

Theoretical description of the interactions between a mixture of vapors and a set of chemical sensors by variable temperature

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A sensor system is expected to detect gas concentrations of interest within low-ranges. The interactions between a sensor array and mixture of vapors hang not only on mixture composition and temperature but also on the partial sensitivities of the array elements. The aim of this paper is to find a useful equation in differential form that relates the change of sensors partial sensitivities to mixture component concentrations and temperature. This kind of equations is known in the thermodynamic of miscellaneous as equations of Gibbs–Duhéme.

KEY WORDS: Adsorption, chemical sensors, sensor array, mixture of vapors, functions of state, equations of Gibbs-duhéme

1. Introduction

The use of chemical sensor arrays for the detection and quantification of volatile compounds is becoming increasingly common due to their small size and cost. These devices operate by arranging multiple partially selective sensors into an integrated sensor system. The data obtained from the array is then used by multivariate statistical methods to calculate analyte concentration or estimate the presence or absence of a particular analyte.

The purpose of this paper is to develop a relationships in differential form that describe the interactions between the vapors mixture and the elements of the sensor array by variable temperature. The effects on the sensor array total

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sensibility of mixture composition and sensors partial sensibilities can be separated, by introducing of two variables a and b which are specific to each system sensor/gas.

2. Chemical gas sensors

Chemical sensors are measurement devices that convert a chemico-physical property of a specific analyte into a measurable signal, whose magnitude is normally proportional to the concentration of the vapor analyte [1]. On the basis of the transducer type chemical sensors can be classified into the following groups: electrochemical, optical, heat-sensitive, and mass sensitive sensors. The working principles of a chemical sensor are primarily based on the interaction between sample input and the chemically sensitive materials on the sensor surface.

2.1. Equilibrium isotherms

Several isotherm models as for instance Langmuir, van Bemmelen-Freundlich, Frumkin-Fowler-Guggenheim, and the Brunauer-Emmett-Teller (BET) were used to describe the equilibrium between adsorbed vapor on the sensitive film of a sensor and free gas particle at constant temperature [2]. The Langmuir isotherm model which equation is given below [3] is the simplest of all models and occurs by the most chemical sensors

$$q_{\text{eq}} = [Q_0 L C_{\text{eq}}] / [1 + L C_{\text{eq}}], \quad (2.1)$$

where q_{eq} is the adsorbed amount at equilibrium, C_{eq} the equilibrium concentration of the vapor, Q_0 is adsorption capacity and L is a constant related to the energy or net enthalpy of adsorption. Q_0 represents a practical limiting adsorption capacity when the surface is fully covered.

2.2. Sensitivity of chemical sensors

The sensitivity of chemical sensors is the amount of change in a sensor's output in response to a change at a sensor's input over the sensor's entire range. The qualitative aspect gives the strength of interaction between the sensor and the analyte, while the quantitative term takes into consideration the concentration of the analyte. The output is used in this paper as sensitivity. Furthermore sensibility, sensitivity and response are used as synonymous. Generally for the isotherm interaction between a chemical sensor and one vapor the sensitivity (output) can be related to the mole number of adsorbed particles (input) via

$$S = \alpha q_{\text{eq}}, \quad (2.2)$$

where, S is the output or response of the sensor, q_{eq} the mole number of adsorbed gas molecules and α is a correlation coefficient.

We assume that the mole number of the adsorbed vapor particles fits well to Langmuir isotherm and consider the equation (2.1).

Let n be the vapor mole number that interact with the sensor

$$n = C_{eq} + q_{eq} \tag{2.3}$$

denoting

$$\beta = [Q_o L] / [1 + LC_{eq}] \tag{2.4}$$

and introducing the equations (2.3) and (2.4) into the relationship (2.1) yields

$$q_{eq} = \beta(n - q_{eq}) \tag{2.5}$$

rearranging equation (2.5) and setting

$$\gamma = \beta / 1 - \beta \tag{2.6}$$

gives

$$q_{eq} = \gamma.n \tag{2.7}$$

substitution of this into equation (2.2) yields

$$S = \alpha.\gamma.n, \tag{2.8}$$

where α and γ are correlation coefficients that hang on the transducer type and the magnitude of the adsorption on the sensor surface, respectively. Generally the sensitivity of chemical sensors by constant temperature can be expressed as:

$$S^T = f(n) = b^T .n, \tag{2.9}$$

where b^T is detector response per mole by constant temperature. b^T depends on the number of adsorbed particles and the transducer type. S^T is the sensibility of the sensor by constant temperature, n is the concentration of the gas.

2.3. *The effect of temperature and humidity on sensor sensitivity*

Some detectors as metal oxide sensors (MOS) or polymeric chemiresistors are strongly influenced by humidity and temperature [4–6]. The temperature acts on the sensitive film of the sensors and changes the electric properties of its transducers. The vapors-sensor interactions are reversible if the chemical vapors readily desorb, but some hysteresis and drift can occur. α the transducer coefficient hangs then on the temperature ($\alpha = \alpha(T)$).

Recalibration after each application has to be used, since the response to a change of temperature and various gas concentrations of such a sensors is not a function of state.

3. Interaction between a chemical sensor array and a vapor mixture

The sensitivity of certain gas sensors to different gases depends on the choice of the sensor material and the operating temperature. By combining several different gas sensors into a sensor array, complex gas mixtures can be analyzed. Although the selectivity of the sensors is limited, qualitative gas analysis can be performed using pattern recognition techniques [7–11].

The sensitivity of each element i of a sensor array depend not only on the temperature and the cross sensitivity (the influence of one measurand on the sensitivity of the sensor for another measurand) but also on the partial sensibilities of the other $i - 1$ sensors.

The interaction between a mixture M of j various vapors and a sensor system composed by i -elements by constant temperature is considered. We assume that α the transducer coefficient is independent of temperature. Let n_j be the concentration of the j th vapor and S_i the sensitivity of the i th sensor. The responses of all sensors to a change of temperature and mixture pressure are then reversible, this is a condition for practically operational and useful sensors. In this case S the total sensitivity of the sensor array is a function of state. Small variation dS as function of the vapors concentrations and the temperature can be expressed as total differential [12].

$$dS = \left\{ \frac{\partial S}{\partial n_1} \right\}_{n_2, \dots, n_j, T} \cdot dn_1 + \dots + \left\{ \frac{\partial S}{\partial n_j} \right\}_{n_1, \dots, n_{j-1}, T} \cdot dn_j + \left\{ \frac{\partial S}{\partial T} \right\}_{n_1, \dots, n_j} \cdot dT. \quad (3.1)$$

The total sensibility S of the sensor array is the sum of the individual sensor sensibilities S_i ,

$$S = \sum_{i=1}^i S_i \quad (3.2)$$

the substitution of this into equation (3.1) yields

$$dS = \sum_{i=1}^i \left(\left\{ \frac{\partial S_i}{\partial n_1} \right\}_{n_2, \dots, n_j, T} \cdot dn_1 + \dots + \left\{ \frac{\partial S_i}{\partial n_j} \right\}_{n_1, \dots, n_{j-1}, T} \cdot dn_j + \left\{ \frac{\partial S_i}{\partial T} \right\}_{n_1, \dots, n_j} \cdot dT \right) \quad (3.3)$$

furthermore the response S_i of the i th detector is the sum of its partial sensibilities S_{ij}

$$S_i = \sum_{j=1}^j S_{ij} \quad (3.4)$$

dS can now be calculated by inserting equation (3.4) into equation (3.3)

$$dS = \sum_{i=1}^i \left(\left\{ \frac{\partial S_i}{\partial n_1} \right\}_{n_2, \dots, n_j, T} \cdot dn_1 + \dots + \left\{ \frac{\partial S_i}{\partial n_j} \right\}_{n_1, \dots, n_{j-1}, T} \cdot dn_j \right) + \left(\sum_{i=1}^i \sum_{j=1}^j \left\{ \frac{\partial S_{ij}}{\partial T} \right\}_{n_1, \dots, n_j} dT \right) \tag{3.5}$$

by denoting $\left\{ \left\{ \frac{\partial S_i}{\partial n_j} \right\}_{n_1, \dots, n_{j-1}, T} \right\} = h_{ij}^T$, $\left\{ \left\{ \frac{\partial S_{ij}}{\partial T} \right\}_{n_1, \dots, n_j} \right\} = h_{ij}^P$, the following equation is obtained:

$$dS = \left(\sum_{i=1}^i \sum_{j=1}^j h_{ij}^T \cdot dn_j \right) + \left(\sum_{i=1}^i \sum_{j=1}^j (h_{ij}^P \cdot dT) \right), \tag{3.6}$$

where h_{ij}^T and h_{ij}^P are the correlation coefficients by isotherm and isobar interactions between the *i*th element of the sensor array and the *j*th component of the vapor mixture, respectively. The total sensibility *S* can be calculate by integrate the relationship (3.4) for small *dn_j* and *dT*

$$S = \left(\int_0^{n_j} \sum_{i=1}^i \sum_{j=1}^j h_{ij}^T \cdot dn_j \right) + \left(\int_0^T \sum_{i=1}^i \sum_{j=1}^j (h_{ij}^P \cdot dT) \right) \tag{3.7}$$

the integral of a sum is the sum of the integrals, this applied to the equation (3.7) gives

$$S = \left(\sum_{i=1}^i \sum_{j=1}^j \int_0^{n_j} h_{ij}^T \cdot dn_j \right) + \left(\sum_{i=1}^i \sum_{j=1}^j \int_0^T (h_{ij}^P \cdot dT) \right) \tag{3.8}$$

by using of some algebra the equation (3.8) can be transformed to

$$S = \left(\sum_{i=1}^i \sum_{j=1}^j h_{ij}^T \cdot n_j \right) + \left(\sum_{i=1}^i \sum_{j=1}^j (h_{ij}^P \cdot T) \right) \tag{3.9}$$

differentiating equation (3.8) and comparing it with equation (3.5), we find a Gibbs–Duhem-like equation [13, 14]

$$F_1 = \left(\sum_{i=1}^i \sum_{j=1}^j (n_j \cdot dh_{ij}^T) \right) + \sum_{i=1}^i \sum_{j=1}^j (T \cdot dh_{ij}^P) = 0, \tag{3.10}$$

which relates the variations of sensors partial sensibilities, the vapors concentrations and the temperature to remain in equilibrium.

For the sensors quoted in paragraph (2.3) the equation (3.10) must be reduced to:

$$F_2 = \left(\sum_{i=1}^i \sum_{j=1}^j (n_j \cdot dh_{ij}^T) \right) = 0, \quad (3.11)$$

while the total sensibility S is a function of state only by isotherm interactions between the sensors and the mixture.

4. The separation of the effects on sensor array total sensitivity of vapors concentrations and sensors partial sensitivities

To separate the influence of the sensors partial sensibilities and the mixture composition on the total sensitivity of a sensor array, the equation

$$\left(\sum_{i=1}^i \sum_{j=1}^j (n_j \cdot dh_{ij}^T) \right) + \sum_{i=1}^i (T \cdot dh_i^P) = 0$$

is considered and transformations such that $h_{ij}^T = a_{ij}^T \cdot b_{ij}^T$ and $h_{ij}^P = a_{ij}^P \cdot b_{ij}^P$, are introduced, the following relationship is got:

$$\begin{aligned} \sum_{i=1}^i \sum_{j=1}^j (n_j a_{ij}^T \cdot db_{ij}^T) + \sum_{i=1}^i \sum_{j=1}^j (n_j \cdot b_{ij}^T \cdot da_{ij}^T) + \sum_{i=1}^i \sum_{j=1}^j (T \cdot b_{ij}^P \cdot da_{ij}^P) \\ + \sum_{i=1}^i \sum_{j=1}^j (T \cdot a_{ij}^P \cdot db_{ij}^P) = 0, \end{aligned} \quad (4.1)$$

where a_{ij}^T and a_{ij}^P are coefficients that express the magnitude of the i th sensor partial sensibilities by isotherm and isobar interactions between the sensor array and the j th component of the mixture, respectively. b_{ij}^T and b_{ij}^P are correlation coefficients, which represent the influence of the j th component concentration by isotherm and isobar interactions between the sensor array and the j th component of the mixture, respectively.

Let R_{ij}^T and R_{ij}^P be the isotherm and the isobar responses of the i th sensor when it interacts separately with the j th component of the mixture, respectively. n_{ij} is the mole part of the j th mixture component that interact with the

*i*th element of the sensor array. Mathematically we have

$$R_{ij}^T = (b_{ij}^T \cdot n_j), \tag{4.2}$$

$$R_{ij}^P = T \cdot b_{ij}^P, \tag{4.3}$$

$$n_{ij} = a_{ij}^T \cdot n_j. \tag{4.4}$$

The relationships (4.2), (4.3) and (4.4) introduced in equation (4.1) gives:

$$F_3 = \left(\sum_{i=1}^i \sum_{j=1}^j (n_{ij} \cdot db_{ij}^T) \right) + \left(\sum_{i=1}^i \sum_{j=1}^j (R_{ij}^T \cdot da_{ij}^T) \right) + \left(\sum_{i=1}^i \sum_{j=1}^j R_{ij}^P \cdot da_{ij}^P \right) + \left(\sum_{i=1}^i \sum_{j=1}^j (T \cdot a_{ij}^P \cdot db_{ij}^P) \right) = 0. \tag{4.5}$$

The mixture *M* that interact with the sensor array is so subdivided into subsets *M*₁, . . . , *M*_{*i*}, we have

$$M_1 \cup, \dots, \cup M_i = M. \tag{4.6}$$

Each partition *M*_{*i*} responds to one element (*i*th sensor) of the array. *n*_{*ij*} is then one component of the mixture *M*_{*i*} and express the mole fraction of the *j*th component of the mixture *M* that interact with the *i*th sensor of the array. If we assume that each element of the sensor array answer reciprocally to a change of temperature and mixture pressure, the application of Gibbs–duhem theory to the interaction between the *i*th sensor and the mixture fraction *M*_{*i*} gives :

$$\sum_{j=1}^j (n_{ij} \cdot db_{ij}^T) + \sum_{j=1}^j (T \cdot a_{ij}^P \cdot db_{ij}^P) = 0 \tag{4.7}$$

equation (4.6) generalized for the sensor array becomes:

$$F_4 = \sum_{i=1}^i \sum_{j=1}^j (n_{ij} \cdot db_{ij}^T) + \sum_{i=1}^i \sum_{j=1}^j (T \cdot a_{ij}^P \cdot db_{ij}^P) = 0 \tag{4.8}$$

the combination of the relationships (4.5) and (4.8) gives:

$$F_5 = \left(\sum_{i=1}^i \sum_{j=1}^j (R_{ij}^T \cdot da_{ij}^T) \right) + \left(\sum_{i=1}^i \sum_{j=1}^j R_{ij}^P \cdot da_{ij}^P \right) = 0. \tag{4.9}$$

The separation of mixture composition and sensor sensibilities effects was also demonstrated, since the differential expression *F*₄ and *F*₅ describe the species concentrations influence and the reciprocal influence of the sensors, respectively.

5. Conclusion

An differential expressions for a sensor array total responses and a relationship in differential form between the changes of sensors partial sensitivities, mixture components concentrations and temperature were deduced using the function of state properties of the sensors sensibilities and the Gibbs-duh me formalism for extensive quantities known in the thermodynamic of miscellaneus. Useful informations about thermodynamic behavior of solid/gas interfaces can be extracted from these equations.

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