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The effusion catastrophe set

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Abstract

The occurrence of topological catastrophes in effusion cells was recently discovered. These chemical events have been termed "effusion catastrophes" (ECats). Side effects from ECats can make it difficult to achieve equilibrium in an effusion cell, and many effusion studies have been compromised thereby. ECats result when the equilibrium potential surface of an effusing chemical system becomes multiple valued in temperature–pressure–composition space. In such a case, discontinuous catastrophic transitions between equilibrium states occur at certain temperatures; these temperatures make up the ECat set. The ECat is modeled here, and equations for the ECat set are derived in terms of $\Delta H^\ominus$ and $\Delta S^\ominus$ of the phase transitions underlying the ECat and of the forced vapor compositions in a passive effusion cell containing the condensed phases involved. Known ECats in the Ga–S and Ga–Se systems are treated with the model. The equations derived here are sufficiently general to be applied to any ECat.

Keywords: Binary system; Catastrophe; ECat; Effusion; Effusion cell; Transition

1. Introduction

For convenience and efficiency, the following symbols and abbreviations will be used in this paper: temperature (T), pressure (P), composition (X), vapor pressure (vP), composition of vapor (vC), and composition of condensed phase (cC). Others will be defined subsequently.

Recently it was shown that condensed-phase transitions in effusion cells can occur on catastrophic paths [1–3] in many chemical systems in effusion cells, e.g., In_2Se_3(s) [3], GaSe(s) [1], and K_2S(s) [1]. In other cases, when appropriate

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conditions obtain, an incremental change in T across the T of a condensed-phase transition results in discrete and measurable changes in the X at equilibrium within the effusion cell. The vP, too, changes, but that change can be small and difficult to measure by effusion methods. The phase transition, then, is discontinuous in T, i.e., the state of the system depends on the direction of approach to the transition T, even in the limit of vanishing orifice area. Over a certain range of T, a system within an effusion cell can have either of two states. Only T is a control variable in a passive effusion cell [1], and thus the change is classified as a fold catastrophe [4]. With independent control of cV, a cusp catastrophe [4] could be effected.

In this paper the equations representing vC curves in $P-X$ phase diagrams are used to find intersections where catastrophic phase transitions occur in effusion cells. These intersections are the effusion catastrophe (ECat) set. For a given phase transition the set comprises two points, one in the direction of increasing T, here denoted by $T^{\uparrow}$, and one in the direction of decreasing T, here denoted by $T^{\downarrow}$. It will be seen that $T^{\uparrow} < T^{\downarrow}$ and that in that interval the equilibrium thermodynamic state function of the system within the effusion cell is double valued.

The discontinuities in such transitions can be understood by recognizing that a condensed-phase transition at equilibrium in an effusion cell requires that at least two condensed phases and the vapor coexist, and thus any such system in an effusion cell has at least two components [2]. At equilibrium, then, two equilibrium constants must be obeyed; X of each condensed phase and the vapor are fixed by the thermodynamic properties of the substances in the effusion cell. These requirements and the conditions imposed by the effusion cell can be contradictory; in such cases, catastrophic phase transitions occur.

It is important to recognize and understand the ECat when it occurs in binary systems, so that data from effusion studies can be correctly acquired and interpreted for chemical and thermodynamic applications. The following derivation of the ECat set is intended to help with such understanding.

2. The effusion catastrophe set

Figure 1 shows two isothermal $P-X$ phase diagrams that illustrate the conditions for ECats. Two segments of isotherms through equilibrium $T-P-X$ space for a binary system with components A and B are shown. The upper isotherm is at a higher T than the lower isotherm. The vertical solid lines represent regions of stability of a condensed phase λ and a condensed phase ρ. The solid curved lines represent vC in equilibrium with the condensed phase at a given P. On the solid horizontal lines, λ, ρ, and vapor are in equilibrium. The broken vertical and curved lines are metastable extensions of stability lines. The vertical dotted lines will be discussed next.

In an effusion cell, the vC and cC have a unique relationship established by the molecular weights of species in the vapor and the relative volatilities of the components. We consider two-component, condensed phases which effuse to give the vapor species A(g) and B(g). Two special conventions will be adopted in writing

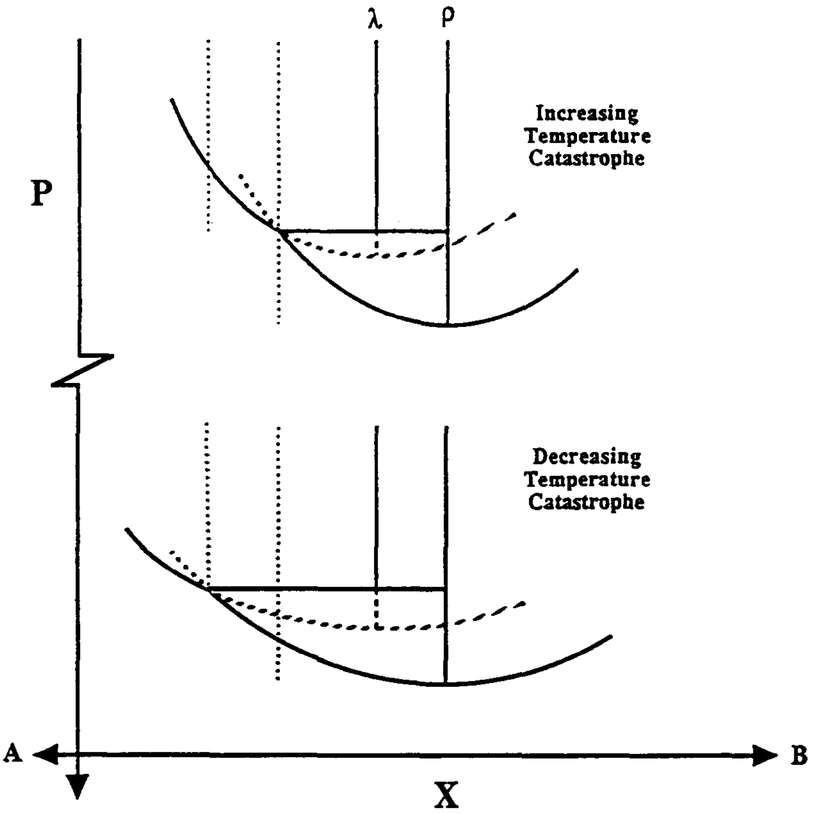

Fig. 1. Two segments of isothermal cuts through the $T-P-X$ phase diagram of the A–B system. The isotherms are at the temperatures of the effusion catastrophe set, $T^{\downarrow}$ and $T^{\uparrow}$, where the cusps in the vC curves cross the forced vC (vertical dotted lines) in the cell.

the chemical formula of the condensed phase: (1) the components of the condensed phase will be taken to be A and B, such that the formula of λ is $A_aB_b(c)$ and of ρ is $A_eB_f(c)$; (2) the sum of the subscripts will be set to unity, i.e., $a+b=1$ and $e+f=1$. The chemical reaction of congruent effusion of $A_aB_b(c)$ is represented by

$$A_aB_b(c) = aA(g) + bB(g) \tag{1}$$

and of $A_eB_f(c)$ by

$$A_eB_f(c) = eA(g) + fB(g) \tag{2}$$

A specific example of such a reaction with an equation written with these conventions would be the vaporization of $K_2S(s)$ [5], accordingly represented by

$$K_{0.8}(S_2)_{0.2}(s) = 0.8K(g) + 0.2S_2(g) \tag{3}$$

A useful effect of the conventions adopted for writing the formula of the condensed phase is that the congruent vaporization reaction produces one mole of vapor;

many of the equations to be developed subsequently will be simpler because of this effect.

The chemical reaction of the transition from λ to ρ would be represented by the equation

$$A_aB_b(c) + (f-b)B(g) = A_eB_f(c) + (a-e)A(g) \tag{4}$$

The transition from ρ to λ would be represented by the reverse of Eq. (4)

$$A_eB_f(c) + (a-e)A(g) = A_aB_b(c) + (f-b)B(g) \tag{5}$$

In the reactions represented by Eqs. (4) and (5), the number of moles of gas produced equals the number of moles of gas consumed.

The Knudsen equation [6] gives the partial pressure P_i of each vapor species within the cell

$$P_i = \dot{n}_i(2\pi RTM_i)^{1/2} \tag{6}$$

where $\dot{n}_i$ is the molar flux of molecular species i through the effusion orifice, M_i is the molecular weight of species i, and the other symbols have their usual meanings.

The vC over congruently effusing $A_aB_b(c)$ is given by either of the equations

$$\chi_A^\lambda = [1 + (b/a)(M_B/M_A)^{1/2}]^{-1} \tag{7}$$

$$\chi_B^\lambda = [1 + (a/b)(M_A/M_B)^{1/2}]^{-1} \tag{8}$$

where χ_A^λ and χ_B^λ are mole fractions of A(g) and B(g), respectively, in the vapor of λ in an effusion cell. The corresponding equations for χ_A^ρ and χ_B^ρ over $A_eB_f(c)$ are

$$\chi_A^\rho = [1 + (f/e)(M_B/M_A)^{1/2}]^{-1} \tag{9}$$

$$\chi_B^\rho = [1 + (e/f)(M_A/M_B)^{1/2}]^{-1} \tag{10}$$

Henceforth, we will adopt the convention that $M_A > M_B$. The vertical dotted lines in Fig. 1 are at χ_A^λ and χ_A^ρ from Eqs. (7) and (9); that on the left corresponds to the vapor of phase λ, and that on the right to the vapor of phase ρ.

The solution laws of components in non-stoichiometric compound phases are rarely known [7] and thus, in this paper we will ignore variations in cC resulting from variations in T and will consider only "line phases". In applications where solution laws are known, the following derivations can easily be modified by substituting the laws appropriately to express the partial pressures of the vapor components. Under the restriction to line phases and at the low P in an effusion cell, the equilibrium constant of reaction (1) K_1 is expressed by either

$$K_1 = P_A^a P_B^b \tag{11}$$

where P_A and P_B are partial pressures of A(g) and B(g), respectively, or

$$K_1 = (X_A^v)^a (X_B^v)^b P \tag{12}$$

where X_A^v and X_B^v are mole fractions in the vapor. For reaction (2) we have

$$K_2 = P_A^e P_B^f \tag{13}$$

and

$$K_2 = (X^{\mathrm{v}}_{\mathrm{A}})^e (X^{\mathrm{v}}_{\mathrm{B}})^f P \tag{14}$$

Moreover, we consider only effusion cells with very small orifices, so effusates within the effusion cells would be at equilibrium.

Equations (7)-(14) can be obeyed simultaneously in an effusion cell when only one condensed phase is present. The resulting equilibrium is illustrated by the schematic isothermal $P-X$ phase diagram in Fig. 2. The horizontal broken line is the tie-line connecting the vapor and condensed phase in equilibrium at P. In an effusion cell, P is the vP of the condensed phase. The vC at equilibrium (tracked on the horizontal axis) is represented as a function of P (tracked on the vertical axis) by the curved solid line. Below the curved line, only vapor is present at equilibrium; above the curved line, vapor is in equilibrium with the condensed phase except exactly at cC. The equation representing the curved line is obtained from Eq. (12)

$$P = K_1(1 - X^{\mathrm{v}}_{\mathrm{B}})^{-a}(X^{\mathrm{v}}_{\mathrm{B}})^{-b} \tag{15}$$

Substitution of $\chi^{\lambda}_{\mathrm{B}}$ from Eq. (8) for $X^{\mathrm{v}}_{\mathrm{B}}$ in Eq. (15) yields the vP at equilibrium over $\mathrm{A}_a\mathrm{B}_b$(c) in an effusion cell; the broken horizontal tie-line in Fig. 2 lies at that vP.

When $\mathrm{A}_e\mathrm{B}_f$(c) is in equilibrium with vapor, P is given by

$$P = K_2(1 - X^{\mathrm{v}}_{\mathrm{B}})^{-e}(X^{\mathrm{v}}_{\mathrm{B}})^{-f} \tag{16}$$

where K_2 is the equilibrium constant of the vaporization reaction of $\mathrm{A}_e\mathrm{B}_f$(c), reaction (2), given by Eq. (14). Substitution of $\chi^{\varrho}_{\mathrm{B}}$ from Eq. (10) for $X^{\mathrm{v}}_{\mathrm{B}}$ in Eq. (16) yields the vP over $\mathrm{A}_e\mathrm{B}_f$(c).

In a binary system with equilibrium among $\mathrm{A}_a\mathrm{B}_b$(c), $\mathrm{A}_e\mathrm{B}_f$(c), and vapor with vC $= X^{\mathrm{v}}_{\mathrm{B}}$, P and vC over either condensed phase are the same, as shown in Fig. 1 on the horizontal solid lines. Equating the right sides of Eqs. (15) and (16) gives the

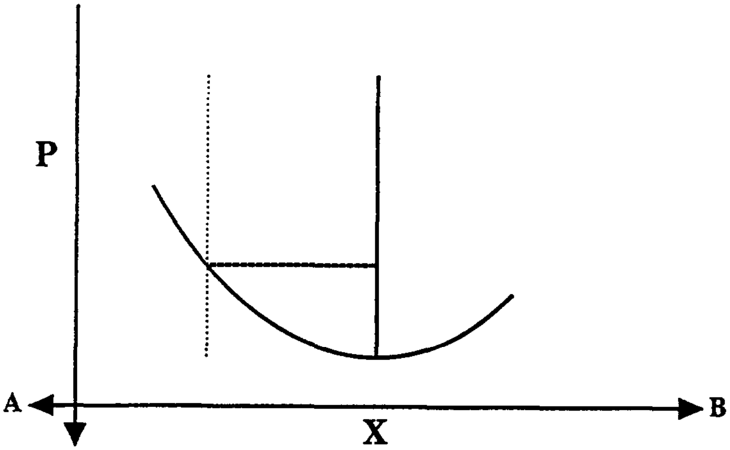

Fig. 2. A segment of an isothermal cut through the $T-P-X$ phase diagram of a vaporizing condensed phase in the A-B system in an effusion cell. The vertical dotted line represents forced vC within the cell.

equation expressing X_B^v when both condensed phases and the vapor are in equilibrium

$$K_1(1-X_B^v)^{-a}(X_B^v)^{-b} = K_2(1-X_B^v)^{-e}(X_B^v)^{-f} \tag{17}$$

The cusps in the solid vC curves in Fig. 1 occur at X_B^v given by Eq. (17). This X, when substituted into either Eq. (15) or (16), gives the P of a solid horizontal line in Fig. 1. Thus, with increasing T, we find $T^{\uparrow}$ where X_B^v in Eq. (17) equals χ_B^ρ from Eq. (10), and with decreasing T, $T^{\downarrow}$, where X_B^v equals χ_B^λ from Eq. (8).

Equation (17) rearranges to the form

$$\ln(K_1/K_2) = (a-e)\ln(1-X_B^v) + (b-f)\ln(X_B^v) \tag{18}$$

which, with the relationship between the Gibbs energy and equilibrium constant, gives

$$\Delta G_4^\ominus/RT = (e-a)\ln(1-X_B^v) + (f-b)\ln(X_B^v) \tag{19}$$

$$\Delta G_5^\ominus/RT = (a-e)\ln(1-X_B^v) + (b-f)\ln(X_B^v) \tag{20}$$

in which $\Delta G_4^\ominus$ and $\Delta G_5^\ominus$ are the Gibbs energy changes of reactions (4) and (5), respectively.

Substituting $\Delta H^\ominus - T\Delta S^\ominus$ for $\Delta G^\ominus$ gives the ECat set

$$T^{\downarrow} = \Delta H_4^\ominus/[\Delta S_4^\ominus + R\ln(1-\chi_B^\lambda)^{(e-a)}(\chi_B^\lambda)^{(f-b)}] \tag{21}$$

in which $\Delta H_4^\ominus$ and $\Delta S_4^\ominus$ are standard enthalpy and entropy changes of reaction (4), and

$$T^{\uparrow} = \Delta H_5^\ominus/[\Delta S_5^\ominus + R\ln(1-\chi_B^\lambda)^{(a-e)}(\chi_B^\rho)^{(b-f)}] \tag{22}$$

in which $\Delta H_5^\ominus$ and $\Delta S_5^\ominus$ are standard enthalpy and entropy changes of reaction (5).

3. Application to gallium sulfide

$T^{\uparrow}$ and $T^{\downarrow}$ in the effusion of gallium sulfide have both been observed experimentally to be within one degree of 1242 K [1, 8]. The condensed phases involved in these ECats can be taken to be $Ga_2S_3(c)$, ρ, and $Ga_{(2.04\pm0.01)}S_3(c)$, λ, after Uram and Edwards [1, 8]. The exact stoichiometry of $Ga_2S_3(c)$ was arbitrarily assigned, and measured changes in X were used to calculate the stoichiometry of the other phase. These are effectively the same stoichiometries found by Roberts and Searcy [9]. In the present notation, these phases are $(Ga_2S)_{0.5}\cdot(S_2)_{0.5}$ and $(Ga_2S)_{(0.5075\pm0.0019)}(S_2)_{(0.4925\mp0.0019)}$, respectively. With the uncertainties temporarily omitted from the subscripts in phase λ, the chemical reaction of the decreasing-T phase transition, equivalent to reaction (4), is

$$\begin{aligned}&(Ga_2S)_{0.5075}\cdot(S_2)_{0.4925}(c) + 0.0075S_2(g)\\&\quad = (Ga_2S)_{0.5}\cdot(S_2)_{0.5}(c) + 0.0075Ga_2S(g)\end{aligned} \tag{23}$$

in which case the exponents in Eq. (21) are $e - a = -0.0075$ and $f - b = 0.0075$, and for the increasing-T transition, equivalent to reaction (5), is

$$(Ga_2S)_{0.5} \cdot (S_2)_{0.5}(c) + 0.0075Ga_2S(g)$$
$$= (Ga_2S)_{0.5075} \cdot (S_2)_{0.4925}(c) + 0.0075S_2(g) \quad (24)$$

in which case the exponents in Eq. (22) are $a - e = 0.0075$ and $b - f = -0.0075$.

Neither $\Delta H^\ominus$ nor $\Delta S^\ominus$ of reactions (23) and (24) are known, but a reasonable estimate of $\Delta H^\ominus$ can be made by analogy with known reactions. It is likely that $(Ga_2S)_{0.5} \cdot (S_2)_{0.5}(c)$ is solid and $(Ga_2S)_{0.5075} \cdot (S_2)_{0.4925}(c)$ is liquid [1], and thus reaction (24) is a fusion. The $\Delta H^\ominus$ of fusion of $K_2S(s)$ is 16 150 J mol^{-1} [10], and thus one might reasonably estimate the $\Delta H^\ominus$ of fusion of $Ga_2S_3(s)$ to be 25 000 J mol^{-1}. Minor contributions to $\Delta H^\ominus$ and $\Delta S^\ominus$ by the small amount of gas can be ignored; the $\Delta H^\ominus$ of reaction (24), $\Delta H^\ominus_{24}$, then, might reasonably be taken to be 12 000 J mol^{-1}. The crudeness of this estimate needs to be noted, but it will be seen that it is sufficiently accurate for the present purposes.

If the $T^\uparrow$ of $Ga_2S_3(s)$ is taken to be at 1242 K [1], one calculates $\Delta S^\ominus_{24}$ with Eq. (22) to be 9.6312 J K^{-1}. By setting $\Delta H^\ominus_{23} = -\Delta H^\ominus_{24}$ and $\Delta S^\ominus_{23} = -\Delta S^\ominus_{24}$, one calculates $T^\downarrow$ with Eq. (21) to be 1241.73 ± 0.13 K where the uncertainty in cC of phase λ has been accounted for. It is seen, then, that $T^\downarrow$ and $T^\uparrow$ of Ga_2S_3 differ by 0.27 ± 0.13 K, a range that would be practically impossible to measure in an effusion experiment. The estimate of 1 K, previously made on the basis of experimental observations [1] is shown, then, to be too large. The corresponding difference in vPs at the ECat boundaries, too, would be hard to measure. Any other reasonable estimate of $\Delta H^\ominus_{24}$ above, would have led to the same conclusion. However, these properties are not the issue in the observable effects from ECats. Changes in cC and vC, and the vP increases during the ECats in both T directions were striking [1, 8], and allowed discovery [9], in effects during effusion of Ga_2S_3, of the phenomenon modeled here.

4. Application to gallium selenide

Dieleman, Sanders, and van Dommelen [11] found that both $Ga_2Se_3(s)$ and a liquid with cC of $X_{Ga} = 0.44$ and $X_{Se} = 0.56$ effused congruently. Perhaps the liquid could be viewed as being $Ga_4Se_5(l)$. An ECat with $T^\uparrow \approx 1250$ K was associated with the solid–liquid transition in this system [1]. The chemical equation for the decreasing-T transition, equivalent to Eq. (4), is

$$(Ga_2Se)_{0.56} \cdot (Se_2)_{0.44}(c) + 0.06Se_2(g)$$
$$= (Ga_2Se)_{0.5} \cdot (Se_2)_{0.5}(c) + 0.06Ga_2Se(g) \quad (25)$$

in which case the exponents in Eq. (21) are $e - a = -0.06$ and $f - b = 0.06$, and the chemical equation for the increasing-T transition, equivalent to Eq. (5), is

$$(Ga_2Se)_{0.5} \cdot (Se_2)_{0.5}(c) + 0.06Ga_2Se(g)$$
$$= (Ga_2Se)_{0.56} \cdot (Se_2)_{0.44}(c) + 0.06Se_2(g) \quad (26)$$

in which case the exponents in Eq. (22) are $a - e = 0.06$ and $b - f = -0.06$. With the same assumptions about $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ as in the case of gallium sulfide and with $T^{\uparrow} = 1250$ K, one calculates $T^{\downarrow}$ to be 1234 K. Such a large difference, 16 K, between $T^{\uparrow}$ and $T^{\downarrow}$ could be measured. This test of the theory is under way.

5. Other systems

The present analysis is applicable to other systems with ECats, where the T interval in the ECat set could be large, e.g., the In–Se system, where the phases $In_4Se_5(l)$ and $In_4Se_6(l)$ are known to form during effusion of $In_2Se_3(s)$ [12], and where $e - a$ and $f - b$ in Eqs. (21) and (22) can be even larger than in the Ga–Se system [3]. In the In–Se system, however, $T^{\uparrow}$ is not known; apparently $T^{\uparrow}$ is too low to give vPs measurable by ordinary effusion methods. $In_2Se_3(s)$ effuses incongruently, through an ECat, even at the lowest useful T. Similar considerations apply to the K–S system, where $K_2S(s)$ effuses incongruently, through an ECat, until the cC of the K_2S_4 is reached [5].

ECats or secondary effects from them can be expected to affect any chemically binary system in an effusion cell if the forced vapor composition fails to intersect with the equilibrium vapor composition of the condensed phase in the cell. In such a case, the chemical reaction and related thermodynamic analysis would need special evaluation.

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