

Chemical Reaction Models for Non-Equilibrium Phase Transitions

F. Schlögl

Institut für Theoretische Physik
der Rheinisch-Westfälischen Technischen Hochschule Aachen

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Chemical model reactions are discussed the steady states of which show the phenomenon of non equilibrium phase transitions. One example shows a phase transition of second order, another one shows a phase transition of first order. If diffusion occurs in the case of first order transition, coexistence of two phases in different domains is possible. For plane boundary layers between the domains the coexistence states are found by a construction analogous to the Maxwellian construction of vapor pressure of a Van der Waals gas. For spherical domains the coexistence dates change similarly as vapor pressure of droplets or bubbles with radius.

1. Introduction

A certain class of thermodynamic non-equilibrium states is formed by such transport states which can be described by relatively few macroscopic thermodynamic variables. These variables may be local variables already occurring in thermostatics, or typical transport variables as flow densities of thermostatic quantities (as heat flow or electrical current density). Of special importance are the steady states of this class for which the thermodynamic variables in an adequate frame of reference are constant in time. If a steady state is sufficiently near to a thermostatic equilibrium state—that means if it lies in the region where linear thermodynamics of irreversible processes is valid—the steady state is characterized by minimal entropy production. This is not valid if the steady state is far away from any thermal equilibrium. Thermodynamics of these states is a relatively unknown field. As thermal equilibrium states are special steady states, it seems reasonable to consider the thermal steady states as a generalization of the thermal equilibrium states.

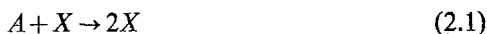
It was pointed out by several authors that in the field of steady states of a system phenomena can occur which best can be described as phase transitions in non-equilibrium states. They should be considered not only as an analogy to phase transitions in thermostatics but as a generalization of these. There should for instance be mentioned the behaviour of

a LASER below and above the threshold¹⁻⁴ and the behaviour of tunnel diode circuits^{5,6}.

Phase transitions in non-equilibrium states are always connected with non linear transport equations the study of which in general is complicated. Therefore it seems reasonable to discuss model systems which show phenomena of this kind of phase transition and which are as simple as possible with respect to mathematical treatment. In the following two such model systems are discussed. These are models of chemical reactions*. The first one shows a non-equilibrium phase transition of second order, the second one a phase transition of first order. The latter is more complicated and shows the possibility of coexistence of two different phases if diffusion takes place. The two phases form separated domains in space. The concentrations and therefore the reaction rates are different in the two phases and depend on the curvature of the surface of the domains. There are strict analogies to the dependence of vapor-pressure on the radius of a droplet.

2. A Phase Transition of Second Order

The following chemical reactions between four chemical species A , B , C , X may be assumed:



The reactions may be possible in both directions. They may occur isothermic and homogeneous in space. All chemical species be rarified gases. The homogeneity of all concentrations can be realized in a stirring vessel. The concentrations a , b , c of the species A , B , C shall be hold constant by appropriate feeding of the reactor. Only the concentration n of the species X can vary with time. Under these conditions, in general, no chemical equilibrium is possible, and the reaction rates of the two

* Similar models of chemical reactions were suggested and discussed by Glansdorff, Prigogine, Nicolis and Lefever. See e.g.: Glansdorff, P., Prigogine, I.: *Structure, stabilité et fluctuations*. Masson, Paris: 1971.

1 Haken, H.: *Verhandlungen der Deutschen Physikalischen Gesellschaft 5/1970. Frühjahrstagung Freudenstadt 1970: Laserlicht — ein Beispiel für eine Phasenumwandlung*. Stuttgart: Teubner 1970.

2 Haken, H.: *Festkörperprobleme X* (ed. O. Madelung). Braunschweig: Vieweg 1970.

3 Graham, R., Haken, H.: *Z. Physik* **243**, 289 (1971).

4 Grossmann, S., Richter, P. H.: *Z. Physik* **242**, 458 (1971).

5 Landauer, R., Woo, J. W. F.: *Proceedings of the Sixth IUPAP Conference on Statistical Mechanics* (eds. S. A. Rice, K. F. Freed, and J. C. Light): University of Chicago Press: to be published.

6 Landauer, R.: *Plenarvorträge der 36. Physikertag. 1971 Essen: Stability and instability in information processing and in steady state dissipative systems*. Stuttgart: Teubner 1971.

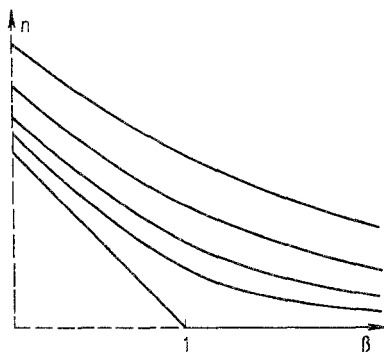


Fig. 1. Diagram of steady states of reactions (2.1), (2.2) for the values 1, 1/2, 1/4, 0 of γ . The value 0 gives a second order phase transition

reactions

$$r_1 = k_1 a n - k'_1 n^2 \quad (2.3)$$

$$r_2 = k_2 b n - k'_2 c \quad (2.4)$$

don't vanish. The derivative of n with respect to time is

$$\dot{n} = r_1 - r_2. \quad (2.5)$$

A steady state is characterized by vanishing \dot{n} .

By an appropriate choice of units of time and concentrations we can put

$$k'_1 = 1, \quad k_1 a = 1. \quad (2.6)$$

Moreover we introduce the abbreviations

$$k_2 b = \beta, \quad k'_2 c = \gamma \quad (2.7)$$

and can write

$$\dot{n} = -n^2 + (1 - \beta)n + \gamma \equiv \varphi(n). \quad (2.8)$$

As \dot{n} vanishes only for one positive value n , there exists always one steady state. \dot{n} is positive for smaller values n and negative for larger values n . Therefore the steady state is stable. That means it regenerates itself if disturbed.

In the steady state is valid

$$\gamma = n^2 - (1 - \beta)n \equiv \psi(n). \quad (2.9)$$

The value n of the steady state is given in Fig. 1 in dependence on β for different values γ . If γ is hold fixed to zero we get

$$n = \begin{cases} 1 - \beta & \text{for } \beta < 1 \\ 0 & \text{for } \beta > 1. \end{cases} \quad (2.10)$$

This is the behaviour of a phase transition of second order. We can compare it with the phase transition of a ferromagnetic substance if we put magnetization M , magnetic field H and temperature T in analogy to n , γ , β . The phase transition takes place for vanishing H , as in our case for vanishing γ . As M vanishes for T higher than the critical temperature T_c , in our case n vanishes for β higher than the critical value which is unit.

The interpretation of n , correspondingly to Eq. (2.3) with the values (2.6), as the forward reaction rate of the first reaction (2.1), shows that symmetry with respect to time-inversion is broken for β below the critical point. We can call the reaction rate n (as any other part of the total reaction rate) an "order parameter". Breaking of a symmetry is typical for phase transitions of second order. In comparison to thermostatics the breaking of time-inversion symmetry is new.

Another analogy to thermostatic phase transitions can be seen in the fact that the regression time of small fluctuations becomes extremely large at the critical point. For small fluctuations δn we get

$$\delta \dot{n} = -\frac{1}{\tau} \delta n \quad (2.11)$$

with

$$\frac{1}{\tau} = \frac{\partial \psi}{\partial n} = 2n - (1 - \beta). \quad (2.12)$$

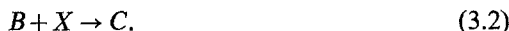
For vanishing γ :

$$\frac{1}{\tau} = |1 - \beta|. \quad (2.13)$$

The regression time τ is infinite in the critical point.

3. A Phase Transition of First Order

Now we discuss the following chemical reactions (compare ⁷):



The second one is the same as (2.1) and therefore its reaction rate r_2 is given by (2.4). The reaction rate of the first reaction, however, is now

$$r_1 = k_1 a n^2 - k'_1 n^3. \quad (3.3)$$

Again we assume the species to be rarified gases in a stirring vessel hold isothermic. Now we put by adequate choice of units:

$$k'_1 = 1, \quad k_1 a = 3. \quad (3.4)$$

⁷ Schlögl, F.: Z. Physik **248**, 446 (1971).

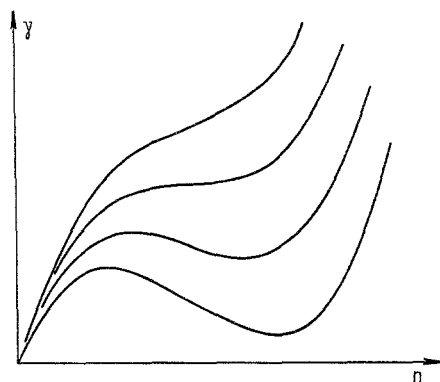


Fig. 2. Diagram of steady states of reactions (3.1), (3.2) for four values of β

With the abbreviations (2.7) we get

$$\dot{n} = r_1 - r_2 = \varphi(n) \quad (3.5)$$

with

$$\varphi(n) = -n^3 + 3n^2 - \beta n + \gamma. \quad (3.6)$$

For certain values β, γ there exist three real positive points n_1, n_2, n_3 in which \dot{n} vanishes. These are steady states. In the following we shall call the smallest steady value n_1 , the largest n_2 . They are attached to stable steady states. Between them lies an unstable steady state n_2 . (The use of the subscripts is different from ⁷.) The stability features are easily seen by the sign of \dot{n} .

In Fig. 2 the diagram of the steady states is given corresponding to the equation

$$\gamma = n^3 - 3n^2 + \beta n \equiv \psi(n) \quad (3.7)$$

for four values of β . There exists a critical value β_c for which the three values n_1, n_2, n_3 coincide:

$$\beta_c = 3. \quad (3.8)$$

Only for values β below β_c exist three different real values n_1, n_2, n_3 . The unstable states n_3 lie on decreasing parts of $\psi(n)$. In the critical point moreover is

$$n_c = 1, \quad \gamma = 1. \quad (3.9)$$

The diagram is similar to that of the equilibrium states of a Van der Waals gas if n, γ, β are replaced by concentration v^{-1} , pressure p and RT where T is temperature, R gaseous constant. If by choice of units the

critical dates become

$$v_c = 1, \quad p_c = 1, \quad R T_c = \frac{8}{3}, \quad (3.10)$$

the thermal state equation of the Van der Waals gas gets the form

$$p = \left(1 - \frac{n}{3}\right)^{-1} \psi(n). \quad (3.11)$$

The analogy becomes complete to a gas with the state equation

$$p = \frac{RT}{v} - \frac{a_1}{v^2} + \frac{a_2}{v^3}. \quad (3.12)$$

That means a gas with two virial coefficients which are independent of T . Adequate choice of units, leads to the form

$$p = \psi(n). \quad (3.13)$$

This analogy justifies to call the transition between the two stable steady states a phase transition of first order. It is not connected with a symmetry breaking. For the same external conditions, given by β , γ , exist two competing states n_1 , n_2 . The system shows yet another analogies to the system liquid and gas as shall be shown in the following chapters.

4. Coexistence of Two Phases

If the reaction occurs in a stirring vessel, all concentrations a , b , c , n are homogeneous in space. In the following we drop this assumption and let $n(\mathbf{r})$ be dependent on the space coordinates \mathbf{r} . It can change not only by the chemical reactions (3.1), (3.2) but by diffusion of the species X as well. The concentrations of the other components A , B , C may be constant in time and in space. This is realized if the mobility of these components is essentially higher than that of X and the concentrations are hold fixed by appropriate feeding of the reactor.

In this case we get with $\varphi(n)$ of Eq. (3.6):

$$\dot{n} = \kappa \Delta n + \varphi(n). \quad (4.1)$$

κ is a diffusion constant, Δ the Laplacian. For the following it is suitable to write

$$\varphi(n) = \frac{\partial}{\partial n} \Phi(n) \quad (4.2)$$

and to apply a method which is developed by van Kampen⁸ for the discussion of an analogous equation in statistical theory of a real gas.

⁸ Kampen, N. G. van: Phys. Rev. **135**, A 362 (1964).

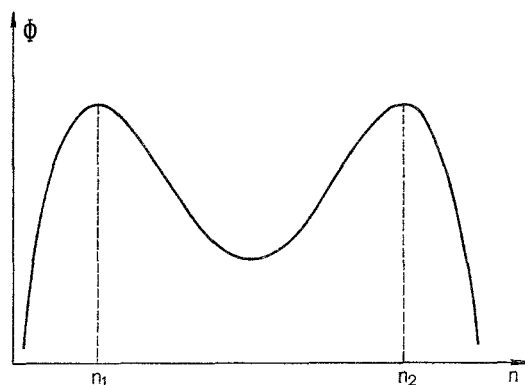


Fig. 3. $\Phi(n)$ in case of coexistence of two phases n_1, n_2 with plane boundary layer

In the special case that n is dependent on one coordinate z only, the steady states are solutions of the equation

$$\kappa \frac{\partial^2 n}{\partial z^2} = - \frac{\partial}{\partial n} \Phi(n). \quad (4.3)$$

This equation has the same structure as a one-dimensional mechanical equation of motion of a mass point in a potential field Φ . This is seen by replacing z, n by time t and the coordinate x of the mass point.

We ask for a steady state in which the two phases n_1, n_2 are in coexistence such that n becomes equal to n_1 if z goes to plus infinity and equal to n_2 if z goes to minus infinity. n_1, n_2 are relative maxima of $\Phi(n)$. Therefore this steady state corresponds to the motion of the mass point from one maximum of the potential Φ where it was at rest to the second maximum where it comes to rest. Compare Fig. 3. This is possible only if the value of Φ in both maxima is the same. That gives the condition of coexistence of both phases:

$$\Phi(n_1) = \Phi(n_2). \quad (4.4)$$

With

$$\Phi(n) - \Phi(n_1) = \int_{n_1}^n dn \varphi(n) \quad (4.5)$$

the condition of coexistence fixes the value

$$\gamma = \frac{1}{n_2 - n_1} \int_{n_1}^{n_2} dn \psi(n). \quad (4.6)$$

This relation corresponds to the Maxwellian construction of vapor pressure of a Van der Waals gas as shown in Fig. 4. γ is exactly the mean

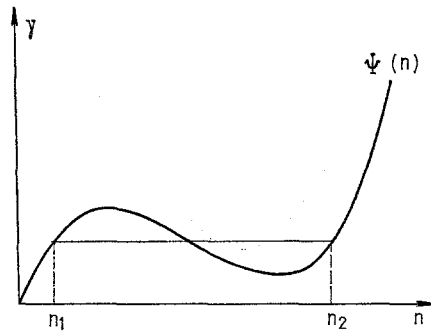
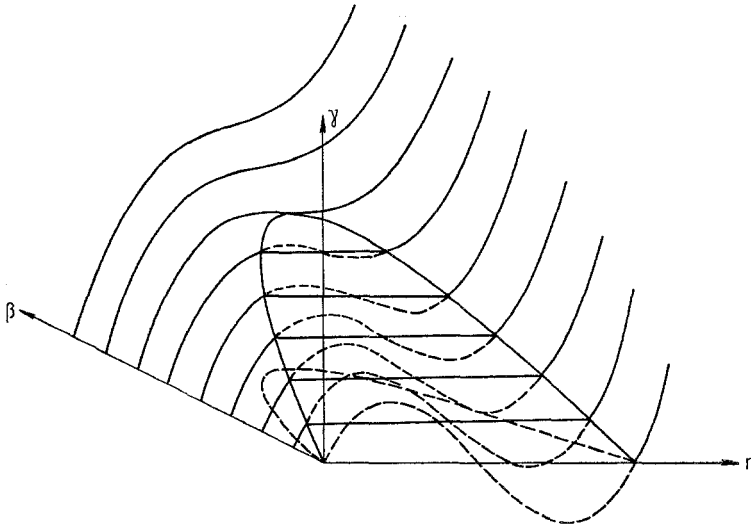
Fig. 4. Maxwellian construction of the coexistence value γ 

Fig. 5. Perspective representation of the three dimensional steady state diagram of reactions (3.1), (3.2) with the coexistence region of the two phases

value of ψ in the interval between n_1 and n_2 . Thus for given β the values γ, n_1, n_2 are fixed. The three dimensional state diagram of the steady states of the system is given in Fig. 5 in perspective representation.

As shown in the *Appendix A.1*, the coexistence values are

$$\gamma = \beta - 2, \quad (4.7)$$

$$n_{1,2} = 1 \mp (3 - \beta)^{1/2}. \quad (4.8)$$

The original value n_3 is then

$$n_3 = 1. \quad (4.9)$$

The width of the layer in which n changes from n_2 to n_1 is finite (compare Appendix A.2):

$$\delta z = 2(2\kappa/(1-\gamma))^{1/2}. \quad (4.10)$$

That means, the layer is thin in comparison to the extension of the domains of homogeneous phases.

5. A Variational Principle

For finding the coexistence states of two phases n_1, n_2 in the general case that n depends on the three dimensions of space, a variational principle is useful which is valid for an equation

$$\dot{n} = \kappa \Delta n + \frac{\partial \Phi}{\partial n}. \quad (5.1)$$

This equation can be written in the form

$$\dot{n} = -\frac{\partial L}{\partial n} + \nabla \frac{\partial L}{\partial \nabla n} \equiv -\frac{\delta L}{\delta n} \quad (5.2)$$

by introducing a Lagrangian

$$L = \frac{\kappa}{2} (\nabla n)^2 - \Phi(n). \quad (5.3)$$

For all variations δn vanishing on the boundary of the domain of integration we get

$$\int d\mathbf{r} (\dot{n} \delta n) = -\delta \Psi \quad (5.4)$$

where

$$\Psi = \int d\mathbf{r} L. \quad (5.5)$$

Thus in the steady states Ψ has an extremum or a saddle point. Eq. (5.4) gives yet more: If $\delta \Psi$ is positive, in the average over the domain δn and \dot{n} (and with it $\delta \dot{n}$) have opposite signs and the absolute value of δn decreases. That means $\delta \Psi$ decreases. If, however, $\delta \Psi$ is negative, the absolute value of δn increases in the average. In any case Ψ decreases if it has not reached an extremum or a saddle point. Stable steady states are reached in minima of Ψ and only an absolute minimum is stable with respect to any perturbation.

6. Minimal Surface of Coexisting Phases

In the following arbitrary surfaces of the domains of homogeneous phases shall be discussed. If the radii of the curvature of these phases are sufficiently large, we can assume that the layers between the two different

phases are nearly as thin as a plane layer. In this case we can make an approximation for solving the variational problem which was applied by van Kampen⁸ in the analogous problem for equilibrium states of a real gas. We divide Ψ in two additive terms:

$$\Psi_1 = - \int dr \Phi, \quad (6.1)$$

$$\Psi_2 = \int dr \frac{\kappa}{2} (Vn)^2. \quad (6.2)$$

The integral Ψ_2 contains only positive contributions of the surface layers. Instead of minimizing the sum Ψ , in the approximation the terms Ψ_1 and Ψ_2 are minimized independently.

To vary Ψ_1 , the total volume V of the reactor is divided into parts v_λ such that in any part v_λ the concentration n has a value n_λ . The variations are made with the subsidiary conditions that

$$V = \sum_\lambda v_\lambda, \quad (6.3)$$

$$N = \sum_\lambda n_\lambda v_\lambda \quad (6.4)$$

are hold fixed.

$$\Psi_1 = - \sum_\lambda v_\lambda \Phi(n_\lambda) \quad (6.5)$$

is to minimize. Introduction of two Lagrange parameters μ, μ' allows to vary all n_λ and v_λ independently. We get

$$\Phi(n_\lambda) = \mu n_\lambda + \mu', \quad (6.6)$$

$$\left(\frac{\partial \Phi}{\partial n} \right)_{n=n_\lambda} = \mu. \quad (6.7)$$

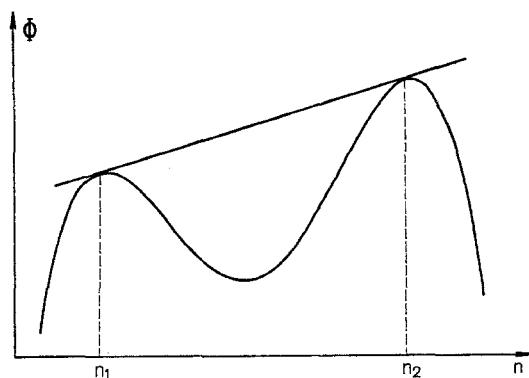


Fig. 6. Condition of minimizing Ψ_1 in case of coexistence of different values n_λ

If there exist different coexisting phases n_λ , the values $\Phi(n_\lambda)$ must lie on a tangent of the curve $\Phi(n)$. The largest possible number of different values n_λ therefore is two. Compare Fig. 6. Then, however, in (6.5) can be minimal for simultaneously non-vanishing v_1 and v_2 only if

$$\Phi(n_1) = \Phi(n_2). \quad (6.8)$$

This condition of coexistence gives again the Maxwellian construction as for plane layers.

The minimalization of Ψ_2 gives the result that the area of the surface between the two phases is minimal.

7. Surface Tension of Phase Domains

The coexistence value γ is dependent on the radius of curvature of the boundary layer between the two phases. There can be seen a close analogy to the dependence of vapor pressure on the radius of a droplet.

To show this, the case may be discussed that n is dependent on r only. We can summarize the case of spherical and of cylindrical symmetry and write r for the distance from a centre, or from an axis respectively. We can characterize these two different cases by the number v of dimensions being 3 for spherical and 2 for cylindrical symmetry. For steady states, that means for vanishing \dot{n} , Eq. (5.1) gets the form

$$\kappa \frac{\partial^2 n}{\partial r^2} = -\kappa \frac{v-1}{r} \frac{\partial n}{\partial r} - \frac{\partial \Phi}{\partial n}. \quad (7.1)$$

This equation has the same structure as the one dimensional mechanical equation of a mass point in a potential field Φ and moreover subject to a time dependent friction force. The analogy becomes obvious if r, n are replaced by t, x .

A coexistence state with

$$n = \begin{cases} n_2 & \text{for } r=0 \\ n_1 & \text{for } r \rightarrow \infty \end{cases} \quad (7.2)$$

corresponds in the spherical case ($v=3$) to a "droplet" of the "condensed" phase n_2 . It is analogous to a mechanical motion for which the mass point is at rest in the maximum point n_2 of $\Phi(n)$ at the beginning of the motion and comes to rest again exactly in the relative maximum point n_1 . Compare Fig. 7. As the mass point has lost energy during the motion by friction, $\Phi(n_1)$ must be smaller than $\Phi(n_2)$. The difference of the two relative maximum values of Φ can be got by multiplication of

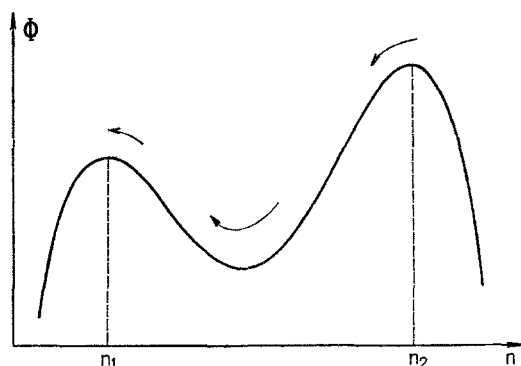


Fig. 7. Coexistence condition of two phases in the "droplet" case

Eq. (7.1) with $\partial n / \partial r$ and integration over r :

$$\Delta\Phi = (v-1)\kappa \int_0^\infty dr \frac{1}{r} \left(\frac{\partial n}{\partial r} \right)^2. \quad (7.3)$$

This quantity is positive definite.

If n_1, n_2 in (7.2) are exchanged, we get a steady state corresponding to a "bubble" of the "rarified" phase n_1 . In this case the relative maximum of Φ in n_1 is higher than that in n_2 and the direction of the arrows in Fig. 6 signifying the direction of increasing r has to be reversed.

In the following equations the upper sign belongs to the "droplet", the lower to the "bubble". Coexistence condition now is

$$\Phi(n_2) - \Phi(n_1) = \pm \Delta\Phi, \quad (7.4)$$

$$\gamma = \frac{1}{n_2 - n_1} \left[\int_{n_1}^{n_2} dn \psi(n) \pm \Delta\Phi \right]. \quad (7.5)$$

The coexistence value γ is higher for "droplets" and lower for "bubbles" than the value γ_∞ for plane boundary layers. The latter was given by the Maxwellian construction, Eq. (4.6).

We can only speak of domains of different phases if the radius r_0 of the "droplet" or the "bubble" is sufficiently large compared to the width of the boundary layer. In this case we can write in good approximation

$$\Delta\Phi = \frac{v-1}{r_0} \kappa \int_{n_1}^{n_2} dn \left| \frac{\partial n}{\partial r} \right| \quad (7.6)$$

and can replace the integral by its value for the plane layer. Moreover, we can approximately replace the difference $n_2 - n_1$ and the integral in

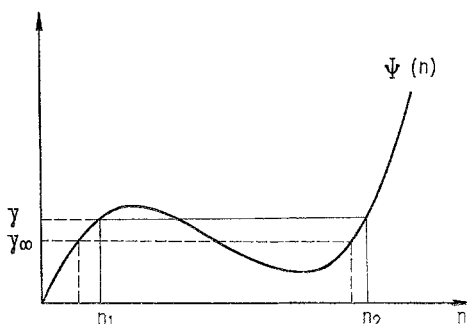


Fig. 8. Maxwellian construction of the coexistence value γ in the "droplet" case

(7.5) by their values for the plane layer. Compare Fig. 8. Then we get (see *Appendix A.3*)

$$\gamma - \gamma_{\infty} = \pm \frac{\gamma - 1}{r} \sigma \quad (7.7)$$

with an "surface tension"

$$\sigma = \frac{1}{n_2 - n_1} \kappa \int_{n_1}^{n_2} dn \left| \frac{\partial n}{\partial r} \right|, \quad (7.8)$$

$$\sigma = (2\kappa)^{1/2} \left(1 - \frac{\beta}{3} \right). \quad (7.9)$$

This quantity is proportional to the maximum value j_m of the diffusion current density

$$\mathbf{j} = -\kappa \nabla n \quad (7.10)$$

in the interior of the boundary layer:

$$\sigma = \frac{2}{3} j_m. \quad (7.11)$$

Now we can see what happens in the stirring vessel. By the stirring process the domains of homogeneous phases will be divided in small "droplets" or small "bubbles". If these have smaller radii r_0 than this one which is connected by (7.7) with the given value γ , they will decrease and vanish. Finally, in the steady state, the chemical mixture in the reactor will be a genuine homogeneous one and will not be a composition of two phases divided in very small domains.

Appendix

A.1. Maxwellian Construction

By Eq. (4.2) we get

$$\Phi(n) - \Phi(n_1) = -\frac{1}{4} n^4 + n^3 - \frac{\beta}{2} n^2 + \gamma n + \text{const.} \quad (\text{A.1.1})$$

This expression has maxima for n equal to n_1 and n_2 . Following the Maxwellian construction (4.4) the expression vanishes in these maxima likewise. Therefore

$$\Phi(n) - \Phi(n_1) = -\frac{1}{4}(n - n_1)^2(n - n_2)^2. \quad (\text{A.1.2})$$

Comparison of coefficients gives

$$n_1 + n_2 = 2, \quad (\text{A.1.3})$$

$$n_1^2 n_2^2 = 4\Phi(n). \quad (\text{A.1.4})$$

On the other hand comparison of coefficients in (3.6) and

$$\varphi(n) = -(n - n_1)(n - n_2)(n - n_3) \quad (\text{A.1.5})$$

gives the relations

$$n_1 + n_2 + n_3 = 3, \quad (\text{A.1.6})$$

$$n_1 n_2 n_3 = \gamma = \psi(n_1). \quad (\text{A.1.7})$$

Thus we get

$$n_3 = 1 \quad (\text{A.1.8})$$

and with (3.7):

$$\psi(n_3) = \psi(n_1) = \psi(n_2) = \beta - 2. \quad (\text{A.1.9})$$

This is the coexistence value of γ . n_3 is also the point of inflection of $\psi(n)$ in which the second derivative vanishes. With (A.1.7) we get

$$n_1 n_2 = \beta - 2 \quad (\text{A.1.10})$$

and as (A.1.3) shows now, n_1, n_2 are the roots of the quadratic equation

$$n^2 - 2n + \beta - 2 = 0. \quad (\text{A.1.11})$$

That means:

$$n_{1,2} = 1 \mp (3 - \beta)^{1/2}. \quad (\text{A.1.12})$$

The limits of the coexistence region in the (n, γ) -diagram of the steady states are given by the parabola

$$\gamma = 1 - (n - 1)^2 \quad (\text{A.1.13})$$

which is gained by elimination of β in Eq. (A.1.11) and (3.7).

A.2. The Plane Boundary Layer

By multiplication of (4.3) with $\partial n / \partial z$ and by integration over z we get in analogy to the law of energy conservation the equation

$$\frac{\kappa}{2} \left(\frac{\partial n}{\partial z} \right)^2 + \Phi(n) = \Phi(n_1). \quad (\text{A.2.1})$$

In the case discussed in Chapter 4 the concentration n decreases with increasing z in the boundary layer between both phases. Then we get by (A.2.1):

$$\frac{\partial n}{\partial z} = - \left[\frac{2}{\kappa} (\Phi(n_1) - \Phi(n)) \right]^{1/2} \quad (\text{A.2.2})$$

and with (A.1.2):

$$\frac{\partial n}{\partial z} = -(2\kappa)^{-1/2} (n - n_1)(n_2 - n), \quad (\text{A.2.3})$$

$$z = -(2\kappa)^{1/2} \frac{1}{n_2 - n_1} \ln \frac{n - n_1}{n_2 - n}, \quad (\text{A.2.4})$$

$$n = 1 - (1 - \gamma)^{1/2} \tanh \left[\left(\frac{1 - \gamma}{2\kappa} \right)^{1/2} z \right]. \quad (\text{A.2.5})$$

This relation gives the width δz of the boundary layer. The diffusion current density in the layer is

$$j = -\kappa \frac{\partial n}{\partial z}. \quad (\text{A.2.6})$$

Its maximal value is

$$j_m = \left(\frac{\kappa}{2} \right)^{1/2} (3 - \beta). \quad (\text{A.2.7})$$

A.3. Surface Tension

With (A.2.3) Eq. (7.8) gives

$$\sigma = \left(\frac{\kappa}{2} \right)^{1/2} \frac{1}{n_2 - n_1} \int_{n_1}^{n_2} dn (n - n_1)(n_2 - n), \quad (\text{A.3.1})$$

$$\sigma = \frac{1}{6} \left(\frac{\kappa}{2} \right)^{1/2} (n_2 - n_1)^2 \quad (\text{A.3.2})$$

and with (A.1.12) the relations (7.9) and (7.11).

Prof. Dr. Friedrich Schlögl
Institut für Theoretische Physik
der Rheinisch-Westfälischen Technischen
Hochschule Aachen
D-5100 Aachen, Templergraben
Germany