Zeitschrift: Helvetica Physica Acta
Band: 49 (1976)
Heft: 3

Artikel: On the thermodynamics of fog
Autor: Tschudi, H.R.
DOI: https://doi.org/10.5169/seals-114773

Nutzungsbedingungen
Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation
L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use
The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 01.12.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

On the Thermodynamics of Fog

by **H. R. Tschudi**[1])

Institut für Theoret. Physik, ETH-Hönggerberg, 8049 Zürich, Switzerland

(28. X. 1975)

Abstract. Fog is considered as a thermodynamic system composed of an atmosphere (vapour and air) and droplets of water which move through the atmosphere. Expressions for the Helmholtz and Gibbs free energy of fog are derived which contain only the thermodynamic potentials of the atmosphere and of a droplet in contact with the atmosphere. It is shown that fog and not the pure phase represents the thermodynamic equilibrium, although the concentration of droplets may often be very small.

We discuss fog without condensation nuclei and fog around soluble nuclei. In the first case practically no droplets occur which contain more than a few dozen molecules. For the second case we show that fog exists only very close to the saturation point. At saturation every soluble nucleus of s molecules (or ions) forms a droplet containing $c \cdot s^{3/2}$ water molecules. Using the calculated value $c = \frac{1}{12}$ for water at 300°K, we obtain good agreement with experiment.

I. Introduction

How does fog, a system of water-droplets in air and vapour, behave in equilibrium? Does fog actually exist in equilibrium? The task of developing the thermodynamics of such heterogeneous systems is interesting and it contributes to a better understanding of nucleation phenomena and condensation.[2])

In 1870 Lord Kelvin [1] showed that the vapour pressure of a droplet is always higher than of a plane surface. At best a droplet can be metastable in a super-saturated vapour. Nearly 70 years later, Frenkel pointed out that nevertheless an ensemble of droplets may be thermodynamically stable. [2] 'We shall assume, in contradistinction from the rough thermodynamic treatment, that even in the range of thermodynamic stability of the phase A, the latter is not strictly homogeneous, but contains embryos of a second phase B (in the form of liquid drops, gas bubbles, small crystals, etc.) .... Our problem consists in the determination of the statistical distribution of the B embryos in the phase A ....' [3].

Frenkel solved the problem in the following way: He considered an embryo containing j water molecules as itself a molecule of some substance A_j and fog as an ideal mixture of the substances A_j. He made the statement:

$$G(T, p, N_1, \ldots, N_j, \ldots) = \sum_j N_j(\tilde{\mu}_j(T, p) + kT \ln x_j) \tag{I.1}$$

for the Gibbs' free energy of fog.

---

[1]) Present address: H. R. Tschudi, Institut de Physique Théorique, Dorigny, CH-1015 Lausanne, Switzerland.

[2]) These questions will be the subject of a succeeding paper.

Where:

N_j: Particle number of the substance A_j
$\tilde{\mu}_j$: Chemical potential per particle of the 'pure' substance j

$$x_j = \frac{N_j}{N} \qquad N = \sum_j N_j.$$

In the fog there are chemical reactions of the following type

$$A_{j+1} \leftrightarrows A_1 + A_j.$$

We look for the equilibrium subject to the condition that the total number N_w of water molecules

$$N_w = \sum_j jN_j$$

is held fixed. The equilibrium concentrations are determined by

$$\tilde{\mu}_j + kT \ln x_j = j(\tilde{\mu}_1 + kT \ln x_1)$$

or equivalently

$$x_j = x_1^j \exp\left(\frac{j\tilde{\mu}_1 - \tilde{\mu}_j}{kT}\right). \tag{I.2}$$

(We have excluded the trivial solutions $x_j = 0$ for all j.)

Substituting x_j from (I.2) into the normalization condition $\sum_j x_j = 1$ yields the equation

$$f(x_1) = \sum_j x_1^j \exp\left(\frac{j\tilde{\mu}_1 - \tilde{\mu}_j}{kT}\right) = 1$$

which determines x_1 as its only positive solution.

Using $N = N_w(\sum_j j\, x_j)^{-1}$, we obtain the particle numbers

$$N_j = N_w\left(\frac{df}{dx_1}\right)^{-1} x_1^{j-1} \exp\left(\frac{j\tilde{\mu}_1 - \tilde{\mu}_j}{kT}\right).$$

Substituting (I.2) into (I.1) yields the value of the Gibbs free energy G of fog as

$$G = N_w(\tilde{\mu}_1 + kT \ln x_1)$$

which is less than $N_w\tilde{\mu}_1$, the Gibbs free energy of a pure gas A_1. The thermodynamical equilibrium is, therefore, not represented by the pure one-molecular phase A_1, but particles of the substances A_j containing several molecules must also exist.

Doubtless, this is the most important statement in this context and we owe it to Frenkel, as mentioned before. But his statement (I.1) must be criticized. In general, one has ideal mixtures only if one can neglect the interactions between the molecules of different constituents. We are, however, interested in embryos which may be considered as small droplets characterized by their volume and surface tension. Thus we must consider at least the interaction between the atmosphere and the droplet: The atmosphere is excluded from the interior of the droplet and the surface tension depends on both the liquid and the gaseous phase. The 'pure gas of droplets of one kind' A_j (i.e. without the atmosphere A_1 present) does not exist and it is not clear

what we have to substitute for the $\tilde{\mu}_j$. Frenkel considers $\tilde{\mu}_j - j\tilde{\mu}_1$ as the amount of free energy to form the droplet from the vapour and he uses Gibbs' expression for $\tilde{\mu}_j$, which is

$$\tilde{\mu}_j = j\mu_{\text{liq}}(T, p) + \sigma A.$$

The quantity μ_{liq} is the chemical potential per water molecule in the liquid phase, σ the surface tension, A the surface area. This last step was reconsidered by several authors who felt that a droplet has certain translational and rotational degrees of freedom appearing nowhere in Gibbs' formula. Ref. [4] gives a survey of these papers.

Another way to express our objections: It is not clear in what respect droplets may be considered as molecules. They are also macroscopic systems and appropriately Frenkel describes their inner properties by the same parameters as describe the whole system—a confusing situation! It is more natural, however, not to identify droplets with the same number of particles from the beginning, considering them as molecules of a substance, but to take every droplet itself as a thermodynamic system which exchanges water-molecules with the atmosphere. The droplets may move in the volume of the atmosphere. One has now to derive an expression for the Helmholtz free energy of this heterogeneous system.

We do this in two steps. First, we establish a set of classical Hamiltonian functions describing fog. Essentially, then, we will have achieved a certain decomposition of the state integral (Postulate 1) and must consequently determine the Liouville measure of the corresponding phase space (Postulate 2). Thereby the Helmholtz free energy of the fog is reduced to a known and simple function of the free energy of the atmosphere and the free energy of a droplet in contact with the atmosphere and whose centre of mass is held fixed. The equilibrium conditions can now be calculated and the thermodynamic potentials determined (Chapter II). Next we derive an explicit expression for the Gibbs free energy of a droplet based on Gibbs' thermodynamics of surfaces (Chapter III). In this framework we discuss fog without nuclei (III.2), fog around soluble (III.3) and insoluble nuclei (III.4).

II. The Thermodynamic Potentials of Fog

II.1. The model

We consider fog as a heterogeneous system which consists of droplets of a substance A (water) floating in the atmosphere, a mixture of the pure gas phase of A and an inert substance B (air). The shape, the volume and the number of droplets containing the same amount of water are inner variables of the whole system. First, we determine the Helmholtz free energy for an arbitrary but fixed value of these variables, whose actual values are calculated from the condition of equilibrium. We assume that no external fields are present and that the mean distance between the droplets is large compared with the range of the molecular interaction. We may, therefore, neglect the interaction between the droplets. The droplets interact only with the atmosphere in a manner which is translationally invariant.

In order to characterize our model precisely, we introduce the following definitions:

V_0: the volume of the atmosphere
N_0: the number of particles of the substance A in the atmosphere

N_B: The number of particles of the substance B in the atmosphere

λ_j: the number of droplets containing j molecules of A

v_{jr}: a symbol parametrising the shape and the volume of the rth droplet with j molecules.

V_{jr}: the volume of the jrth droplet

$N_A = N_0 + \sum_j j\,\lambda_j$: the total number of particles of the substance A

$V = V_0 + \sum_{jr} V_{jr}$: the total volume of the system

$\mathbf{x}_{jr} = (x_{jr}^{(1)}, x_{jr}^{(2)}, \ldots, x_{jr}^{(j)})$

$\mathbf{p}_{jr} = (p_{jr}^{(1)}, p_{jr}^{(2)}, \ldots, p_{jr}^{(j)})$

contain the coordinates and the momenta of all molecules of the droplet jr.

$\mathscr{X}_{jr}$: the coordinates of the centre of mass of the jr droplet jr.

$\boldsymbol{\xi}_{jr} = (x_{jr}^{(1)} - \mathscr{X}_{jr}, x_{jr}^{(2)} - \mathscr{X}_{jr}, \ldots, x_{jr}^{(j)} - \mathscr{X}_{jr})$: the coordinates of all molecules of the droplet jr relative to its centre of mass

$$\boldsymbol{x}_0 = (x_0^{(1)}, x_0^{(2)}, \ldots, x_0^{(N_0)}; x_B^{(1)}, x_B^{(2)}, \ldots, x_B^{(N_B)})$$
$$\boldsymbol{p}_0 = (p_0^{(1)}, p_0^{(2)}, \ldots, p_0^{(N_0)}; p_B^{(1)}, p_B^{(2)}, \ldots, p_B^{(N_B)})$$

contain the coordinates and the momenta of all molecules in the atmosphere.

$$\boldsymbol{X}_{jr} = (\mathscr{X}_{jr}, \mathscr{X}_{jr}, \mathscr{X}_{jr}, \ldots, \mathscr{X}_{jr}, \mathscr{X}_{jr})$$

$\mathscr{X}_{jr}$ is taken $N_0 + N_B$ times.

Our model of fog contains two assumptions:

(a) The Hamiltonian of fog has the following form

$$H = H_0 + \sum_{jr} H_{jr} + \sum_{jr} (W_{jr}^0 + W_{jr}^1)$$

where $H_0(\boldsymbol{p}_0, \boldsymbol{x}_0)$ contains the kinetic energy and the interaction of the particles in the atmosphere between themselves, and $H_{jr}(\mathbf{p}_{jr}, \boldsymbol{\xi}_{jr})$ contains the kinetic energy and the interaction of the particles in the droplet jr between themselves.

The phenomenological potentials W_{jr}^0, W_{jr}^1 describe globally the interaction between the atmosphere and the droplet jr. W_{jr}^0, W_{jr}^1 shall depend on the distance of the molecules from the centre of mass of jr, the shape and the volume of the droplet jr and on the intensive thermodynamic variables characterizing the atmosphere:

$$W_{jr}^0 = W^0\left(\boldsymbol{x}_0 - \boldsymbol{X}_{jr}; j, v_{jr}, T, \frac{N_0}{V_0}, \frac{N_B}{V_0}\right)$$

$$W_{jr}^1 = W^1\left(\boldsymbol{\xi}_{jr}; j, v_{jr}, T, \frac{N_0}{V_0}, \frac{N_B}{V_0}\right).$$

Since the interaction between the droplets is neglected, we achieve the following factorized form of the partition integral

$$\int dp\, dx\, e^{-\beta H} = \int \left(\prod_{jr} d^3 X_{jr}\right) d\boldsymbol{p}_0\, d\boldsymbol{x}_0\, e^{-\beta(H_0 + \sum_{es} W_{es}^0)}$$
$$\times \prod_{jr} \left\{\int d\mathbf{p}_{jr}\, d\mathbf{x}_{jr}\, \delta^3\left(\sum_{h=1}^{j} \boldsymbol{\xi}_r^{(h)}\right) e^{-\beta(H_{jr} + W_{jr}^1)}\right\}.$$

(b) We assume that

$$\int dp_0\, dx_0\, e^{-\beta(H_0+\sum_{es} W^0_{es})} = N_0!\, N_B!\, h^{3(N_0+N_B)} Z_0(T, V_0, N_0, N_B) \times \prod_{es} \omega\left(e, v_{es}, T, \frac{N_0}{V_0}, \frac{N_B}{V_B}\right)$$

Z_0 is the partition function of the pure atmosphere, i.e. the integral above shall not depend on the positions of the droplets.

We combine the assumptions (a) and (b) in the following postulate which defines our model.

Postulate 1

$$\int dp\, dx\, e^{-\beta H_{fog}} = h^{3N_A+3N_B} N_0!\, N_B! \prod_j (j!)^{\lambda_j} \times Z_0(T, V_0, N_0, N_B) \prod_{jr} \left\{ V_0 \tilde{Z}\left(T, v_{jr}, j; \frac{N_0}{V_0}, \frac{N_B}{V_0}\right)\right\}$$

where $\tilde{Z}$ is the partition function of a droplet in the atmosphere whose centre of mass is held fixed ($\tilde{Z}$ has the dimension (Volume)$^{-1}$).

II.2. Statistics

The phase space corresponding to the factorization in postulate 1 is a rather complicated submanifold of $\mathbb{E}^{3N_A+3N_B} \times \mathbb{R}^{3N_A+3N_B}$ ($\mathbb{E}^{3N_A+3N_B}$ denotes the space of the coordinates of all particles in the system which form an $3N_A + 3N_B$ dimensional Euclidean space; $\mathbb{R}^{3N_A+3N_B}$ denotes the space of the momenta of all particles, which is a $3N_A + 3N_B$ dimensional real vector space; $\times$ denotes the cartesian product.) This phase space is characterized by the condition that all particles of the substance B and the particles with number $1, 2, 3, \ldots, N_0$ of the substance A have to be in the volume V_0 of the atmosphere, number $N_0 + 1, N_0 + 2$ in the volume $V_{2,1}$ of the first 'droplet' containing 2 molecules etc. V_0 and V_{jr} are disjoint and they build together the system's volume V. Apart from these constraints the droplet may move freely in V. We need some information about the statistical weight of a point in this phase space.

Let us first consider a system of N identical particles which all can move without restrictions in the same volume.

The notions 'state' and 'observable', familiar usually in quantum mechanics only, have a good meaning also in classical mechanics. A state φ is represented by a probability measure μ_φ over the phase space Γ, an observable A is represented by a measurable real function Φ_A over Γ. The expectation value of A in the state φ is given by

$$\langle A\rangle_\varphi = \int_\Gamma \Phi_A(q) d\mu_\varphi(q) = \int_\Gamma \Phi_A(q)\rho_\varphi(q)\, dq$$

where

$$q = (p_1 x_1, p_2 x_2, \ldots, p_N x_N)$$

denotes a point in the phase space $\Gamma = \mathbb{E}^{3N} \times \mathbb{R}^{3N}$ and $dq = dp^{3N}\, dx^{3N}$. ρ_φ is the probability density corresponding to the measure μ_φ. ρ_φ is positive and normalized:

$$\rho_\varphi \geqslant 0 \qquad \int_\Gamma \rho_\varphi(q)\, dq = 1.$$

'Identical particles' means physically that no observable exists, which distinguishes one particle from another. All observables must, therefore, be represented by symmetric functions, i.e.

$$(U_\pi \Phi_A)(q_1 \cdots q_N) \equiv \Phi_A(q_{\pi(1)} \cdots q_{\pi(N)}) = \Phi_A(q_1 \cdots q_N)$$

for all permutations π. $q_j \equiv \not{p}_j x_j$ denotes the momentum and the coordinates of the particle j.

Or one may say that the only identifying mark of a particle is the point in space it actually occupies. $\not{p}_i$ (the momentum of the ith particle) is, therefore, no observable but the momentum density of the system given

$$\Phi_{\not{p}(x)}(q) = \sum_{i=1}^{N} \not{p}_i \delta^3(x - x_i)$$

is an observable (which means: The momentum of the particle being at the place x).

What are the pure states of the system? The classical pure states are characterized by the requirement that all observables have sharp values. We assume for simplicity that all functions

$$\Phi\colon \Gamma \to \mathbb{R} \quad \text{with} \quad \Phi, \Phi^2 \quad \text{measurable,}$$

correspond to observables. One easily sees that the probability densities with the property that

$$\langle \Phi \rangle^2 = \left(\int_\Gamma \Phi \rho \, dq \right)^2 = \int_\Gamma \Phi^2 \rho \, dq = \langle \Phi^2 \rangle$$

for all the Φ's considered must have the form

$$\rho(q) = \sum_\pi \alpha_\pi \delta^{6N}(q - U_\pi q_0)$$

$$\alpha_\pi \geqslant 0 \qquad \sum_\pi \alpha_\pi = 1.$$

The expectation value of an observable does not depend on the choice of the α_π: every set α_π gives the same pure state for fixed q_0. The phase space is, therefore, not the space of the pure states; we have to identify first the points $U_\pi q_0$. Nevertheless, it is possible to parametrize the classical pure states by the points of the phase space, but we must then choose $1/N!\, dq$ as a volume element; every point q_0 carries only the $1/N!$-th part of a pure state.

If we now confine the phase space by constraints (for instance by dividing the system into spacially disjoint parts) and if we integrate only over the restricted space, we have to distribute a pure state among less than $N!$ points. The space of the pure state is the same in both cases, we only have changed the parametrization.

Thus, we are led to the following statistical postulate:

Postulate 2: Let $\Gamma \subset \mathbb{E}^{3N} \times \mathbb{R}^{3N}$ be the phase space of a system of N identical particles ($\mathbb{E}^{3N}$: space of the coordinates $\mathbb{R}^{3N}$ space of the momenta),

$$q_j = x_j \not{p}_j \qquad \text{the coordinates and momenta of particle } j$$

$$q = (q_1, \ldots, q_N)$$

$$dq = d^{3N}x \, d^{3N}p.$$

Then the partition function is given by

$$Z(T, N, \Gamma) = \int_\Gamma \frac{dq}{h^{3N}\mathscr{Z}_\Gamma(q)} \exp\left(-\frac{H(q)}{kT}\right).$$

$\mathscr{Z}_\Gamma(q)$ being the number of permutations π of N elements with the property, that $q \in \Gamma$ implies

$$U_\pi q = (q_{\pi(1)}, q_{\pi(2)}, \ldots, q_{\pi(N)}) \in \Gamma.$$

Let us check some consequences:

(i) We denote by $\Gamma_j \subset \mathbb{E}^3 \times \mathbb{R}^3$ the phase space of the point mass number j. If

$$\Gamma_1 = \Gamma_2 = \cdots = \Gamma_N,$$

we obtain for the phase space

$$\Gamma = \bigtimes_{j=1}^{N} \Gamma_j$$

of the N-particle system that

$$\mathscr{Z}_\Gamma(q) = N! \qquad \forall q \in \Gamma.$$

(ii) The N-particle system shall now be divided in z subsystems l ($l \in \{1, 2, \ldots, z\}$) containing n_l particles, each occupying a different volume. The n_1 particles of the subsystem 1 carry always the indices $1, 2, \ldots, n_1$ those of system 2 the indices $n_1 + 1, \ldots, n_1 + n_2$ and so on. Then

$$\mathscr{Z}_\Gamma(q) = \prod_{l=1}^{z} n_l! \qquad \forall q \in \Gamma.$$

If the interaction between particles in different systems can be neglected, the Helmholtz free energy is the sum of the free energies of the subsystems.

(iii) The N particles build a rigid body ($N \geqslant 3$). The phase space is a 12 dimensional surface in $\mathbb{E}^{3N} \times \mathbb{R}^{3N}$. Only permutations generating rigid rotations and translations of the body contribute to $\mathscr{Z}_\Gamma$ [5] (and one has also to replace h^{3N} by h^6).

We now determine $\mathscr{Z}_\Gamma$ for the fog. If the droplets could not move, then

$$\mathscr{Z} = N_B!\, N_0! \prod_j (j!)^{\lambda_j}. \tag{II.1}$$

What does their mobility change? First, the integral

$$\int d\mathbf{p}_{jr}\, d\mathbf{x}_{jr} \exp(-\beta(H_{jr} + W^1_{jr}))$$

augments by a factor V_0/V_{jr} at least. This is already taken into consideration in postulate 1. Secondly, the phase space grows. The droplets may exchange their positions. But as we keep the partition of the molecules into the droplets fixed and neglect the collisions, only the exchange of droplets with the same number of particles will add new permutations, totally $\prod \lambda_j!$ for each permutation of (II.1). This last step shows that macroscopic systems of same composition can be identified as molecules of a substance from the point of view of statistics.

We therefore write definitively:

$$\mathscr{Z}_{\mathrm{Fog}}(q) = N_B!\, N_0! \prod_j (\lambda_j)!\, (j!)^{\lambda_j}$$

and the partition function of fog becomes

$$Z = Z_0(T, V_0, N_0, N_B) \prod_j \left(\frac{V_0^{\lambda_j}}{\lambda_j!} \prod_r \tilde{Z}\left\{ T, v_{jr}, j; \frac{N_0}{V_0}, \frac{N_B}{V_0} \right) \right\}. \tag{II.2}$$

The partition function of a mixture of ideal gases with particle numbers λ_j masses m_j occupying the volume V_0 is given by

$$\prod_j \frac{V_0^{\lambda_j}}{\lambda_j!} \left(\frac{2\pi m_j kT}{h^2} \right)^{(3/2)\lambda_j}.$$

If in equilibrium the v_{jr} are the same for the same j we may consider the droplets of fog as an ideal mixture of ideal gases whose molecular mass depends on the 'quasivacuum' of the atmosphere [6].

II.3. The Helmholtz and Gibbs free energy

Applying Stirlings approximation

$$\ln \lambda! = \lambda(\ln \lambda - 1) + 0(\ln \lambda)$$

we obtain from (II.2) the following expression for the Helmholtz free energy of fog

$$F = -kT \ln Z = F_0(T, V_0, N_0, N_B) + \sum_{jr} F_j'\left(V_0; T, v_{jr}; \frac{N_0}{V_0}, \frac{N_B}{V_0} \right)$$
$$+ kT \sum_j \lambda_j(\ln \lambda_j - 1) \tag{II.3}$$
$$F_j' = -kT \ln \left(V_0 \tilde{Z}\left(T, v_{jr}; \frac{N_0}{V_0}, \frac{N_B}{V_0} \right) \right).$$

The equilibrium is given by minimizing F for the inner variables V_0, v_{jr}, N_0, λ_j, and observing that

$$N_0 + \sum_j j\lambda_j = N_A = \text{const} \tag{II.4a}$$

$$V_0 + \sum_{jr} V_{jr} = V = \text{const} \tag{II.4b'}$$

$$N_B = \text{const} \tag{II.4c}$$

$$T = \text{const} \tag{II.4d}$$

These restrictions concern only the volume V_{jr} of the droplet jr, not its shape. The latter may, therefore, be adapted individually and the actual shape is given by the minimum of F_{jr}', the number of particles of the droplet jr, its volume V_{jr}, T, N_0/V_0 and N_B/V_0 held fixed.

We denote this minimum by

$$F_j\left(V_0; T, V_{jr}; \frac{N_0}{V_0}, \frac{N_B}{V_0} \right) \tag{II.5}$$

and replace F_j' in (II.3) by (II.5). We make the assumption throughout the text that no isomerism occurs i.e., that the equilibrium conditions determine the value of the inner variables uniquely, which is the usual situation.

We now keep the λ_j fixed and vary only the V_{jr}, considering V_0 as a function of the V_{jr}. The total differential of the Helmholtz free energy F is then given by

$$dF = \sum_{jr} \left\{ -\frac{\partial F_0}{\partial V_0} - \frac{\partial F_j}{\partial V_0}\bigg|_{V_{jr}} + \frac{\partial F_j}{\partial V_{jr}} \right\} dV_{jr}.$$

The condition of equilibrium yields

$$-\frac{\partial F_j}{\partial V_0} + \frac{\partial F_j}{\partial V_{jr}} = \frac{\partial F_0}{\partial V_0},$$

which is the same condition for all r. We, therefore, set $V_{jr} = V_j \ \forall r$ and replace (II.4b′) by

$$V_0 + \sum_j V_j \lambda_j = V_0 = \text{const} \tag{II.4b}$$

and (II.3) by

$$F = F_0(T, V_0, N_0, N_B) + \sum_j \lambda_j \left\{ F_j\left(V_0; T, V_j; \frac{N_0}{V_0}, \frac{N_B}{V_0}\right) + kT(\ln \lambda_j - 1) \right\}. \tag{II.5}$$

It remains to find the minimum of (II.5) varying V_0, V_j, N_0, λ_j observing the restrictions (II.4). This is most easily achieved by the method of Lagrange multipliers which leads to

$$p = -\frac{\partial F}{\partial V}\bigg|_{N_A N_B T} = -\frac{\partial F_0}{\partial V_0} - \sum_l \lambda_l \frac{\partial F_l}{\partial V_0} = -\frac{\partial F_j}{\partial V_j} \tag{II.6a}$$

$$\mu_A = \frac{\partial F}{\partial N_A}\bigg|_{V N_B T} = \frac{\partial F_0}{\partial N_0} + \sum_l \lambda_l \frac{\partial F_l}{\partial N_0} \tag{II.6b}$$

$$\mu_B = \frac{\partial F}{\partial N_B}\bigg|_{V N_A T} = \frac{\partial F_0}{\partial N_B} + \sum_l \lambda_l \frac{\partial F_l}{\partial N_B} \tag{II.6c}$$

$$\lambda_j = \exp\left(\frac{j\mu_A - G_j}{kT}\right) \qquad G_j = F_j - V_j \frac{\partial F_j}{\partial V_j}. \tag{II.6d}$$

From (II.5) and (II.3) we deduce that F_j has the form

$$F_j = -kT \ln V_0 + \tilde{F}_j(T, V_j; \rho_0, \rho_B). \tag{II.7}$$

The dependency on ρ_0, ρ_B takes into account that the surface energy of a droplet may depend on the density of the atmosphere. The pressure p is, therefore, the sum of the atmospheric pressure

$$p_0 = -\frac{\partial F_0}{\partial V_0}$$

and an osmotic pressure, i.e. the partial pressures of ideal gases in the volume V_0 and with particle numbers

$$\lambda_l \left(1 + \frac{1}{kT}\left(\rho_0 \frac{\partial \tilde{F}_l}{\partial \rho_0} + \rho_B \frac{\partial \tilde{F}_l}{\partial \rho_B}\right)\right).$$

Let us now insert the equilibrium values (II.6) of the λ_j into (II.5). We suppose F_0 to be homogeneous of degree one in the parameters N_0, N_B, V_0.

Then

$$F = \frac{\partial F_0}{\partial N_0} N_0 + \frac{\partial F_0}{\partial N_B} N_B + \frac{\partial F_0}{\partial V_0} V_0 + \sum_j \lambda_j \left(j\mu_A + \frac{\partial F_j}{\partial V_j} V_j - kT \right)$$

$$= \mu_A N_A + \mu_B N_B - pV - \sum_j \lambda_j \left(N_0 \frac{\partial F_j}{\partial N_0} + N_B \frac{\partial F_j}{\partial N_B} + V_0 \frac{\partial F_j}{\partial V_0} + kT \right)$$

$$= \mu_A N_A + \mu_B N_B - pV$$

by reason of (II.7). F is, therefore, homogeneous of degree one in V, N_A, N_B. The quantities p, μ_A, μ_B are intensive and it is easy to show that λ_j, N_0, V_0 are extensive due to the special form (II.7) of F_j.

The Gibbs free energy is given by

$$G = F + pV = G_0(N_0, N_B, p_0, T) + V_0(p - p_0)$$
$$+ \sum_j \lambda_j \{ G_j(V_0; p, T; \rho_0, \rho_B) + kT(\ln \lambda_j - 1) \} \tag{II.8}$$

with

$$N_0 = N_A - \sum_j j\lambda_j \tag{II.9a}$$

$$p_0 = p + \sum_j \lambda_j \frac{\partial F_j}{\partial V_0} \tag{II.9b'}$$

$$V_0 = \frac{\partial G}{\partial p_0} \tag{II.9c}$$

$$G_j = -kT \ln V_0 + \tilde{G}_j(p, T; \rho_0, \rho_B). \tag{II.9d}$$

An easy calculation yields further

$$V_j = \left. \frac{\partial \tilde{G}_j}{\partial p} \right|_{T, \rho_0, \rho_B} \tag{II.10a}$$

$$\left. \frac{\partial \tilde{F}_j}{\partial \rho_0} \right|_{V_j T \rho_B} = \left. \frac{\partial \tilde{G}_j}{\partial \rho_0} \right|_{p T \rho_B} \tag{II.10b}$$

$$\left. \frac{\partial \tilde{F}_j}{\partial \rho_B} \right|_{V_j T \rho_0} = \left. \frac{\partial \tilde{G}_j}{\partial \rho_B} \right|_{p T \rho_0}. \tag{II.10c}$$

We may, therefore, replace (II.9b') by

$$p_0 = p + \sum_j \lambda_j \left. \frac{\partial G_j}{\partial V_0} \right|_{p, T, N_0, N_B} \tag{II.9b}$$

and have so eliminated the droplet volumes V_j; they can be calculated by (II.10a).

We now have to calculate the equilibrium distribution of the λ_j. We first consider N_B, p, N_0, λ_j, p_0 and V_0 as independent variables and hold T fixed. This leads to an

expression for the total differential dG of the Gibbs free energy given by

$$dG = \left(\frac{\partial G_0}{\partial N_B} + \sum_l \lambda_l \frac{\partial G_l}{\partial N_B}\right) dN_B + \left(V_0 + \sum_l \lambda_l \frac{\partial \tilde{G}_l}{\partial p}\right) dp$$
$$+ \left(\frac{\partial G_0}{\partial N_0} + \sum_l \lambda_l \frac{\partial \tilde{G}_l}{\partial N_0}\right) dN_0 + \sum_j (G_j + kT \ln \lambda_j)\, d\lambda_j$$
$$+ \left(\frac{\partial G_0}{\partial p_0} - V_0\right) dp_0 + \left(p - p_0 + \sum_l \lambda_l \frac{\partial G_l}{\partial V_0}\bigg|_{p,T,N_0,N_B}\right) dV_0.$$

Equations (II.9b,c) show that G does not depend at all on p_0 and V_0 and we get equations (II.6b,c,d) back now with p, T, N_A, N_B as independent variables. The homogeneity of G_0 and the structure (II.9d) of G_j imply the homogeneity of G in N_A, N_B and the extensivity of the λ_j as before.

Inserting (II.6d) into (II.8) and neglecting all terms containing $\partial \tilde{G}_l/\partial \rho_0$, $\partial \tilde{G}_l/\partial \rho_B$ we get

$$G = G_0(N_0, N_B, p, T) - \frac{1}{2}\frac{\partial G_0}{\partial p}(p - p_0)^2$$
$$+ \sum_j j\lambda_j \left(\frac{\partial G_0}{\partial N_0}\bigg|_p + \frac{\partial V_0}{\partial N_0}(p_0 - p)\right) - kT \sum_j \lambda_j$$
$$\Rightarrow$$
$$G = G_0(N_A, N_B, p, T) - kT \sum_j \lambda_j \left(1 + 0\left(\frac{\sum j\lambda_j}{N_0 + N_B}\right)\right).$$

This formula shows that (II.6d) gives indeed the equilibrium values of the λ_j.

Fog is in a stable equilibrium if the matrix

$$G_{mn} = \frac{\partial^2 G}{\partial \lambda_m \partial \lambda_n}\bigg|_{p,T,N_A,N_B}$$

is positive definite. The condition

$$\frac{\partial^2 G_0}{(\partial N_0)^2} + \sum_j \lambda_j \left\{\frac{\partial^2 \tilde{G}_j}{(\partial N_0)^2} - \left(\frac{\partial \tilde{G}_j}{\partial N_0}\right)^2\right\} > 0 \tag{II.11}$$

assures stability of fog (see Appendix A).

III. A Phenomenological Model of the Droplet

III.1. The model

The Gibbs free energy of a droplet in a metastable equilibrium with the atmosphere is given by

$$G_{\text{liq}}(j, N_C, p_0, T) + 3\left(\frac{4\pi}{3}\right)^{1/3} \sigma V^{2/3}. \tag{III.1}$$

(See for instance Ref. [6], §25.) σ denotes the surface tension and N_C indicates that the

droplet may contain a soluble substance C. We assume the following expression for the G_j of (II.6d):

$$G_j = -kT \ln \frac{V_0}{V^*} + G_{\text{liq}}(j, N_C, p_0, T) + 3\left(\frac{4\pi}{3}\right)^{1/3} \sigma V_j^{2/3} \tag{III.2}$$

V^* is a phenomenological parameter the dimension of which has to be a volume. It should be noted that G_j in (II.6d) is calculated with fixed center of mass. This is not taken into account in (III.1). Considering the correction factor so caused as weakly dependent on j we get a first contribution to V^*.

A second contribution is due to the fact that the thermodynamic potentials have to be considered as thermodynamical limits, i.e.:

$$F(j, V, T) = -kTj \lim_{n \to \infty} \frac{\ln Z(nV, nj, T)}{nj} = j \cdot f\left(\frac{j}{V}, T\right)$$

which assures the homogeneity of F. Introducing surface energies allows for contributions proportional to $j^{2/3}$; we incorporate the remainder in V^*. This remainder may give rise to large corrections: Rigid rotations of a water droplet by room temperature cause, for instance, a factor of about $10^5 j^{5/2}$ to λ_j [7].

The question if (III.1) contains rigid rotations, or, how they have to be taken into account cannot be answered in this thermodynamical framework, because these terms disappear in the thermodynamical limit. One has to calculate the state sum for a model of a explicitly finite droplet.

The measurements of the rate of (homogeneous) nucleation in super-saturated vapour indicate that $V^* \simeq 10^{-19}\ \text{cm}^3$ [8].

The terms of order $j^{1/3}$ taken into V^* become important for very small clusters. If the diameter of the droplet is comparable to the range of the intermolecular forces it is inappropriate to consider the surface as an infinitesimally thin dividing surface.

There is another reason why our model (1.1) may become less applicable as j decreases. We consider the interior of the droplet as a homogeneous phase characterized by its thermodynamic potentials, which makes sense only if the mean values tower the thermodynamic fluctuations; the fluctuations determine the minimal size of a piece of matter which can be reasonably described by thermodynamics. According to a well-known formula of statistical physics

$$\frac{\overline{(\Delta j)^2}}{j^2} = \frac{kT}{V_j} \varkappa_T$$

where $\varkappa_T$ is the isothermic compressibility. We have, therefore, the condition that

$$j \gg \frac{kT\varkappa_T}{v} \qquad v = \frac{V_j}{j}$$

which is always fulfilled by liquid droplets.

$kT\varkappa_T v^{-1} = 1$ for ideal gases: it makes no sense to speak of gas bubbles containing less than say 100 molecules.

In the rest of the paper we discuss the statement (III.2) for the case of pure fog and for fog around soluble nuclei.

III.2. Pure fog ($N_C = 0$)

We put $N_C = 0$ and $V_j = v_1 j$ in (III.2) and get

$$G_j = -kT \ln \frac{V_0}{V^*} + j\mu_1 + 3\left(\frac{4\pi}{3}\right)^{1/3} \sigma v_1^{2/3} j^{2/3} \qquad v_1 = \frac{\partial \mu_1}{\partial p}. \tag{III.3}$$

The index 1 denotes the pure liquid phase of the substance A. Equations (III.3), (II.6b), (II.6c) and (II.10b) give the following partition function for the droplets of pure fog

$$\lambda_j = \frac{V_0}{V^*} \exp(-\alpha j - \gamma j^{2/3}) \tag{III.4a}$$

with

$$\gamma = 3\left(\frac{4\pi}{3}\right)^{1/3} \frac{\sigma v_1^{2/3}}{kT}. \tag{III.4b}$$

$$\alpha = \frac{1}{kT}(\mu_1(p_0, T) - \mu_0(p_0, T)) - kT \sum_l \lambda_l \frac{\partial \tilde{G}_l}{\partial N_0}$$

$$\simeq \frac{1}{kT}(\mu_1(p_1 T) - \mu_0(p_1 T)) + \frac{\sum \lambda_l}{V_0}\left(\frac{\partial \mu_0}{\partial p} - \frac{\partial \mu_1}{\partial p}\right) \tag{III.4c}$$

if we neglect terms containing $\partial\sigma/\partial\rho_0$ and $\partial\sigma/\partial\rho_B$. We observe further that

$$\frac{1}{V_0} \sum_l \lambda_l \left(\frac{\partial \mu_0}{\partial p} - \frac{\partial \mu_1}{\partial p}\right) \simeq \frac{\sum_l \lambda_l}{N} \ll 1$$

which means that α is approximately given by

$$\alpha = \frac{1}{kT}(\mu_1(p, T) - \mu_0(p, T)). \tag{III.5}$$

For water droplets in air $\gamma \simeq 8$. ($T = 300°\text{K}$, $p = 10^6$ dyn cm^{-2}, $\sigma \simeq 70$ dyn cm^{-1}). The value of V^* mentioned above ($V^* \simeq 10^{-19}$ cm^3) shows that the concentration of the droplets which are reasonably described by our simple model ($j \geqslant 50$) is practically zero.

III.3. Fog around soluble nuclei

Our formula for the concentration λ_j of droplets containing j water molecules

$$\lambda_j = \exp \frac{j\mu_A - G_j}{kT} \tag{III.6}$$

has a general and discouraging property: λ_j is an exponential function of a difference of two terms which both have the order of magnitude j. We must either restrict ourselves to small j (which does not interest us here) or know G_j very accurately, in order to obtain a reasonable value for the λ_j given (III.6); or we introduce a fit-parameter as V^* i.e.; we use (III.6) only to calculate ratios λ_j/λ_l. We can, therefore, expect powerful results only in a situation where the total number of droplets is given as a fixed parameter: we consider fog around (soluble) dirt nuclei.

For simplicity, we assume that only one kind of soluble dirt is present; generalizations are evident. A species of droplets is now characterized by two indices: λ_{js} means the number of droplets containing j water molecules and s molecules or ions of

the dirt. The total number n_s of nuclei containing s dirt molecules (ions) is taken to be a fixed external parameter of the system, and is given by

$$n_s = \sum_{j=0} \lambda_{js} \qquad \lambda_{js} \geqslant 0. \tag{III.7}$$

The generalization of (II.5) is

$$F = F_0(T, V_0, N_0, N_B) + \sum_{js} \lambda_{js}\{F_{js}(V_0; T, V_{js}; \rho_0, \rho_B) + kT(\ln \lambda_{js} - 1)\}, \tag{III.8}$$

with

$$F_{js} = -kT \ln V_0 + \tilde{F}_{js}(T, V_{js}; \rho_0, \rho_B).$$

We look for the minimum of F, varying the inner parameters V_0, V_{js}, N_0, λ_{js}, under the restrictions

$$\sum_{js} V_{js}\lambda_{js} + V_0 = V \tag{III.9a}$$

$$\sum_{js} j\lambda_{js} + N_0 = N_A \tag{III.9b}$$

$$\sum_{j \geqslant 0} \lambda_{js} = n_s \tag{III.9c}$$

$$T = \text{const} \qquad N_B = \text{const} \tag{III.9c}$$

We write the result in the following manner:

$$\lambda_{js} = \Lambda_s^0 \frac{\exp \frac{1}{kT}(j\mu_A - g_{js})}{\sum_l \exp \frac{1}{kT}(\rho\mu_A - g_{ls})} \tag{III.10a}$$

$$\Lambda_s^0 = \sum_{j>0} \lambda_{js} = n_s - \lambda_{0s} = \frac{n_s}{1 + \left(\sum_l \exp \frac{1}{kT}(G_{0s} + \rho\mu_A - G_{ls})\right)^{-1}} \tag{III.10b}$$

$$\mu_A = \frac{\partial F}{\partial N_A} = \frac{\partial F_0}{\partial N_0} + \sum_{js} \lambda_{js} \frac{\partial F_{js}}{\partial N_0} \simeq \mu_0 \tag{III.10c}$$

g_{js} is given by G_{js} minus all terms in G_{js} not depending on j.

$(1/kT)(G_{0s} + j\mu_A - G_{js})$ is a difference of macroscopic energies measured with the microscopic unit kT. Λ_s^0 is, therefore, always practically equal to n_s or to zero. g_{js} does not contain any constant V^*. The restrictions (III.9c) convert the peculiar structure (III.6) of λ, we had complained at the beginning, into a help, leading to the beautiful law (III.10)!

What is G_{js}? We expect that typically $j \gg s \gg 1$ i.e., that we are in the osmotic limit. In this case we have that (see Appendix B and (III.2))

$$G_{js} = -kT \ln \frac{V_0}{V^*} + skT\left(\ln s + \frac{\tilde{\mu}_2}{kT} + \varphi_2^1 - 1\right)$$
$$+ j\tilde{\mu}_1 + kT\gamma j^{2/3} - kTs\left(\ln j + 0\left(\left(\frac{s}{j}\right)^{\epsilon}\right) + 0(j^{-1/3})\right). \tag{III.11a}$$

The term $s0(j^{-1/3})$ takes into account that the volume of the droplet depends on s also.

If $j \gg s \gg 1$ we have, therefore,

$$\frac{1}{kT}(g_{js} - j\mu_A) \equiv \varphi(j, s) = \alpha j + \gamma j^{2/3} - s \ln j \tag{III.11b}$$

α, γ are as in (III.4). For fixed s, $\varphi(j, s)$ has in $0 < j < \infty$ one minimum which is very sharp for the values of α, γ, s in which we are interested. We may, therefore, put

$$\frac{e^{-\varphi(j,s)}}{\int_0^\infty dj e^{-\varphi(j,s)}} = \delta(j - j_0) \tag{III.12}$$

with $j_0(\alpha, \gamma, s)$ as the only positive solution of

$$\frac{\partial \varphi}{\partial j} = \alpha + \tfrac{2}{3}\gamma j^{-1/3} - sj^{-1} = 0. \tag{III.13}$$

The quantity,

$$\left(j_0^2 \frac{\partial^2 \varphi}{(\partial j)^2}\bigg|_{j_0}\right)^{-1} = \frac{\partial \ln j_0}{\partial s}, \tag{III.14}$$

is the relative width of the distribution $e^{-\varphi(j)}$.

(III.13) is a cubic equation in j which may be solved exactly. But the algebraic representation of the one positive solution $j_0(\alpha)$ changes as α grows; equation (III.13) has three real roots for $\alpha = 0$ and one real and two conjugate complex roots for big α's. We, therefore, proceed in a different way. We write (III.13) in the form

$$x = a + x^{1/3}$$

$$x = \frac{s}{j}\left(\frac{3s^{1/3}}{2\gamma}\right)^{3/2} \qquad a = \alpha\left(\frac{3s^{1/3}}{2\gamma}\right)^{3/2} \geqslant 0$$

and solve it by iteration:

$$x_0 = x|_{a=0} = 1$$

$$x_n = a + x_{n-1}^{1/3} \qquad n \in \mathbb{N}.$$

How fast does the iteration converge? We see that for $n \geqslant 2$

$$\Delta_n = \frac{x_n - x_{n-1}}{x_{n-1}} = x_{n-1}^{-2/3}(1 - (1 + \Delta_{n-1})^{-1/3})$$

and $\Delta_1 = a \geqslant 0$, i.e. $x_{n+1} \geqslant x_n \geqslant \cdots \geqslant x_0 = 1$, and

$$0 \leqslant \Delta_n \leqslant x_1^{-2/3}\frac{\Delta_{n-1}}{3} = \frac{\Delta_{n-1}}{3(1 + a)^{2/3}} \leqslant \Delta_2\left(\frac{1}{3(1 + a)^{2/3}}\right)^{n-2}$$

$$\Delta_2 = (1 + a)^{-2/3} - (1 + a)^{-1}.$$

Therefore ($n \in \mathbb{N}$)

$$\frac{x_\infty - x_n}{x_\infty} \leqslant \sum_{l=n+1}^{\infty} \Delta_l \leqslant \frac{1 - (1 + a)^{1/3}}{(1 + a)^{2/3} - \frac{1}{3}}(3(1 + a)^{2/3})^{1-n} < 0.18(3(1 + a)^{2/3})^{1-n},$$

and thus x_1 is a good approximation for our purpose and we obtain

$$j_0 = s\left(\alpha + \left(\frac{2\gamma}{3}\right)^{2/3} s^{-1/2}\right)^{-1}. \tag{III.15}$$

Formula (III.14) indicates a relative width of the order s^{-1}.

We now have to calculate the quantity Λ_s^0 in formula (III.10b). The statement (III.11) for G_{js}

$$G_{js} = -kT \ln \frac{V_0}{V^*} + s\tilde{\mu}_2 + kTs(\ln s - 1 + \varphi_2^1) + g_{js}$$

and a statement of the type (III.2) for G_{0s}

$$G_{0s} = -kT \ln \frac{V_0}{V_s^*} + s\tilde{\mu}_2 + kT\gamma_s s^{2/3}$$

together with the form (III.12) of the droplet distribution yield

$$\begin{aligned}\frac{\Lambda_s^0}{\lambda_{0s}} &= \sum_j \exp \frac{1}{kT}(G_{0s} + j\mu_A - G_{js}) \\ &\simeq \exp\left(\gamma_s s^{2/3} + \ln \frac{V_s^*}{V^*} - s(\ln s - 1 + \varphi_2^1) - \varphi(j_0, s)\right) \\ &\simeq \exp(s\{\ln Q - \tfrac{1}{3}\gamma s^{-1/3} Q^{2/3} - \varphi_2^1\}).\end{aligned}$$

To perform the last step we use equation (III.15) and the conditions

$$s \gg 1, \qquad Q = \frac{j_0}{s} \gg 1.$$

We finally obtain

$$\Lambda_s^0 = n_s\left(1 + \frac{\lambda_{0s}}{\Lambda_s^0}\right)^{-1} \simeq n_s \Theta(\ln Q - \tfrac{1}{3}\gamma s^{-1/3} Q^{2/3} - \varphi_2^1) \tag{III.16a}$$

with

$$\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} \tag{III.16b}$$

and

$$Q = (\alpha + (\tfrac{2}{3}\gamma)^{3/2} s^{-1/2})^{-1}. \tag{III.16c}$$

It follows from equations (III.16) that

$$\ln Q > \varphi_2^1 + \tfrac{1}{2}$$

is a sufficient condition that $\Lambda_s^0 \simeq n_s$. But the solubility of substance 2 in substance 1 implies only that

$$\frac{\Delta G}{kT} = -s(\ln Q - \varphi_2^1 + 1 + 0(Q^{-\epsilon})) < 0$$

i.e.

$$\ln Q > \varphi_2^1 - 1 + 0(Q^{-\epsilon}).$$

Therefore, we cannot expect that every soluble substance causes fog.

We illustrate (III.15) by an example. α given by formula (III.5) is approximately

$$\alpha \simeq \frac{p_s - p}{p_s}. \tag{III.17}$$

(We expand the chemical potentials around the saturation pressure $p_s(T, N_0/N_B)$, consider air as an ideal gas and neglect the specific volume of the liquid.) Let s be of the order 10^{10}, $(\frac{2}{3}\gamma)^{3/2} = 12.3$ for water–air by 300°K. (III.15) shows that j_0 falls very rapidly if α becomes different from zero.

$$j_0 = \left(\frac{3s}{2\gamma}\right)^{3/2} \quad \text{if } \alpha = 0 \qquad j_0 \simeq 10^{14} \quad \alpha = 0$$

$$j_0 = \frac{s}{\alpha} \quad \text{if } \alpha > \left(\frac{2\gamma}{3}\right)^{3/2} s^{-1/2} \simeq 10^{-4} \begin{cases} j_0 \simeq 10^{13} & \alpha = 10^{-3} \\ j_0 \simeq 10^{12} & \alpha = 10^{-2}. \end{cases}$$

Fog, therefore, exists only very near saturation and then

$$j_0 = \left(\frac{3s}{2\gamma}\right)^{3/2}. \tag{III.18}$$

This formula is in agreement with experiment. Droplets in sea clouds have radii between $2.5 \cdot 10^{-4}$ cm and $2 \cdot 10^{-3}$ cm, droplets with radius $1.1 \cdot 10^{-3}$ cm are the most frequent [9].

If we assume saturation and NaCl as nuclei, we get

r [cm]	j_0 measured	s calculated with (III.18)	m_{NaCl} [gr]
2.5×10^{-4}	2.3×10^{12}	9.2×10^{8}	4.4×10^{-14}
1.1×10^{-3}	1.6×10^{14}	1.6×10^{10}	7.8×10^{-13}
2.0×10^{-3}	1.1×10^{15}	5.8×10^{10}	2.8×10^{-12}

The observed masses of salt nuclei lie between 10^{-15} gr and 5×10^{-10} gr [10].

III.4. A remark about fog around insoluble nuclei

In contradistinction to the situation discussed in III.3 every nucleus has its distinct form which corresponds to a metastable state rather than to equilibrium. But to assure the right homogeneity behaviour of the system – i.e.: the additivity of the Helmholtz free energy – we have nevertheless to introduce classes s of identical nuclei which may be characterized by the same number of particles, the same form of the surface, etc. The numbers n_s of the nuclei of the species s are fixed parameters of the system. We proceed as in III.3 and obtain the result

$$\lambda_{js} = n_s \frac{\exp(1/kT)(j\mu_A - G_{js})}{\sum_l \exp(1/kT)(l\mu_A - G_{ls})}. \tag{III.19}$$

But the classes s of identical nuclei and, therefore, the λ_{js} are rather artificial. It is not possible to separate these classes by experiment. A quantity which is measurable is

$$\lambda_j = \sum_s \lambda_{js} = \sum_s n_s \frac{\exp(1/kT)(j\mu_A - G_{js})}{\sum_l \exp(1/kT)(l\mu_A - G_{ls})} \tag{III.20}$$

Equation (III.20) shows that the identification of nuclei depends only upon the functions G_{js}, which means that a phenomenological thermodynamic description of the nuclei is enough to determine the total number λ_j of droplets containing j water molecules.

Acknowledgements

The author feels much indebted to Prof. Baltensperger and Prof. Jost of the ETH in Zürich for their encouragement and for many helpful discussions. He also thanks Dr. Haley who eliminated numerous grammatical errors and improved much the formulation of the paper.

Appendix A: Stability

$$G_{mn} = \left.\frac{\partial^2 G}{\partial\lambda_m \partial\lambda_n}\right|_{pTN_A N_B} = D_m D_n - C_m C_n + \frac{\delta_{mn}}{\lambda_m}$$

with

$$\lambda_m > 0$$

$$C_m = \frac{\partial \tilde{G}_m}{\partial N_0}\left(\frac{\partial^2 G_0}{(\partial N_0)^2} + \sum_l \lambda_l \frac{\partial^2 \tilde{G}_l}{(\partial N_0)^2}\right)^{-1/2}$$

$$D_m = \frac{m}{C_m}\frac{\partial \tilde{G}_m}{\partial N_0} - C_m$$

G_{mn} is positive definite, if and only if

$$\sum_{mn} x_m(\sqrt{\lambda_m}\, G_{mn}\sqrt{\lambda_n})x_n \geqslant 0 \qquad \forall x_m \in \mathbb{R}$$

and

$$\sum_{mn} x_m(\sqrt{\lambda_m}\, G_{mn}\sqrt{\lambda_n})x_n = 0 \Rightarrow x_m = 0\ \forall_m$$

or: the corresponding eigenvalue-problem

$$(\mathscr{d}, \mathscr{x})\mathscr{d} - (\mathscr{c}, \mathscr{x})\mathscr{c} = (E - 1)\mathscr{x}$$

$$\mathscr{d} = (d_1, d_2, \ldots, d_m, \ldots) \qquad d_m = \sqrt{\lambda_m}\, D_m$$

$$\mathscr{c} = (c_1, c_2, \ldots, c_m, \ldots) \qquad c_m = \sqrt{\lambda_m}\, C_m$$

has only positive eigenvalues E.

$\mathscr{x}$ lies in the plane spanned by $\mathscr{c}$ and $\mathscr{d}$ if $E \neq 1$. We choose, therefore, coordinates so that

$$\mathscr{d} = d(1, 0, \ldots, 0, \ldots)$$

$$\mathscr{c} = c(u, v, 0, \ldots, 0, \ldots)$$

$$c, d > 0 \qquad u^2 + v^2 = 1.$$

We have then to diagonalize the 2×2 matrix

$$\begin{pmatrix} d^2 - c^2u & -c^2uv \\ -c^2uv & -c^2v^2 \end{pmatrix}$$

The eigenvalues are

$$E_\pm = 1 + \frac{d^2 - c^2}{2} \pm \sqrt{\left(\frac{d^2 - c^2}{2}\right)^2 + d^2c^2v^2}$$

$\min(E_+, E_-) = E_- > 0$ is equivalent to

$$(1 - c^2)(1 + d^2) + (\mathscr{d}, \mathscr{c})^2 > 0 \qquad \text{and} \qquad 1 + \frac{d^2 - c^2}{2} > 0$$

$c^2 < 1$ (i.e. (II.11)) is, therefore, sufficient for stability.

Appendix B: The Thermodynamics of Mixtures

B.1. Ideal mixtures

Let $A_1, \ldots, A_M$ denote M different substances each characterized by its Helmholtz free energy $F_m(N_m, V, T)$.

Definition: The mixture of the substances $A, \ldots, A_M$ is called ideal, if the free energy of the mixture is given by

$$F(\mathscr{N}, V, T) = \sum_{m=1}^{M} F_m(N_m, V, T)$$

$$\mathscr{N} = (N_1, N_2, \ldots, N_M).$$

Dalton's law is valid for ideal mixtures

$$p = -\frac{\partial F}{\partial V} = \sum_m -\frac{\partial F_m}{\partial V} = \sum_m p_m(N_m, V, T)$$

and

$$S(\mathscr{N}, V, T) = \sum_{m=1}^{M} S_m(N_m, V, T)$$

$$G(\mathscr{N}, p, T) = \sum_m G_m(N_m, p_m, T).$$

Definition: We call the mixing part of the Gibbs' free energy

$$\Delta G(\mathscr{N}, p, T) = G(\mathscr{N}, p, T) - \sum_m G_m(N_m, p, T).$$

In the case of an ideal mixture, we have

$$\Delta G = \sum_m \int_p^{p_m} V_m(N_m, p', T)\, dp'$$

and for an ideal mixture of ideal gases

$$\Delta G(\mathcal{N}, p, T) = kT \sum_m N_m \ln x_m$$

$$\Delta S(\mathcal{N}, p, T) = -k \sum_m N_m \ln x_m$$

$$\mu_m(x, p, T) = \tilde{\mu}_m(p, T) + kT \ln x_m$$

$$x_m = N_m \left(\sum_n N_n \right)^{-1}$$

$\tilde{\mu}_m$ being the chemical potential of the pure mth substance.

B.2. Non ideal mixtures

One expects that the mixture becomes an ideal mixture of ideal gases in the limit $p \to 0$ and makes the statement

$$\Delta G(\mathcal{N}, p, T) = kT \sum_m N_m (\ln x_m + \Phi_m(x, p, T))$$

where

$$\lim_{p \to 0} \Phi_m(x, p, T) = 0$$

and

$$\lim_{x_j \to 1} \Phi_j(x, p, T) = 0 \qquad \text{by definition.}$$

The homogeneity of G implies

$$\sum_m x_m \, d\Phi_m \Big|_{pT} = 0$$

or marking the substance number 1

$$q_m = \frac{x_m}{x_1} \qquad m \in \{2, 3, \ldots, M\}$$

$$d\Phi_1 = \sum_{l=2}^{M} - \left(\sum_{m=2}^{M} q_m \frac{\partial \Phi_m}{\partial q_l} \right) dq_l = \sum_{l=2}^{M} f_l(q, p, T) \, dq_l$$

$\Phi_1(o) = 0$ and we get, therefore, for fixed p, T

$$\Phi_1(\mathcal{Q}) = \int_{\mathcal{P}} (\mathbf{f}, d\mathbf{s}) = -(\mathcal{Q}, \mathbf{\Phi}) + \int_{\mathcal{P}} (\mathbf{\Phi}, d\mathbf{s})$$

$$\mathbf{f} = (f_2, \ldots, f_m) \qquad (\mathcal{Q}, \mathbf{\Phi}) = \sum_{m=2}^{M} Q_m \Phi_m$$

and $\mathcal{P}$ is a (sufficiently smooth) path, connecting $\mathcal{Q}$ with the origin of the $\mathcal{Q}$-space.

The homogeneity of ΔG means that $\mathbf{\Phi}$ is a gradient field. The integral depends only from the boundary points of $\mathcal{P}$ i.e.: Φ_1 is completely determined by the other Φ_m.

If there exist positive real figures a, ϵ, δ so that

$$\|\text{grad } \Phi_m(q)\| \leqslant a\|q\|^{1-\epsilon} \qquad m \in \{2, \ldots, M\}$$

for all

$$\|q\| = \left(\sum_{m=2}^{M} q_m^2\right)^{1/2} \leqslant \delta$$

one easily shows that (for $\|q\| \leqslant \delta$)

$$|\Phi_1(q)| \leqslant \frac{a\sqrt{M-1}}{1+\epsilon} \|q\|^{1+\epsilon}$$

$$|\Phi_m(q) - \Phi_m(o)| \leqslant \frac{a}{\epsilon} \|q\|^{\epsilon} \qquad m \in \{2, \ldots, M\}.$$

$\Phi_m(o) = \varphi_m^1(p, T)$ is determined by the components A_1 and A_m only. These inequalities indicate a general law for the Gibbs' free energy of dilute mixtures [11], which in the case of a two component mixture reads as

$$G = N_1\tilde{\mu}_1(p, T) + kTN_2\left(\ln \frac{N_2}{N_1} + \frac{\tilde{\mu}_2(p, T)}{kT} + \varphi_2^1(p, T) - 1 + 0\left(\left(\frac{N_2}{N_1}\right)^{\epsilon}\right)\right)$$

REFERENCES

[1] Kelvin, Lord, Proc. R. Soc. Edinb. *7*, 63 (1870).
[2] Frenkel, J., *Kinetic theory of liquids* (Dover publications, Inc., New York 1955), p. 366ff.
[3] Frenkel, J., loc. cit. p. 382.
[4] Lothe, J. and Pound, G. M., J. Chem. Phys. *45*, 630 (1966).
[5] Ehrenfest, P., Trkal, V., Annalen der Physik *65*, 609 (1921).
[6] Falk, G., *Theoretische Physik II. Thermodynamik* (Heidelberger Taschenbücher 27, Springer-Verlag 1968), § 28, p. 161ff.
[7] Lothe, J., Pound, G. M., J. Chem. Phys. *36*, 2080 (1962).
[8] Tschudi, H. R., to be published.
[9] Mason, B. J., *The physics of clouds* (Clarendon Press, Oxford 1971), p. 112.
[10] Mason, B. J., loc. cit. p. 75ff.
[11] Kortüm, G., *Einführung in die chemische Thermodynamik* (Vandenhoeck & Ruprecht, Göttingen 1966), p. 207ff.