneity of F is closely related to the First Law of thermodynamics and the convexity of F is closely related to the Second Law. We intend to explore

the relationship of various properties of F to the thermodynamic laws in a subsequent publication.

Let A be a real m by n matrix and $b \in E^m$. Define H , the constraint space by

$$H = \{x \in Q \mid Ax = b\}.$$

The system $Ax = b$ thus represents the mass balance laws.

Let D be the set of points in H at which F achieves its minimum on F . More precisely, let

$$D = \{x \in H \mid F(x) \leq F(y) \text{ for all } y \in H\};$$

that is, D is the set of solutions to the problem. We are primarily interested in obtaining conditions for D to be nonempty; and secondarily in conditions for D to be bounded.

For the sake of completeness we repeat Theorem 9.9 of [1].

PROPOSITION I. If H is bounded and nonempty then so is D .

Proof. H , as the intersection of a linear manifold and Q , is closed and F is continuous. Hence D is nonempty. Since $D \subseteq H$, D is bounded. Q.E.D.

We will hereafter assume that H is unbounded. It is then well known that there are $x \in Q - \{0\}$ such that $Ax = 0$. (See, for example, Lemma 3 below.) Thus if we define H_0 by

$$H_0 = \{x \in \Delta \mid Ax = 0\},$$

where Δ is the set of elements of Q the sum of whose coordinates is one, H_0 will be a bounded nonempty subset of E^n . The problem of minimizing $F(x)$ relative to the constraint that $x \in H_0$ is itself a chemical equilibrium problem, but one with a bounded constraint set H_0 . By Proposition 1 this problem has a solution. That is, F takes on a minimum value, F_0 , on D .

Our results (Theorems 2, 4 and 5) are based on the trichotomy $F_0 > 0$, $F_0 = 0$, $F_0 < 0$. Note that (using the homogeneity of F):

- (1) $F_0 > 0$ means $F(x) > 0$ for all $x \in Q - \{0\}$ with $Ax = 0$.
- (2) $F_0 = 0$ means $F(x) \geq 0$ for all $x \in Q$ with $Ax = 0$ but $F(x) = 0$ for some $x \in Q - \{0\}$ with $Ax = 0$.
- (3) $F_0 < 0$ means $F(x) < 0$ for some $x \in Q$ with $Ax = 0$.

THEOREM 2. If H is unbounded and $F_0 > 0$, then D is non-empty and bounded.

To prove Theorem 2 we will need the following well-known lemma.

LEMMA 3. Let C be a closed, unbounded, convex subset of E^n . There is a $y \in E^n - \{0\}$ such that $x + ty \in C$ for all $x \in C$, $t \geq 0$.

Proof. Since C is unbounded, there are $a \in C$ and an unbounded sequence $\{z_i\}$ of elements of $C - \{a\}$. The set of $\frac{z_i - a}{|z_i - a|}$ is an infinite, bounded subset of E^n which possesses

a limit point, y . By forming a subsequence of $\{z_i\}$ we may, without loss of generality, assume that

$$(4) \quad y = \lim_{i \rightarrow \infty} \frac{z_i - a}{|z_i - a|}$$

and

$$(5) \quad \lim_{i \rightarrow \infty} |z_i - a| = \infty.$$

Let $x \in C$ and $t \geq 0$. For all $\epsilon > 0$ and all positive integers i , define

$$w(\epsilon, i) = (1 - \epsilon)x + \frac{tz_i}{|z_i - a|} + \left(\epsilon - \frac{t}{|z_i - a|}\right)a.$$

It follows from the convexity of C that $w(\epsilon, i) \in C$ for all ϵ with $0 < \epsilon \leq 1$ and for all i so large that (using (5)) $|z_i - a| > \frac{t}{\epsilon}$. Hence, since C is closed, and using (4):

$$\begin{aligned} x + ty &= \lim_{\epsilon \rightarrow 0^+} \left((1 - \epsilon)x + \epsilon a + ty \right) \\ &= \lim_{\epsilon \rightarrow 0^+} \lim_{i \rightarrow \infty} \left((1 - \epsilon)x + \epsilon a + \frac{t(z_i - a)}{|z_i - a|} \right) \\ &= \lim_{\epsilon \rightarrow 0^+} \lim_{i \rightarrow \infty} w(\epsilon, i) \in C. \end{aligned}$$

By (4), $|y| = 1$; hence $y \neq 0$. Q.E.D.

Proof of Theorem 2. Since H is unbounded it is certainly nonempty. Let $z \in H$. Define

$$W = \{x \in H \mid F(x) \leq F(z)\}.$$

Since F is continuous and convex, W is closed and convex.

Suppose that W is unbounded. By the Lemma there is a $y \in E^n - \{0\}$ such that $z + ty \in W$ for all $t \geq 0$. But $W \subseteq H$. Hence $A(z + ty) = b$ for all $t \geq 0$. Hence $Ay = 0$. If $y \notin Q$, then we would have $z + ty \notin Q$ for some $t \geq 0$. Hence $y \in Q$. By the definition of W we have $F(z + ty) \leq F(z)$ for all $t > 0$. Hence, by the homogeneity of F , $F\left(\frac{z}{t} + y\right) \leq \frac{1}{t} F(z)$ for all $t > 0$. Hence, by the continuity of F , $F(y) \leq 0$, but $Ay = 0$ and $y \in Q - \{0\}$, contradicting (1). We have shown that W is bounded.

Since $z \in W$, W is nonempty. Hence, since F is continuous, it achieves its minimum on W at some $x \in W$.

Clearly, for any $u \in H - W$, we have $F(x) \leq F(z) < F(u)$. Thus x minimizes F on H , and u does not. That is, $x \in D$ (which is therefore nonempty), and $D \subseteq W$ so that (since W is bounded) D is bounded. Q.E.D.

THEOREM 4. If $F_0 = 0$, then D is either empty or unbounded.

Proof. Suppose D is nonempty. Let $x \in D$. By (2) there is a $y \in Q - \{0\}$ with $F(y) = 0$ and $Ay = 0$. Since $x \in D \subseteq H$, $Ax = b$. Hence $A(x + ty) = b$ for all $t \geq 0$. But $x, y \in Q$; hence $x + ty \in H$ for all $t \geq 0$. Using the convexity and homogeneity of F , we have for all $t \geq 0$

$$\begin{aligned}
 F(x + ty) &= (t + 1)F\left(\frac{x}{t + 1} + \frac{ty}{t + 1}\right) \\
 &\leq (t + 1)F\left(\frac{x}{t + 1}\right) + (t + 1)F\left(\frac{ty}{t + 1}\right) \\
 &= F(x) + tF(y) \\
 &= F(x) + t \cdot 0 \\
 &= F(x).
 \end{aligned}$$

Since $x \in D$, $x + ty \in D$ for all $t \geq 0$. Thus D is unbounded.
Q.E.D.

Remark. We are unable to obtain any chemically relevant results which distinguish between the two cases of Theorem 4. If F is linear, then D is unbounded when $F_0 = 0$. Chemically, F is linear if each phase contains only one species. In the more general nonlinear case, D may be empty.

THEOREM 5. If $F_0 < 0$, then D is empty.

Proof. The argument is close to that of the proof of Theorem 4. Suppose D is nonempty. Let $x \in D$. By (3) there is a $y \in Q$ with $F(y) < 0$ and $Ay = 0$. As before we have that for all $t \geq 0$, $x + ty \in H$ and $F(x + ty) \leq F(x) + tF(y)$. But now $F(y) < 0$. Hence $F(x + y) \leq F(x) + t \cdot F(y) < F(x)$ for $t > 0$. So $x \notin D$, a contradiction. Q.E.D.

3. Use of an unbounded constraint set to solve a steady state problem. We select a relatively simple chemical system to illustrate the practical utility of the concept of unbounded constraint sets. The system consists of gases in

contact with an aqueous buffer solution at a uniform total hydrostatic pressure of one atmosphere and a uniform temperature of 37°C . Energy may exchange with the environment to maintain this constant temperature, the volume of the gas phase may vary to maintain one atmosphere pressure, and chemical substance may exchange with the environment in a manner to be described.

More specifically, the aqueous phase consists of one kilogram of water containing a buffer system made up of 0.04 mole of sodium hydroxide, NaOH , and 0.06 mole of an acid, HA , and its conjugate base, A^- . The pK (negative \log_{10} of the dissociation constant) of the weak acid is approximately 8. The gas phase consists of .647 mole of O_2 , 3.614 moles of N_2 , .304 mole of H_2O , and an unknown amount of CO_2 . When this gas phase is placed in contact with the buffered aqueous phase, the gaseous substances dissolve, and the aqueous phase contains these species in solution, plus the reaction products of CO_2 and water, and the buffer-system species. A tableau representing this system is shown in Fig. 1. Note that the column sum CO_2 and the row $^*\text{CO}_2$ are an accounting device for keeping track of the total CO_2 in the system. (See [5] for a fuller explanation of this device, as well as other background information.) The reactions which occur in this system between the gas and aqueous phases and within the aqueous phase are shown in more conventional chemical notation in Table 1. The associated free energy parameters, c_j , are also listed in this

COMPONENTS		GAS PHASE				AQUEOUS PHASE										SUM	b(moles)			
Designation		O ₂	CO ₂	N ₂	H ₂ O	O ₂	CO ₂	N ₂	H ⁺	OH ⁻	H ₂ O	Na ⁺	A ⁻	HA	HCO ₃ ⁻	H ₂ CO ₃ [*]		CO ₃ ⁼	SUM CO ₂	
O ₂		1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	b ₁
N ₂		0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	b ₂
H ⁺		0	0	0	1	0	0	0	1	0	1	0	0	1	0	1	-1	0	0	b ₃
OH ⁻		0	0	0	1	0	0	0	0	1	1	0	0	0	1	1	1	0	0	b ₄
A ⁻		0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0	b ₅
NA ⁺		0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	b ₆
*CO ₂		0	-1	0	0	0	-1	0	0	0	0	0	0	0	-1	-1	-1	1	1	b ₇ = 0
CO ₂		0	1	0	0	0	1	0	0	0	0	0	0	0	1	1	1	0	0	b ₈ = ?
Free Energy Parameters c _j		c ₁	c ₂	c ₃	c ₄	c ₅ =0	c ₆ =0	c ₇ =0	c ₈ =0	c ₉ =0	c ₁₀	c ₁₁ =0	c ₁₂ =0	c ₁₃	c ₁₄	c ₁₅	c ₁₆	c ₁₇ =0		

Fig. 1 -- Tableau for Illustrative Buffered Soda-Water System

Table 1

CHEMICAL REACTIONS IN BUFFERED SODA WATER SYSTEM AND
ASSOCIATED FREE ENERGY PARAMETERS

Reactions	Free Energy Parameter ^a $\ln K_j = c_j$
$O_2(\text{gas}) \rightleftharpoons O_2(\text{aq})$	$c_1 = -10.85$
$CO_2(\text{gas}) \rightleftharpoons CO_2(\text{aq})$	$c_2 = -7.69$
$N_2(\text{gas}) \rightleftharpoons N_2(\text{aq})$	$c_3 = -11.52$
$H_2O(\text{gas}) \rightleftharpoons H^+(\text{aq}) + OH^-(\text{aq})$	$c_4 = -36.61$
$H_2O(\text{aq}) \rightleftharpoons H^+(\text{aq}) + OH^-(\text{aq})$	$c_{10} = -39.39$
$HA(\text{aq}) \rightleftharpoons H^+(\text{aq}) + A^-(\text{aq})$	$c_{13} = -22.44519$
$HCO_3^-(\text{aq}) \rightleftharpoons CO_2(\text{aq}) + OH^-(\text{aq})$	$c_{14} = -20.86$
$H_2CO_3(\text{aq}) \rightleftharpoons CO_2(\text{aq}) + OH^-(\text{aq}) + H^+(\text{aq})$	$c_{15} = -33.61$
$CO_3^{2-}(\text{aq}) + H^+(\text{aq}) \rightleftharpoons CO_2(\text{aq}) + OH^-(\text{aq})$	$c_{16} = 6.73$

^aThese free energy parameters are on the mole-fraction scale and are dimensionless. Methods for deriving these constants from the equilibrium constants contained in the literature, which are often on other scales, are given in [5].

table. The values of the b_i for the system are given in Table 2.

As an example of the practical use of the unboundedness concept, we choose to simulate the operation of a CO_2 -stat operating with the buffered soda-water system described above. That is, a chemical goal is set for the system in terms of, say, a specific partial pressure of CO_2 in the gas phase that is to be established and maintained in the system by adding an appropriate amount of CO_2 to be obtained from the environment; the amount of CO_2 to be added depends in a complex way on the values of the parameters.

The numerical problem of determining the amount of CO_2 to be added, and the composition of the system after it has been added, could be solved in a variety of ways. For example, the linear and nonlinear equations describing the problem could be written down and numerically solved by some special purpose method peculiar to this particular problem. Alternatively, one could guess at the amount of CO_2 to be added, solve the resulting chemical equilibrium problem with a standard chemical equilibrium program, systematically varying the amount of CO_2 to be added to obtain the desired partial pressure of CO_2 in the gas phase, and hopefully converge to the correct answer.

However, by using a procedure suggested by the concept of unbounded constraint sets, this problem can be solved by

Table 2

VALUES OF CONSTRAINTS FOR BUFFERED SODA-WATER SYSTEM

Component	From Gas Moles	From Water Moles	Total, b_i , Moles
O ₂	0.647104	0.0	$b_1 = 0.647104$
N ₂	3.613650	0.0	$b_2 = 3.613650$
H ⁺	.304375	55.5660	$b_3 = 55.870375$
OH ⁻	.304375	55.5460	$b_4 = 55.850375$
A ⁻	0.0	0.060	$b_5 = 0.060$
Na ⁺	0.0	0.040	$b_6 = 0.040$
*CO ₂	0.0	0.0	$b_7 = 0.0$
CO ₂	?	0.0	$b_8 = ?$

solving a single "chemical equilibrium problem." Using the device described below and a general-purpose chemical equilibrium program (written entirely in Fortran IV), we solved the problem in 2.8 seconds of execution time on the IBM 7044.

To accomplish the partial pressure goal set for CO_2 , we subtracted $c_2 + \ln g$ (where g is the goal mole fraction, .9, of CO_2 in the gas phase) from c_2 , c_6 , c_{14} , c_{15} , and c_{16} , removed the last constraint (the CO_2 constraint), and solved the resulting "chemical equilibrium" problem. Note the peculiarity of the resulting problem: For example, the number of moles of CO_2 in the gas phase is effectively unconstrained; thus the mass balance space is unbounded. The computed composition of the buffered soda-water system is shown in Table 3.

In accomplishing the partial pressure goal set for CO_2 , the volume of the gas phase became 2823 liters as about 100 moles (approximately 2540 liters) of CO_2 were added to the system from the environment. The size of the gas phase was also influenced by evaporation (approximately .119 kg) of liquid H_2O from the aqueous phase, and its movement into the gas phase to maintain water saturation as dry CO_2 was added to the system. The pH of the aqueous phase became about 6.58 as a result of the acidifying influence of the added CO_2 .

The interested reader may verify the validity of this procedure.*

*We do not claim that the device illustrated will solve any chemical steady state problem, although it is applicable to a wide variety of such problems.

Table 3
COMPUTED COMPOSITION OF A BUFFERED SODA-WATER SYSTEM

Species	Composition (Moles)	Concentration
Gas Phase		
Total	111.650 (2823.182 l)
O ₂	0.647	4.405 mm Hg.
CO ₂	100.485	684.000 "
N ₂	3.614	24.598 "
H ₂ O	6.904 (0.12438 kg)	46.997 "
Aqueous Phase		
Total	49.066	
pH	6.577
O ₂	5.518×10^{-6}	6.268×10^{-6} Moles/kg H ₂ O
CO ₂	2.020×10^{-2}	2.292×10^{-2} "
N ₂	1.580×10^{-5}	1.790×10^{-5} "
H ₂ O	48.908 (0.88113 kg)
H ⁺	2.342×10^{-7}	2.658×10^{-7} "
OH ⁻	8.013×10^{-8}	9.094×10^{-8} "
Na ⁺	4.000×10^{-2}	4.540×10^{-2} "
A	2.166×10^{-3}	2.458×10^{-3} "
HA	5.783×10^{-2}	6.564×10^{-2} "
HCO ₃ ⁻	3.782×10^{-2}	4.292×10^{-2} "
H ₂ CO ₃	6.218×10^{-5}	7.057×10^{-5} "
CO ₃ ⁼	8.256×10^{-6}	9.370×10^{-6} "
Sum CO ₂	100.543

Note: The actual calculations from which these values were derived were made using mole fractions throughout. In converting to the more familiar concentration scales shown here, the following conversion factors were used; 55.506 moles H₂O equals 1 kg H₂O, 1 atm pressure equals 760 mm Hg. At 37°C and 1 atm pressure the volume of a mole of O₂, N₂ or H₂O is assumed to be that of a perfect gas, 25.43l; and the volume of a mole of CO₂ is assumed to be 25.27l.

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