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Notes on the Discovery and Theory of Vapor Condensation in the Supersaturated State.*

Die drei Phasen der Materie (fest, flüssig, gasförmig) befinden sich im allgemeinen im thermodynamischen Gleichgewicht. Unter ungewöhnlichen Umständen - z. B. Abwesenheit von Kondensationskernen, sehr schnelle Zustandsänderungen, usw. - ist es aber möglich, daß übersättigte Zustände eines Dampfes auftreten. Dann entstehen Nichtgleichgewichtsprozesse, die sich der thermodynamischen Beschreibung entziehen; die Theorie des Phasengleichgewichts muß zu einer kinetischen Theorie erweitert werden. Die neue Betrachtung ist der Beschreibung chemischer Reaktionen verwandt. Die Frühgeschichte der Entdeckung dieser ungewöhnlichen Zustände im letzten Jahrhundert wird beschrieben und Theorie und Experiment werden bis zu ihrem jetzigen Status verfolgt. Dies interessante Gebiet hat viele Anwendungen grundsätzlicher und angewandter Art. Die Entstehung unseres Sonnensystems, die Stratosphärenchemie und die Strömung in Dampfturbinen sind Beispiele von Prozessen, die nur im Zusammenhang mit dem Verständnis der Kondensation übersättigter Dämpfe verstanden werden können.

All around us we find matter in its three phases; gaseous, liquid and solid. If phase transformations occur, they normally take place in thermodynamic equilibrium. The falling rain, the crystallization of sugar in honey, and many other examples testify to this effect. However, here we shall look at the condensation of supersaturated vapors, an unusual process of intrinsic interest. Yet in addition important practical aspects in fields as diverse as stratospheric chemistry and steam turbine technology draw on the difficult aspects of non-equilibrium condensation. A vapor is called supersaturated if its state - i. e. pressure and temperature - lie in a range in which normally the vapor would be liquefied or solidified, while in fact it remains in gaseous form. At such states it will condense only under certain circumstances in case no aerosols, surfaces, etc. are available for the deposition of the higher phase. If condensation takes place, a *kinetics* of phase change - not unlike chemical kinetics - arises. Dunning (1969) notes that James Thomson in 1859 proposed the principle that »particles of a substance when existing all in one state only and in continuous contact with one another or in contact only under special circumstances

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with other substances experience a difficulty of making a beginning of their change of state -«. In 1886 Robert von Helmholtz, the brother of the famous physicist, observed supersaturation in a jet of water vapor issuing from a small orifice. No droplets were observed at states where normally the vapor would have condensed. He was the first to note that supersaturation depended in part on the time scale of a given experiment with very rapid expansions delaying condensation. Thermodynamics deals with equilibrium states, time does not enter and therefore at this early stage of studies of supersaturated systems an apparently strange blending of thermodynamics and chemical kinetics arose. This oddity led for a time to the isolation of the field from the main corpus of physical chemical theory to paraphrase Dunning. In our generation Mayer's statistical mechanical theory of condensation has reconciled these initial difficulties.

In 1880 Aitken started his life-long studies of condensation nuclei in atmospheric physics. He categorized the various tiny particles of dust, salts, large ions, etc. that float around in air and that form the centers of condensation for rain and snow. Here condensation occurs at equilibrium, i.e. at a relative humidity of 100%. The invention of the supersonic steam nozzle by de Laval in 1889 led to continuous research in condensation in conjunction with steam turbines. Here the steam does indeed supersaturate before condensing as a consequence of the very rapid expansion at cooling rates of about one degree per microsecond. Wilson began his classical cloud chamber work in 1887. Expanding highly purified moist air in a piston cloud chamber led to the first quantitative experiments in the field. Wilson achieved vapor pressures prior to condensation that were from about four to six times the value of the equilibrium vapor pressure before fog was formed by clustering of water molecules forming small droplets without one of Aitken's aerosols in their center. Wilson's chamber provided an essential tool in physics to trace the path and interaction of subatomic particles. The field entered aerodynamics in 1935 at the Volta Congress in Rome when Prandtl of Göttingen - the founder of modern fluid dynamics - produced photographs of strange disturbances in the flow of supersonic nozzles. In such nozzles moist air moves at speeds faster than the speed of sound (340 m/s at room temperature), and at cooling rates equal to those of Laval's steam nozzles, condensation of the water vapor is delayed. This puzzle was clarified by Wieselsberger of Aachen in the discussion that followed Prandtl's remarks. Oswatitsch finally in 1942 combined the theory of nucleation in the absence of aerosols (see later) with a solution of the equations of motion of the flow and his basic ideas prevail today.

Prior to the earliest observations of delayed condensation Laplace in discussing the mechanical equilibrium of a liquid surface in 1806, laid the foundation of our understanding of condensation in the supersaturated

state. He demonstrated that the pressure in a drop is higher than the surrounding pressure by a value that is given by twice the surface tension of the liquid divided by the drop radius. In 1870 William Thomson (later Lord Kelvin) derived the complete expression for this fact. This work proved that a vapor may be saturated with respect to a drop of large - or even infinite - radius and not be saturated with respect to small droplets. This result furthermore pointed the way to an understanding of the problem at hand - for decreasing droplet radii the vapor pressure increases strongly with respect to that at equilibrium for a flat surface. In parallel J. Willard Gibbs - possibly the greatest scientist of the United States to date - did his seminal work in thermodynamics in isolation at Yale University in Connecticut. He derived the same equation as Kelvin and found an expression for the work needed to form a droplet in the vapor phase. He was the first to relate equilibrium thermodynamics to the stability of phases. He introduced the notion of a *critical nucleus* - a droplet of a certain critical radius that could grow dramatically once its size is minutely increased. The determination of the energy required to form this critical nucleus in a given vapor at a certain pressure and temperature, is the first requirement of a theory of phase change in the supersaturated state.

The second problem in this theory relates to the rate of formation per unit volume of these critical droplets in the pure vapor. An expression for this nucleation rate was first suggested by Volmer and Weber in 1926. With these two formulations - energy and rate of formation of critical nuclei - a theory of homogeneous nucleation was established, a theory that is applicable only in the complete absence of surfaces and foreign substances such as aerosols like dust, salts, large ions and the like.

To give an outline of the theory of *homogeneous nucleation* of a single vapor we first turn to the thermodynamic model of the energy required to form a droplet in the supersaturated vapor. We assume an isothermal, reversible process consisting of five steps. We start with the removal of n molecules (or atoms) from the vapor space, an isothermal expansion to the equilibrium vapor pressure, condensation on a flat surface, formation of a spherical droplet of these n molecules - here the work against the surface tension of the liquid must be performed -, and a return of the droplet to the original state. Since the energy of the system must be identical before and after droplet formation, an amount of heat equal to the energy of drop formation must be removed to the extended vapor space. In carrying out this calculation as a function of the number of molecules in the drop we note the remarkable fact that the energy difference of molecules in the vapor or in a spherical liquid drop shows a maximum at a given value of n . At this energy maximum we define the *critical nucleus* previously discussed. Once the drop grows beyond this

critical size, rapid complete condensation ensues. The state at the energy maximum has been termed metastable by Volmer (1939) since conversely the removal of a single molecule from the critical droplet leads to its total disintegration. This classical approach to determine the energy, size, etc. of a droplet of critical size is described as the *capillarity* or *liquid drop* model. A similar approach was independently found useful in nuclear physics to estimate the energy of atomic nuclei.

To prepare the way for the complete theory of homogeneous nucleation we must next determine the rate of nucleation of nuclei of the critical size. This is the second required component of the theory and we move to a statistical view. Let us recall that unless critical nuclei are formed, condensation will not occur although the vapor is supersaturated. Smaller than critical droplets will disintegrate, while rapid further drop growth is only assured once the critical energy hump is surpassed. An equilibrium distribution of droplets of all sizes including the critical one can be found by applying the law of mass action to the »chemical reaction« of capture and expulsion of single molecules by droplets. This approach is independent of an a priori assumption of a certain droplet model, e.g. solid crystalline or amorphous clusters could be equally treated. The solution to the problem lies in the assignment of the proper partition functions for a droplet of a certain size in the bulk liquid of infinite size versus the same droplet in the vapor space. This assignment requires a better understanding of the fundamental problems of the liquid state. Again - as in the energy calculation using the liquid drop model - we have to resort to a certain model. In fact Kuhrt in 1952 pointed out that our simple drop model omits energy contributions due to Brownian motion and he was the first to extend the simple approach given here.

Volmer and Weber (1926) gave the first expression for the rate of formation of nuclei of the critical size. Based on Einstein's theory of fluctuations (1910) they assumed that this rate is proportional to a Boltzmann factor. The work to form one nucleus is accompanied by an entropy *decrease* of equal magnitude. However, as stated before the latent heat of condensation is ignored owing to the great extent of the vapor space. Volmer's resulting equation for the rate of formation is reminiscent of the Arrhenius activation energy for a chemical reaction. The rate is proportional to an inverse exponential whose exponent is equal to the previously derived work of formation of the critical droplet - or cluster in the case of solids. Volmer's original work gave this functional relationship, the missing kinetic factor was provided by Farkas one year later in 1927. Every collision of vapor molecules is a potential start toward nucleus formation. Continually dimers, trimers, etc. are formed or disintegrated due to random collisions. Based on an idea of Szilard as cited by Farkas, a differential equation for the diffusion flux of growing and

disappearing droplets describes the missing kinetics. A fictitious steady state is postulated for the nucleation of critical droplets in order to integrate the flux equation. Whenever a critical nucleus is born it is discarded and the system is replenished by a number of monomers equal to the number of molecules (or atoms) in the critical drops. The combination of drop energy computed for the liquid drop model and the Farkas approach yield the complete theory of homogeneous nucleation. A great deal of work was, however, performed to study refinements, modifications, improvements, etc., none of which have drastically altered what has been said here. Finally experimental methods have been much extended and improved in recent years, they still encompass modern versions of Wilson's cloud chamber. The steady-state diffusion cloud chamber and the double piston chamber have been added in parallel to extended use of gasdynamic methods like the supersonic nozzle, shock tube, and combinations thereof. Remarkable agreement of theory and experiment was found for many vapors, among them water vapor, alcohol vapors, benzene, sulfur hexafluoride, nitrogen, and tetrachloride. The theory was further extended to treat binary nucleation, the simultaneous condensation of a mixture of two supersaturated vapors. It is here that serious environmental interest exists in handling the acid-water systems present in automotive emissions, emissions from power plants, etc.

The final advance in the theory of homogeneous nucleation relates to the recent advances in chemical physics connected with numerical solutions of the structure of complex assemblies of atoms. Clearly at low temperatures and low pressures when critical nuclei approach molecular dimensions, thermodynamics is expected to fail. The liquid drop model must be replaced by cluster energy calculations of a more fundamental type. Assuming atoms obey e.g. a Lennard-Jones interaction potential, minimum energies to form clusters can be computed by a solution of the appropriate partition function. Such calculations have been carried out e.g. for argon assuming non-crystalline structures (Hoare and Pal 1975). Calculating appropriate energies of formation of the argon cluster and embedding this calculation in the rate equation for nucleation gave excellent agreement with experiments as shown by Hoare, Pal and Wegener (1980). Using for the same purpose molecular dynamics (McGinty 1973) and Monte-Carlo type calculations (Garcia and Torroja 1981), agreement with experiment could also be achieved (Wegener 1986). Indeed such calculations could be extended to a molecule, here nitrogen (Pal 1984) yielding good agreement with experiment at low temperatures (Wegener 1986). It is to be hoped that in the future the important practical vapors, in particular water can be handled theoretically in view of the many applications. Such work might even include quantum mechanical models.

In sum, non-equilibrium condensation studies have come a long way since the middle of the last century and recent advance in theory and experiment pave the way for the understanding of new domains in chemical physics. It may be assumed that these developments will impinge on astrophysical problems on clustering in the early days of the solar system or the formation of galaxies.