Diffusion of an Equilibrium Mixture of a Dissociating Gas

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ABSTRACT: A single diffusion equation describing the transport in a condensed medium of an equilibrium mixture of a dissociating gas is derived. A single concentration-dependent diffusion coefficient characterizes this diffusion. The theory is developed with reference to current interest in the diffusion of N_2O_4-NO_2 mixtures in polymers.

1. Introduction

We wish to provide a simple mathematical description of transient as well as steady-state diffusion of an equilibrium mixture of a dissociating gas through a film of a condensed medium such as a polymer membrane. The diffusion of N_2O_4-NO_2 mixtures is an excellent example to which we can refer our theory. Recent interest in N_2O_4-NO_2 diffusion, particularly in poly(tetrafluoroethylene) (PTFE), has arisen in regard to two technological applications. The first application deals with low-permeability, inert expulsion bladders for storable propellants such as nitrogen dioxide in liquid space propulsion systems. The second application is to the design and calibration of a "permeation tube," a sealed tube containing a liquified gas which escapes through the walls at a relatively constant measured rate.[1] Once calibrated, it is to be used as a source of the confined gas released at a specified rate to be used in calibrating instruments which detect gases such as NO_2 and SO_2.

Pasternak *et al.*[2] have discussed only the steady state of permeation of such an equilibrium mixture of NO_2-N_2O_4 subject to three simplifying assumptions. We will develop in the next section a single effective transport equation valid at all times for the diffusion of a dissociating gas mixture, subject only to one of the assumptions made by Pasternak *et al.* that the equilibrium

$$2 \text{ monomer} \rightleftarrows \text{dimer}$$

viz.

$$2NO_2 \rightleftarrows N_2O_4 \tag{1.1}$$

is maintained in the gas phase and everywhere in the condensed phase (the polymer membrane). We employ this equation in the third section to derive relevant mathematical expressions needed to interpret experimental data obtained from permeation and sorption measurements.

2. Effective Diffusion Equation

Denote by a_i, c_i, γ_i $(c_1, c_2; T) = a_i/c_i$, $i = 1, 2$, the thermodynamic activity, concentration, activity coefficient in the condensed phase of the dissolved monomer (1) and dimer (2) species of the dissociating gas. Choosing an appropriate frame of reference, the application of Fick's laws of diffusion yields in the condensed phase

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x}\left\{D_{11}\frac{\partial c_1}{\partial x} + D_{12}\frac{\partial c_2}{\partial x}\right\} - R(c_1, c_2) \tag{2.1}$$

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x}\left\{D_{12}\frac{\partial c_1}{\partial x} + D_{22}\frac{\partial c_2}{\partial x}\right\} + \frac{1}{2}R(c_1, c_2) \tag{2.2}$$

with $R(c_1,c_2)$ the net, local rate of conversion of monomer to dimer species, and $D_{12} = D_{21}$ the single cross-diffusion coefficient of this ternary gas-polymer mixture. By virtue of eq 1.1, eq 2.1 and 2.2 are not independent since the concentrations C_i are related *via* the equilibrium condition

$$a_2/a_1^2 = K_a(T)$$

or

$$\frac{c_2}{c_1^2} = \frac{K_a(T)\gamma_1^2(c_1, c_2; T)}{\gamma_2(c_1, c_2; T)} = K(c_1, c_2; T) \tag{2.3}$$

with $K_a(T)$ the thermodynamic (activity) equilibrium constant corresponding to the equilibrium eq 1.1, a function of temperature T. Thus diffusion in this system involves only a single transport equation which we can choose to describe the time evolution of the total concentration c of the dissociating gas, where

$$c = c_1 + 2c_2 \tag{2.4}$$

Denote by

$$c_1 = \phi(c; T) = \phi(c) \tag{2.5}$$

$$c_2 = \frac{1}{2}[c - \phi(c)]$$

the unique, positive solutions of the two simultaneous equations (2.3 and 2.4) for c_1 and c_2. Multiplying eq 2.2 by two and adding the result to eq 2.1 yields

$$\frac{\partial(c_1 + 2c_2)}{\partial t} = \frac{\partial}{\partial x}\left\{(D_{11} + 2D_{12})\frac{\partial c_1}{\partial x} + (D_{12} + 2D_{22})\frac{\partial c_2}{\partial x}\right\} \tag{2.6}$$

which, using eq 2.4 and 2.5, can be rewritten as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left\{D(c)\frac{\partial c}{\partial x}\right\} \tag{2.7}$$

with

$$D(c) = \left(D_{11} - D_{22} + \frac{3}{2}D_{12}\right)\phi'(c) + (D_{22} + (1/2)D_{12})$$

$$\phi'(c) = \left[\frac{\partial\phi(c, T)}{\partial c}\right]_T \tag{2.8}$$

In general

$$D_{ij} = D_{ij}(c_1, c_2; T) = D_{ij}(\phi(c, T), \frac{1}{2}[c - \phi(c)]; T)$$
$$= D_{ij}(c, T) \qquad i, j = 1, 2 \tag{2.9}$$

in eq 2.8, where the concentration dependence of the diffusion coefficients D_{ij} arises both from their thermodynamic and mobility factors. Equations 2.7 and 2.8 are our main result. Diffusion of an equilibrium mixture of a dissociating gas is described by a single diffusion equation for c with an effective, concentration-dependent diffusion coefficient $D(c)$. In practice, experimental measurements are conducted in such a fashion that sorption equilibrium

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(1) G. T. Davis, Polymer Division, National Bureau of Standards, private communication, and D. P. Lucero, *Anal. Chem.*, 43, 1744 (1971).

(2) R. A. Pasternak, M. V. Christensen, and J. Heller, *Macromolecules*, 3, 366 (1970).

is achieved almost instantaneously at the interface between the gas and the condensed phase, which implies in turn that the appropriate boundary condition on c at the interface, c_B, is given, without loss of generality, by

$$c_B = pS(p;T) \tag{2.10}$$

with p the total pressure of the dissociating gas in the gas phase. The solubility coefficient $S(p;T)$, a function of p and T, can be determined experimentally by an equilibrium sorption measurement using a sorption balance.[3]

The analytic form of $D_{ij}(c, T)$, $\gamma_i(\phi(c), (1/2)[c - \phi(c)];T) = \gamma_i(c,T)$ and $\phi(c,T)$ can be quite complicated and for sufficiently large values of p, the behavior of the system is best described by the composite function $D(c;T)$ which can be obtained experimentally (*cf.* section 3) from combined steady state permeation and equilibrium sorption data. For sufficiently low values of p, for which the ternary, condensed phase mixture becomes sufficiently dilute in the dissociating gas so that the γ_i approach closely their limiting Henry's law values,

$$\gamma_i^0(T) = \lim_{c \to 0} \gamma_i(c;T) \tag{2.11}$$

and the diffusional mobilities approach their limiting constant values so that

$$\lim_{c \to 0} D_{ij}(c,T) = D_{ij}^{(0)}(T) \tag{2.12}$$

further simplification of eq 2.8 is possible. Using eq 2.11 in 2.3 one obtains

$$\frac{c_2}{c_1^2} = \frac{K_a(T)\gamma_1^0(T)^2}{\gamma_2^0(T)} = K_0(T) \tag{2.13}$$

From eq 2.13 and 2.4 one has

$$\begin{aligned} c_1 = \phi_0(c) &= \frac{1}{4K_0}[(1 + 8K_0c)^{1/2} - 1] \\ c_2 &= \frac{1}{2}[c - \phi_0(c)] \end{aligned} \tag{2.14}$$

Equation 2.14 can be used as a starting point for an iterative solution of eq 2.3 and 2.4 which converges in the vicinity of $c_1 = \phi_0(c)$, *viz.*

$$\frac{[\phi_{k+1}(c)]^2}{\frac{1}{2}[c - \phi_{k+1}(c)]} = K_k(c,T) = \frac{K_a(T)[\gamma_1(\phi_k(c),(1/2)[c - \phi_k(c)];T)]^2}{\gamma_2(\phi_k(c),(1/2)[c - \phi_k(c)];T)} \tag{2.15}$$

$k = 0, 1, 2, \ldots$, if $\gamma_i(c,T)$ is known. In any case for sufficiently small p we can employ eq 2.12 and 2.14 in eq 2.8 to give the limiting form of $D(c)$,

$$\begin{aligned} D_0(c) = {} & (D_{11}^{(0)} - D_{22}^{(0)} + \frac{3}{2}D_{12}^{(0)})(1 + 8K_0c)^{-1/2} + \\ & (D_{22}^{(0)} + (1/2)D_{12}^{(0)}) = D_{01}(1 + 8K_0c)^{-1/2} + D_{02} \approx \\ & (D_{11}^{(0)} - D_{22}^{(0)})(1 + 8K_0c)^{-1/2} + D_{22}^{(0)} \end{aligned} \tag{2.16}$$

with

$$D_{01} = D_{11}^{(0)} - D_{22}^{(0)} + \frac{3}{2}D_{12}^{(0)}$$

and

$$D_{02} = D_{22}^{(0)} + (1/2)D_{12}^{(0)}$$

since in this limit $D_{12}^{(0)} < D_{11}^{(0)}, D_{22}^{(0)}$. Unfortunately, the thermodynamics of irreversible processes only implies that $D_{12} \leq (D_{11}D_{22})^{1/2}$, but plausible models (*e.g.*, the Chapman Enskog theory of the Boltzmann gas) suggest $D_{12}^{(0)} \approx 0$. In this limiting Henry's law region the sorption boundary condition eq 2.10 reduces to

$$c_B = pS_0(T) \tag{2.17}$$

with S_0 the so-called Henry's law solubility, a function of temperature only.

3. Treatment of Permeation and Sorption Data

The treatment of permeation and sorption data for a concentration-dependent diffusion coefficient $D(c)$ has been extensively treated in the literature and has been aptly summarized in ref 3 and 4. For permeation through a polymer film of width l adjacent to a gas reservoir at pressure p_0 at $x = 0$ and vacuum at $x = l$ one has for the experimentally accessible steady-state flux $J(c_0)$ and time lag $L(c_0)$

$$J(c_0)l = \int_0^{c_0} D(c)\mathrm{d}c \tag{3.1}$$

and

$$\frac{L(c_0)}{l^2} = \int_0^{c_0} cD(c)\left[\int_0^{c_0} D(u)\mathrm{d}u\right]\mathrm{d}c \Big/ \left[\int_0^{c_0} D(c)\mathrm{d}c\right]^3 \tag{3.2}$$

with (*cf.* eq 2.10)

$$c_0 = p_0S(p_0;T) \tag{3.3}$$

obtained from equilibrium sorption measurements. Numerical differentiation of $J(c_0)l$ with respect to c_0 yields $D(c_0)$ *via*

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}c_0}[J(c_0)l] &= D(c_0) \\ c_0 &= p_0S(p_0) \end{aligned} \tag{3.4}$$

from data obtained at various pressures p_0. The correctness of the analytic form of $D(c)$ derived in this fashion can be checked by computing $L(c_0)$ from eq 3.2 and comparing the result with experimental values. The data of Pasternak *et al.* show that at 30.1° the solubility at 1 atm of NO_2–N_2O_4 in PTFE is about 2% by weight. Thus at or below 1 atm eq 2.16 may be obeyed, at least in first approximation. Using eq 2.16 in eq 3.1 gives

$$\begin{aligned} J(c_0)l &= \frac{D_{01}}{4K}[\sqrt{1 + 8K_0c_0} - 1] + D_{02}c_0 \\ &= D_{01}\phi_0(c_0) + D_{02}c_0 \\ &= (D_{01} + D_{02})c_0 - \frac{D_{01}K_0c_0^2}{4} + 0(K_0^2c_0^3) \end{aligned} \tag{3.5}$$

If the flux is measured for three values of p_0 for which eq 2.16 applies and the Henry's law solubility is known (*cf.* eq 2.17) then eq 3.5 can be used to compute the three constants D_{01}, D_{02}, and K_0 which characterize this system.

Alternatively using sorption data alone one can employ the experimental initial gradient for sorption I_s

$$I_s = \lim_{t \to 0} \frac{1}{4} \frac{\mathrm{d}(M_t/M_\infty)}{\mathrm{d}(t^{1/2}\pi^{1/2}l)} \tag{3.6}$$

to give approximately

$$\left[1/c_0 \int_0^{c_0} D(c)\mathrm{d}c\right]^{1/2}$$

where M_t is the amount of the dissociating gas taken up by the film of thickness l in a time t. An even better approximation is to use the unweighted mean of the initial gradients for sorption, I_s, and desorption, I_d, *viz.*

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(3) "Diffusion in Polymers," J. Crank and G. S. Park, Ed., Academic Press, London, 1968.

(4) J. Crank, "The Mathematics of Diffusion," Oxford, Oxford Univ, 1956.

$$\frac{1}{2}(I_s^2 + I_d^2) \simeq 1/c_0 \int_0^{c_0} D(c)\mathrm{d}c \qquad (3.7)$$

Other methods such as use of successively smaller intervals and weighted mean diffusion coefficients for systems such as this are fully discussed in ref 3 and 4.

Diffusion in samples of different geometry require solutions of the equation

$$\frac{\partial c}{\partial t} = \mathrm{div}\{D(c)\ \mathrm{grad}\ c\} \qquad (3.8)$$

Swelling effects can be minimized by employing a section fixed frame of reference. It is desirable to have both sorption and permeation measurements on such a system to verify the basic equilibrium assumption of the theory. Agreement must exist between values of $D(c)$ obtained from transient and steady-state measurements. The theory has been developed for homogeneous polymer-gas systems that are studied sufficiently well above their glass transition temperatures so that non-Fickian transport effects could be neglected.

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Aspects of Polymer–Polymer Thermodynamics

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ABSTRACT: It has been observed that most polymer–polymer pairs exhibiting partial miscibility decrease in solubility as temperature is increased. One origin of the observed behavior has been found to arise from free volume effects. Using a modified form of Flory's "equation of state" thermodynamics, it has been shown that lower critical solution temperature (lcst) behavior should generally be anticipated for polymer–polymer systems. Rather modest differerences in pure-component thermal expansion coefficients are responsible for the lcst. Computations have been made which show the effect of molecular weight, pure-component equation of state parameters, the interaction energy parameter, and other mixture parameters on polymer–polymer mutual solubility. In addition, the effects of pressure and polydispersity have been considered. The cloud point curves for two polymer–polymer pairs have been measured; comparison of these curves with the theoretical curves show them to have less temperature sensitivity. Reasons for this quantitative discrepancy are discussed.

During the last few years considerable effort has been expended by the polymer industry to identify compatible polymer pairs. The reason for the effort is that thermodynamic solubility of one polymer in another is the exception rather than the rule. Hence, if such systems can be found, the probability of obtaining a proprietary compatible material is high. For the same reason, research aimed at finding mutually soluble polymer pairs can be futile since the probability of success is often small. Techniques have been developed based upon use of the multidimensional solubility parameter[1-5] to aid in finding compatible polymer pairs. These procedures, although helpful, have not been entirely successful when applied to polymer–polymer systems.

In the course of research at this laboratory, it has been observed that several polymer liquids which are mutually soluble at a low temperature exhibit a liquid–liquid phase transition at higher temperatures. This lower critical solution temperature (lcst) behavior has been observed rather than the more conventional upper critical solution temperature (ucst) behavior. The purpose of this paper is to explain this rather unusual thermodynamic behavior using Flory's new "equation of state" thermodynamics.[6,7]

The model predicts why most polymer pairs show a decrease in mutual solubility as temperature is increased. This trend is contrary to predictions of the original Flory–Huggins model[8] of polymer solution thermodynamics. It is also contrary to the behavior of most polymer–solvent systems far below the critical point of the solvent. The model also predicts the qualitative effects of pressure and molecular weight distribution on the polymer thermodynamics.

An additional need for such a thermodynamic model arises when one is concerned with phase transition phenomena in binary and multicomponent polymer systems. Predictions of the mode of phase separation and the ultimate structure require a detailed thermodynamic model.

Cloud point curves have been measured experimentally for two polymer pairs. These data are used to make a qualitative comparison with the model. However, no attempt is made to determine model parameters for either experimental system.

Theoretical Development

A. The Flory "Equation of State" Thermodynamic Model. In this section, a generalized version of Flory's equation of state thermodynamics will be presented. Both similarities to and differences from the original Flory–Huggins theory of polymer solution thermodynamics will be indicated. The intention of this comparison is to provide a basis of presentation which is familiar to most polymer scientists. Of course, much of the phenomena discussed below can also be quantitatively described by the use of the Flory–Huggins theory with an empirical concentration and temperature-dependent interaction parameter. However, such empiricism provides little understanding of the underlying causes of observed thermody-

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(1) P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

(2) J. L. Gardon, *J. Paint Technol.*, 38, 43 (1966).

(3) R. F. Blanks and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **3**, 1 (1964).

(4) C. M. Hansen, *J. Paint Technol.*, **39**, 104 (1967).

(5) J. D. Crowley, G. S. Teaque, Jr., and J. W. Lowe, Jr., *J. Paint Technol.*, **38**, 269 (1966).

(6) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Amer. Chem. Soc.*, **86**, 3515 (1964).

(7) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).

(8) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.