Computation of Physicochemical Parameters, Namely pH, in Complex (Bio)chemical Systems: Extension to Gas–Liquid Systems[1]

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The first model has been proposed to compute, in complex liquid (bio)chemical systems, a number of physicochemical parameters, namely pH, concentration of one of any chemical species, partition between acid–base forms, global charge, or ionic strength, assuming the physicochemical equilibrium state. The extension of the present model, described here, permits moreover the computation of gas–liquid distributions, specific gas volumes, or total pressures. The model solely requires the knowledge of existing thermodynamic constants and of the concentration of every chemical species other than the species under examination. The model elicites a unique equilibrium state. Computed values agreed with experimental measurements, thereby validating the model. Digital computer programs were prepared to use the proposed algorithms. © 1989 Academic Press, Inc.

Physical chemistry plays an essential part in the control of complex (bio)chemical and biological processes. The prediction of physicochemical state parameters, such as pH, generally requires a complex mathematical tool (1) and often yields only approximate solutions (2). Assessing the physicochemical state by existing mathematical systems does not permit an easy understanding of the related process.

In a previous paper (3), rational algorithms were developed to compute, for any aqueous (bio)chemical system at equilibrium, state parameters, such as pH or the partition of a chemical species among its different acid–base forms. However, the former model only considers a single aqueous phase. This assumption limits its range of application. The present paper proposes the extension of the former model to gas–liquid systems.

Figure 1 is the computation algorithm for the determination of the concentration of any given species, $C(m)$, as established in the previous paper (3). Computation of the global charge, Z, requires the knowledge of the value of the concentrations, $C(s)$, of the chemical species in the aqueous phase. In a gas–liquid system, the latter concentrations depend furthermore upon the distribution of the species between the gas and the liquid phase. Hence, the extension of the algorithm to gas–liquid systems involves defining the distribution of the chemical species between the aqueous and the gaseous phase, before computing the concentrations of the chemical species in the aqueous phase.

SYSTEM DEFINITION

The systems considered in this paper are limited to aqueous solutions in equilibrium with a gas phase. Only proton exchange and gas–liquid transfer are taken into consideration. The systems are reduced to 1 liter of aqueous phase, and all extensive parameters are defined per unit aqueous phase volume.

One chemical species is defined as the sum of its dissolved acid–base forms and a single gaseous form, if any. For example, inorganic carbon is one chemical species composed of three dissolved forms (CO_2 or H_2CO_3, HCO_3^- and CO_3^{2-}) and a single gaseous form (CO_2). On the other hand, $NaNO_3$ is composed of two chemical species (Na^+ and NO_3^-). s and m are indexes to define species.

The different forms, H_iA (or H_jA) of one acid–base species, s, are defined by the number of protons (i or j),

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        │ C(m) = 0│
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   │ For every species s, compute the │
   │   partition between different    │
   │   acid-base forms, φ(i), and     │
   │ the molar mean charge, ζ(s)      │
   └───────────────────────────────┘
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      │ Z = Σs ζ(s) C(s) │
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    │ Adjust C(m) until Z = 0 │
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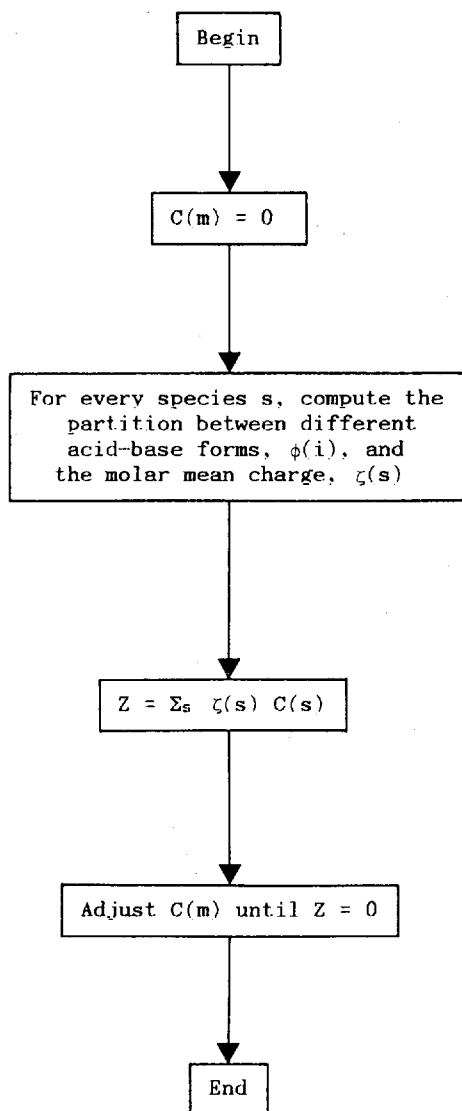
FIG. 1. Computation of the concentration, $C(m)$, of any given chemical species, without taking ionic strength effects into consideration, according to [3].

carried by these forms and released when passing to the most alkaline form. Index g is reserved to define the number of protons carried by the gaseous form or carried by the aqueous form in equilibrium with the gaseous form. In the case of inorganic carbon, detailed above, g equals 2.

EXPRESSIONS OF THE CONCENTRATION IN GAS–LIQUID SYSTEMS

A quantity of a given chemical species in a gas–liquid system can be expressed by:

—the total quantity of that species, $Q(s)$, in the system, generally obtained by a mass balance;

—the concentration of that species in solution, $C(s)$, often obtained by analysis of a sample, as for example, by liquid chromatography for volatile fatty acids;

—the concentration of an aqueous form, $[H_iA]$, of that species, also obtained by analysis of a sample, as for example, alkalinity for bicarbonate concentrations;

—the partial pressure, $p(s)$, of the gaseous form of that species;

—the molar gas fraction of the gaseous form of that species, $X(s)$, as obtained by gas chromatography for example;

—or by the quantity of the gaseous forms of that species, $N(s)$.

Each of these different expressions for a quantity, $q(s)$, can be converted into the total species quantity, $Q(s)$, as follows. The distribution coefficient, $d(s)$, is defined as the fraction of the chemical species, s, in the aqueous phase, and, hence, as the concentration of that species in solution, $C(s)$, divided by the total quantity of that species in the system, $Q(s)$:

$$C(s) = d(s)Q(s). \qquad [1]$$

The concentrations of an aqueous species in solution, $C(s)$, and of one of its acid–base forms, $[H_iA]$, are related by

$$[H_iA] = \phi(i)C(s), \qquad [2]$$

where $\phi(i)$ is the partition of the form, H_iA, of the species, s, which can be computed from the pH value and from thermodynamic constants (1). Combining Eqs. [1] and [2] yields

$$[H_iA] = \phi(i)d(s)Q(s). \qquad [3]$$

By definition, in 1 liter of the aqueous phase of a system, the total quantity, $Q(s)$, of one chemical species, s, equals the sum of the aqueous concentration, $C(s)$, and the gaseous quantity, $N(s)$:

$$Q(s) = C(s) + N(s). \qquad [4]$$

Combining Eqs. [1] and [4] leads to

$$N(s) = [1 - d(s)]Q(s). \qquad [5]$$

Assuming that the gas phase behaves as an ideal gas, one can write

$$p(s)V = N(s)RT, \qquad [6]$$

where V is the specific gas volume, namely the gas volume per unit liquid phase volume, T is the temperature,
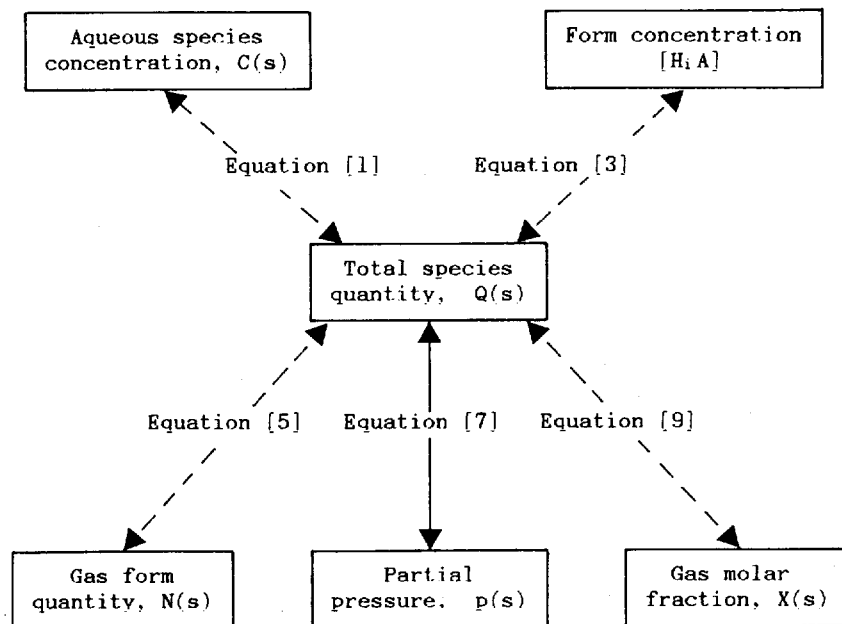
FIG. 2. Conversion flow sheet for the expressions of the quantity of any given species or form.

and R is the ideal gas constant. Combining Eqs. [5] and [6] yields

$$p(s) = [(1 - d(s))RT/V]Q(s). \qquad [7]$$

Finally, Dalton's law links the molar fraction, $X(s)$, to the partial pressure, $p(s)$,

$$X(s) = p(s)/P, \qquad [8]$$

where P is the total pressure. Combining Eqs. [7] and [8] leads to

$$X(s) = [(1 - d(s))RT/PV]Q(s). \qquad [9]$$

Equations [1], [3], [5], [7], and [9] compose a set of equations which permits the conversion of any expression for the quantity of a chemical species or form into the total quantity of that species. These conversion processes are summarized in Fig. 2.

The former set of equations can be written in a generic form

$$q(s) = \psi(s, q)Q(s), \qquad [10]$$

where $q(s)$ is the generic expression for a quantity, and $\psi(s)$ is the family of the first term of the right-hand side portion of the set of equations. Equation [10] states that the expression of the quantity of a chemical species or form, $q(s)$, is proportional to its corresponding $\psi(s, q)$. Hence, the conversion between one of the expressions

for a quantity, q_1, and another expression for a quantity, q_2, is given by

$$q_2(s) = q_1(s)\psi(s, q_2)/\psi(s, q_1). \qquad [11]$$

GAS–LIQUID DISTRIBUTION COEFFICIENT

Henry's law links the concentration of the form, $[H_gA]$, of a chemical species, s, in equilibrium with this gaseous form to the partial pressure, $p(s)$, of that gaseous form

$$[H_gA] = K_H(s)p(s), \qquad [12]$$

where $K_H(s)$ is Henry's constant for the species s. Combining Eq. [3] with i equal to g with Eqs. [1] and [12] yields

$$C(s) = K_H(s)p(s)/\phi(g). \qquad [13]$$

Introducing Eqs. [6] and [13] into Eq. [4] yields

$$Q(s) = (K_H(s)/\phi(g) + V/Rt)p(s). \qquad [14]$$

According to Eq. [1], the gas–liquid distribution coefficient, $d(s)$, is obtained by dividing the aqueous species quantity, $C(s)$, given by Eq. [13] by the total species quantity, $Q(s)$, given by Eq. [14]. Thus

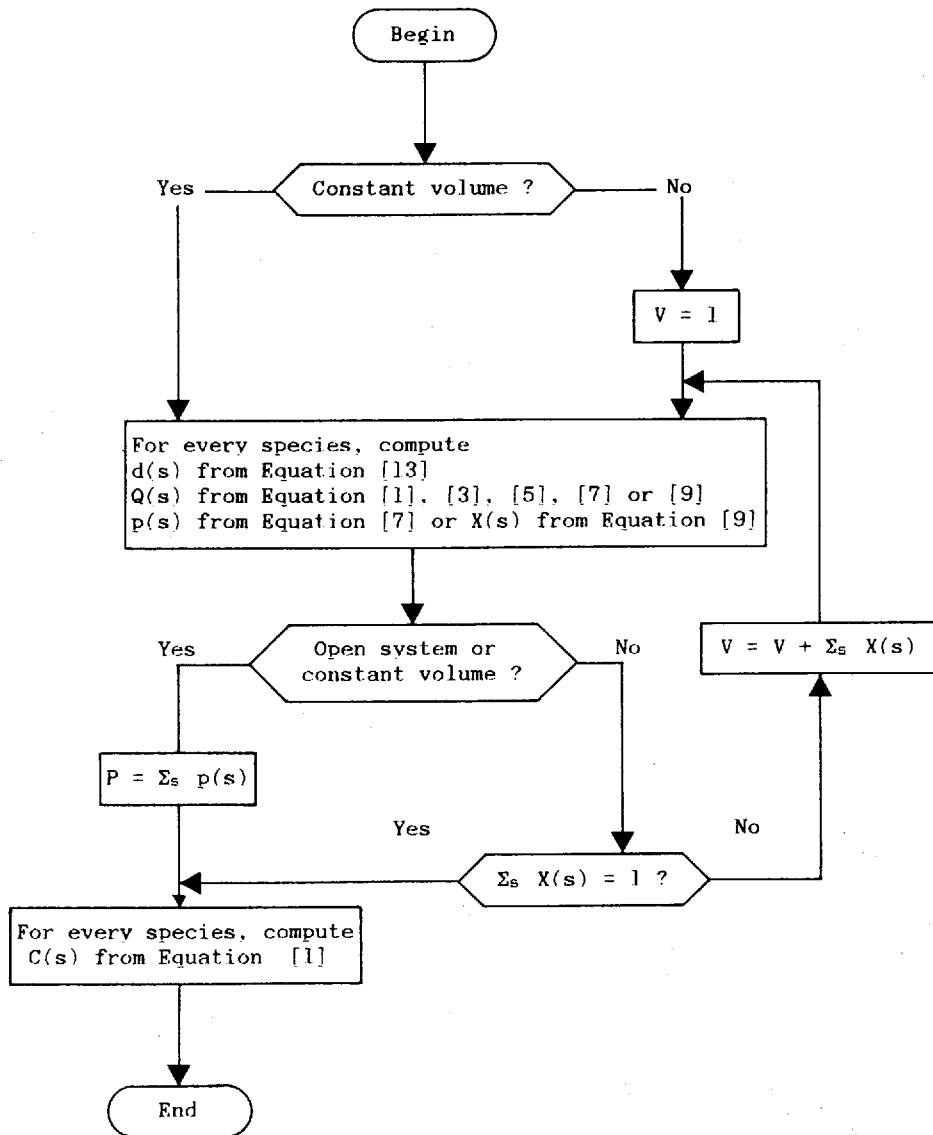$$d(s) = K_H(s)RT/(K_H(s)RT + \phi(g)V). \qquad [15]$$

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         Yes ──────⟨ Constant volume ? ⟩────── No
          │                                      │
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          │                                  ┌───────┐
          │                                  │ V = 1 │
          │                                  └───────┘
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          ▼                                      ▼
┌──────────────────────────────────────────────────────┐
│ For every species, compute                            │
│ d(s) from Equation [13]                               │
│ Q(s) from Equation [1], [3], [5], [7] or [9]          │
│ p(s) from Equation [7] or X(s) from Equation [9]      │
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   Yes ──⟨ Open system or        ⟩── No      ┌──────────────────┐
    │     ⟨ constant volume ?    ⟩    │       │ V = V + Σs X(s)  │
    │                                 │       └──────────────────┘
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│ P = Σs p(s)  │                      │              │
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│ For every species, compute │
│ C(s) from Equation  [1]    │
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│   End   │
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FIG. 3. Computation of gas–liquid distribution and gas parameters (general case).

INTEGRATION OF THE GAS–LIQUID EXTENSION IN THE GLOBAL ALGORITHM

Equation [15] permits the extension of the algorithm to gas–liquid systems. Gas–liquid systems can be divided in three classes. In the first two classes, all products are introduced in a closed vessel. The evolution of the system to the physicochemical equilibrium state can then occur either at constant volume or at constant pressure. The third class can be described as an aqueous solution open to an atmosphere considered with an infinitely large gas volume.

In a system with a fixed gas volume, V, the distribution coefficients, $d(s)$, can be directly calculated with the help of Eq. [15]. The total pressure, P, is given by

$$P = \Sigma_s p(s). \tag{16}$$

In a system with a limited, but unknown gas volume and a fixed total pressure, P, the distribution coefficients, $d(s)$, cannot be directly computed because the specific gas volume, V, used in Eq. [15], is unknown. However, the volume, V, used in Eq. [15] can be calculated by iterative approximations. Indeed, the sum of the gas molar fractions, $X(s)$, must be equal to one:

$$\Sigma_s X(s) = 1. \tag{17}$$

Equations [9] and [15] are solved for an arbitrary value of the specific gas volume, V. If one chooses too large a specific gas volume, V, the computed distribution co-

TABLE 1

Composition of the Mixture Used for the Experimental Validation of the Model

Species	Concentration (mM)
Acetate	13.88
Propionate	17.64
Phosphate	14.95
Carbonate	30.93
Methane	25.02
Sodium cation	54.55

efficients, $d(s)$, and the gas molar fractions, $X(s)$, are lower than the real values. Hence, the sum of the gas molar fractions will be less than 1. On the contrary, an estimate of too low a specific gas volume, V, results in a sum of the gas molar fractions greater than 1. This observation leads to an iterative equation to find the correct specific gas volume, V,

$$V_2 = V_1 \Sigma_s X(s), \qquad [18]$$

where V_2 is the new arbitrary value of the specific gas volume, V, and V_1 is the previous value, for example initially made equal to 1. The iteration is pursued until a prerequisite accuracy on the specific gas volume, V, is reached.

In the case of a system open to an atmosphere, and assuming homogeneity of the gas phase, the gas volume is to be considered as infinite. The total quantity, $Q(s)$, the gas quantity, $N(s)$, and the distribution coefficients, $d(s)$, have no meaning. Moreover, the equilibration of the liquid with the gas phase should not change the gas composition.

The equilibrium state of an open system can be defined by the former mathematical treatment. The gas volume may be considered limited to 1 liter and the concentration of the gas–liquid species is (and must be) introduced as partial pressure, $p(s)$, or gas molar fraction, $X(s)$. The treatment becomes then identical to the case with a constant specific gas volume, V.

Figure 3 gives the general procedure to extend the physicochemical model to a gas–liquid system. The extension task must be introduced in the algorithm 1 (Fig. 1) before the global parameter computation, needed to define the concentration of the aqueous species, but after the molar parameter computation, used to compute the gas–liquid distribution coefficients. The extension task can be introduced in the same way in the other algorithms proposed in the first paper [3].

The Pascal version of the global algorithm is available from the authors or from the European Bank of Computer Programs in Biotechnology (EBCD), Laboratoire

EXPERIMENTAL VALIDATION OF THE MODEL

A mixture of five chemical species, the composition of which is given in Table 1, was introduced into an experimental vessel with a fixed specific gas volume, V. pH, total pressure, gas composition, and bicarbonate concentration were measured after the system had reached equilibrium, respectively, with a pH electrode, by barometry, by gas chromatography, and by titrimetry. The physicochemical parameters of this system were computed with the presented model. The prerequisite accuracy for ionic strength, I, and pH were, respectively, fixed to 0.01 I and 0.01. The results are given in Table 2. There is good agreement between the experimental and the computed data, thereby validating the effectiveness of the computation of these physicochemical parameters.

With the proposed model, each chemical system so far examined, exhibited a unique equilibrium state, namely regarding pH. This uniqueness is predicted by Gibbs' phase rule.

DISCUSSION

The mathematical prediction of physicochemical state parameters of a complex (bio)chemical system is a tedious problem. This paper presents algorithms which ease computation. The global model has a modular structure. It is simple to integrate in more complex tasks. It only consists of simple and iterative equations easily solved by computer.

The model is basically exact as no approximations are made. It yields a unique and correct solution. The model is general as it is extendible to any number of chemical species with any number of acid–base forms.

The present model must be considered more as a laboratory tool than as a universal physicochemical state description of complex gas–liquid systems. It yields easily a good representation of a chemical system, and it allows quick testing of different assumptions, such as quantita-

TABLE 2

Experimental Validation of the Model

Parameters	Measured value	Experimental error (%)	Computed value
T(°K)	295		—
P(atm)	0.898	±0.002	—
V(−)	1.000	±2	0.945
pH(−)	6.09	±0.05	6.14
%CO$_2$	34.8	±3	33.4
%CH$_4$	62.6	±3	63.9

tive influence of activity coefficients and impact of the omission of the concentration of one chemical species or one chemical process before performing real experiments.

Note that the model is based on the hypothesis of equilibrium in the aqueous phase and between the liquid and the gas phase. No complexation or precipitation is, as yet, taken into consideration. The equation to estimate the activity coefficient can be adapted to any particular case.

Finally, the more complex the model, namely the number of integrated loops, the larger the incertitude on the final value will be and the greater the test number to ensure a correct computation will be. For this reason, a commented version of the proposed software is in preparation, with emphasis on its possible uses and with a strategy to build specific applications.

As the model is simple to use and gives direct informations on the physicochemical state, it can be used for tasks generally performed only for simple systems on an intuitive basis. It helps to select suitable acid or base forms in complex media. Analysis of the inhibition by one specific form is simplified (5). The model proved useful to explain the pH impact on diffusion through a membrane (6) or on partition of acid–base species between an aqueous and an organic phase (7).

Poncelet *et al.* (7) integrated their model in a model of microcapsule membrane formation by nylon interfacial polymerization. Analysis of pH effects on the membrane formation and its feedback on pH value was then possible. Swardal and Kroiss (8) extended the previous model to simulate neutralization in anaerobic wastewater treatment. In their work, they have estimated concentrations of organic compounds from chemical oxygen demand, total organic carbon, and total Kjeldahl nitrogen. The model remains a useful tool even when the system is not exactly defined. However, conclusions must then be drawn more carefully.

APPENDIX: SYMBOLS AND UNITS

Symbol	Definition	Unit
$C(s)$	Global concentration of the aqueous form of the chemical species, s, referred to in the text as concentration of the aqueous species	mol liter^{-1}
$d(s)$	Gas–liquid distribution coefficient for the chemical species, s	—
I	Ionic strength	mol liter^{-1}
$K_H(s)$	Henry's constant of the chemical species, s	mol liter^{-1} atm^{-1}
$N(s)$	Gaseous quantity of the chemical species, s, in equilibrium with one unit of aqueous phase volume	mol
P	Total pressure	atm
$p(s)$	Partial pressure of the gaseous form of the chemical species, s	atm
$q(s)$	Any expression for the concentration of the chemical species, s, or one of its forms, i	
$Q(s)$	Total quantity of the chemical species, s, in a unit volume of aqueous phase	mol
R	Ideal gas constant	atm liter mol^{-1} °K^{-1}
T	Temperature	°K
V	Specific gas volume, in equilibrium with one unit volume of aqueous phase	liter
X	Gas molar fraction	—
$[H_iA]$	Concentration of the acid–base form, i, of the chemical species, s, in aqueous solution	mol liter^{-1}
$\phi(i)$	Partition of the chemical species, s, in the acid–base form, i	—
$\psi(s,q)$	Relation between any expression for the concentration of the chemical species, s, or one of its forms, i, $q(s)$ and the concentration of the chemical species, s, in solution $C(s)$	Variable
$\zeta(s)$	Molar mean charge of the chemical species, s	—
Indexes		
g	Refers to the gaseous form	
i or j	Refers to the form containing i or j protons	
s or m	Refers to a given chemical species	

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