

6) Temperature differences between a liquid and the vapor evolving from it

a) A solution and its vapor

Similar to molecules in a vertical column of gas that have a potential energy with respect to the bottom, molecules in a vapor that is in contact with the liquid phase have a potential energy relative to the surface of the liquid phase (from which they rose). The role of gravity is replaced by a different force field, namely the field of the attractive forces of the surface, whose reach is very short. As will be shown below, noticeable differences in temperature between the liquid and the vapor can occur.

aa) The proof consists in a “reductio ad absurdum”: It starts from the assumption that the vapor evolving from a liquid solution (e.g., salt in water) has the same temperature as the liquid. Two principles are applied to this assumption: The principle of conservation of energy, and Boltzmann’s law of distribution of potential energies among particles whose average kinetic energy does not depend on height. It is shown that this leads to contradictions.

In detail:

A saturated solution (salt in water) shall have a vapor pressure of 0.5 bar at a temperature of 100° Celsius. (It is well known that solving salt in water leads to a reduction in vapor pressure at a given temperature of the liquid phase.) We shall, for a short while, suppose that the vapor (0.5 bar) is as hot as the liquid (100°C), and is hence superheated. During a complete evaporation of the water (leaving behind the salt) at constant temperature as a first step of a cycle, the following amounts of heat **Q** and work **W** have been given off or have been added (amounts of work or heat added to the system are given a positive sign in front of the respective variable, whereas amounts of heat or work given off by the system have a negative sign in front of the respective variable; the numerical values of all variables **Q** and **W** are thus positive numbers):

(1)

$$\begin{aligned} Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{W\text{-extern-superheated-1}} - W_{\text{superheated-1}} + Q_{\text{solution}} \\ = Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{\text{solution}} \end{aligned}$$

$Q_{W\text{-intern-1}}$ is the amount of heat added from outside in order to compensate for the internal work done by the molecules when rising from the surface of the liquid in case the liquid is pure water at 100°C and 1 bar; $Q_{W\text{-intern-extra-1}}$ is the additional amount of heat added in order to compensate for the work done by extra intermolecular forces that are present in case the liquid is not pure water, but a saturated salt solution whose vapor pressure at 100°C is only 0.5 bar. The amount of heat $Q_{W\text{-intern-extra-1}}$ can be larger than zero, smaller than zero, or zero (we will have to find out which of the three alternatives is true). Compared to a saturated vapor of 1 bar at 100°C, the density **q** of that vapor (0,5 bar, 100°C) can be assumed to be about 1/2. $Q_{W\text{-extern-superheated-1}}$ is the amount of heat added from outside in order to compensate for the external work done by the superheated vapor (100°C, 0.5 bar) when it is evolving from the surface of the liquid and is shifting a piston. $W_{\text{superheated-1}}$ is the amount of that work

(of isobaric/isothermal expansion) done on a piston by the superheated vapor. $Q_{W\text{-extern-superheated-1}}$ and $W_{\text{superheated-1}}$ are equal in absolute amount. Q_{solution} is the solution heat that comes into play when the salt crystallizes. The right-hand-side of (1) is thus a short way of expressing all the amounts of heat and work involved during the first step.

As a next step (second step) of the cycle, the superheated vapor (100°C, 0.5 bar) shall be isothermally (but not isobaricly) compressed until it is saturated (100°C, 1 bar). For the amounts of Q and W involved during this step, we get:

(2)

$$W_{\text{compr-2}} - Q_{\text{compr-2}} = W_{\text{compr-2}} - (Q_{W\text{-extern-2}} + Q_{W\text{-intern-2}}) = -Q_{W\text{-intern-2}}$$

W_{compr2} is the external work of (isothermal) compression. Q_{compr2} is the total heat that leaves the vapor during that (isothermal) compression. That heat consists of two parts. The first part, that is $Q_{W\text{-extern2}}$, is the heat leaving the vapor in order to compensate for the external compression work done on the vapor. The second part, that is $Q_{W\text{-intern2}}$, is the heat leaving the vapor in order to compensate for the internal work done by the mutual attraction of the vapor molecules. W_{compr2} and $Q_{W\text{-extern2}}$ are equal in absolute amount. The very right-hand side of (2) is thus a short way of expressing all the amounts of heat and work involved during the second step.

In a third and last step of the cycle, the saturated vapor (100°C, 1 bar) is made to condensate on the surface of the pure liquid (100°C, 1 bar). After this has been done, the salt is added to the liquid (100°C). For the amounts of Q and W involved during this step, we get:

(3)

$$-Q_{W\text{-intern3}} - Q_{W\text{-extern-satur3}} + W_{\text{satur3}} - Q_{\text{solution}} = -Q_{W\text{-intern3}} - Q_{\text{solution}}$$

$Q_{W\text{-intern3}}$ is the amount of heat leaving the substance in order to compensate for the internal work given off by the molecules when being absorbed by the surface of the liquid (at 100°C and 1 bar). $Q_{W\text{-extern-satur3}}$ is the heat leaving the system in order to compensate for the external (isobaric) compression work done on the saturated vapor, W_{satur3} is the amount of that external work (of isobaric compression) done on the saturated vapor. $Q_{W\text{-extern-satur3}}$ and W_{satur3} are equal in absolute amount. Q_{solution} is the heat involved when salt is eventually dissolved in the pure liquid. The right-hand side of (3) is thus a short way of expressing all the amounts of heat and work involved during the third step.

The overall-sum of the right-hand sides of (1), (2), and (3) should add up to zero as a consequence of the principle of conservation of energy. In other words:

(4)

$$Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{\text{solution}} - Q_{W\text{-intern-2}} - Q_{W\text{-intern-3}} - Q_{\text{solution}} = 0$$

Since $Q_{W-intern1}$ and $Q_{W-intern3}$ are equal in numerical value, (63) reduces to:

(5)

$$Q_{W-intern-extra-1} = Q_{W-intern-2}$$

bb) Let us now determine the values of those two remaining parameters in (5)(that should be equal to each other).

aaa) In order to determine the value of $Q_{W-intern-extra-1}$ (that is the additional amount of heat added from outside during the first step – isothermal/isobaric evaporation -- needed to compensate for the extra intermolecular forces that are present in case the liquid is not pure water, but a saturated salt solution whose vapor pressure at 100°C is only 0.5 bar), we use the general principle that the number of atoms per unit volume in two different regions is $n_2/n_1 = e^{-(E_2-E_1)/kT}$, presuming Boltzmann's distribution is applicable. With this presumption, there would be a perfect analogy between an isothermal gas in a vertical column subject to gravity, and the vapor rising from the surface of a liquid. We would hence find: As regards the potential energy of the molecules (into which heat has been converted) that rose from the surface of the saturated salt solution, the difference between that potential energy and the potential energy of vapor molecules that rose from the surface of pure liquid water at the same temperature (100°C) would be the same as the difference between the gravitational potential energy of molecules in a column of gas at height h above the bottom and the potential energy of molecules right above the bottom of that column of gas at height $h=0$, given the ratios of the densities and the densities themselves are the same for the two compared cases.

(See for this equality: *R.P. Feynman, Lectures on Physics I*, chapters 40-2 and 42-1, especially chapter 42-1, page 42-1: “There is a certain difference, W , in the energy of a molecule in the liquid from what it would have if it were in the vapor, because we have to pull it away from the other molecules which attract it. Now we use the general principle that the number of atoms per unit volume in two different regions is $n_2/n_1 = e^{-(E_2-E_1)/kT}$. So the number n per unit volume in the vapor, divided by the number ... per unit volume in the liquid, is equal to ... $e^{-W/kT}$, because that is the general rule. It is like the atmosphere in equilibrium under gravity, where the gas at the bottom is denser than that at the top because of the work mgh needed to lift the gas molecules to the height h . In the liquid, the molecules are denser than in the vapor because we have to pull them out through the energy ‘hill’ W , and the ratio of the densities is $e^{-W/kT}$.”)

The density at the bottom of the column of gas – and also the density of the vapor rising from pure liquid water at 100°C and 1 bar – is q_0 . We hence get (with q being the density of the gas in the vertical column at height h and also the density of the vapor rising from the salty solution, with m being the mass of a single molecule; with T being the temperature; with k being Boltzmann's constant; with E_{potMol} being the numerically positive potential energy of a single vapor molecule with respect to the surface of the liquid, where the potential energy is defined to be zero; with R being equal to Nk ; with N being equal to the number of molecules per kmol; with M being equal to Nm ; and with E_{pot} being the potential energy per kmol of the vapor):

(6)

$$q = \frac{1}{2}q_0 = q_0 e^{-\frac{mgh}{kT}} = q_0 e^{-\frac{E_{potMol}}{kT}}$$

$$mgh = E_{potMol} = -kT \ln \frac{1}{2}$$

$$Mgh = E_{pot} = -RT \ln \frac{1}{2} = 2170 \text{ kJ/kmol} = 120 \text{ kJ/kg} = Q_{W-intern-extra-1}$$

bbb) Let us now determine the value of $Q_{W-intern2}$ (that is the heat leaving the vapor during step 2 – isothermal, but not isobaric compression of the vapor – in order to compensate for the internal work done by the mutual attraction of the vapor molecules). What we get from Van-der Waals' equation is:

(7)

$$Q_{W-intern-2} = \int_{V_1=V_{saturated-vapor}}^{V=\infty} \frac{a}{V^2} dV = \left[-\frac{a}{V} \right]_{V_1}^{\infty}$$

With $a=555000 \text{ Nm}^4/\text{kmol}^2$, and with a specific volume of the saturated vapor (100° C, 1 bar) of $30,157 \text{ m}^3/\text{kmol}$ (with 1 kmol corresponding to $18,015 \text{ kg}$), we obtain:

(8)

$$Q_{W-intern-2} = 18.40 \frac{\text{kJ}}{\text{kmol}} = 1.02 \frac{\text{kJ}}{\text{kg}}$$

We realize that $Q_{W-intern-extra-1}$ is more than 100 times larger than $Q_{W-intern2}$, though the two parameters should be equal to each other (based on the assumption of a sameness of temperatures of the liquid solution and the vapor evolving from it).

The hypothesis of the sameness of temperature of a salty solution and its vapor has thus been subject to a “reductio ad absurdum”.

From this follows: The vapor evolving from a salt solution cannot have the same temperature as the liquid salt solution.

cc) Conversely, the temperature of the vapor and of the liquid from which it evolves could only be the same if the inner evaporation/condensation heat $Q_{W-intern-1}$ at a given temperature of the liquid were the same regardless of whether or not the liquid contains a solute (salt). Then $Q_{W-intern-extra-1}$ would vanish, and no inner contradiction would exist.

But experiments show that the inner evaporation/condensation heat $Q_{W-intern-1}$ at a given temperature *is* increased by the presence of a solute. E.T. Whittaker, Proceedings of the

Royal Society A, Vol. 81 (1908), p. 21, cited in Bakker, Handbuch der Experimentalphysik, edited by W. Wien und F. Harms, Vol. 6: Kapillarität und Oberflächenspannung, Leipzig 1928, § 4 b, p. 211, set up the following equation for $Q_{W-intern}$:
(9)

$$Q_{W-intern-1} = \frac{H-T \frac{dH}{dT}}{kT}$$

H denotes the surface tension of the liquid, **T** its temperature, **k** is Boltzmann's constant. The specific evaporation/condensation heat at a given temperature is thus increasing in case the surface tension does.

As regards the effect on the surface tension of a liquid when adding a solute, we find (Bakker, op. cit., § 5 a, p. 238):

“When adding a dissolving substance to a liquid, for instance NaCl in water, the surface tension is modified. The surface tension of the solution is larger than that of the pure liquid and increases roughly proportionally with concentration.”

We thus state: The non-zerosness of $Q_{W-intern-extra-1}$ is not only arrived at by an application of Boltzmann's law (of distribution of energy) to a column of gas of presumably homogeneous temperature under gravity (as was done in Equation 6 in accordance with a proposal by R.P. Feynman), but also by experiment.

dd) As Edwin Edser puts it (*Heat for advanced students*, Macmillan & Co, London 1923, pp. 188, 189):

“The actual temperature of the vapour above a boiling solution is generally slightly lower than the temperature of the solution. Thus above a salt solution, the temperature of which is 110°C, the steam may reach a temperature, say, of 105°C. A thermometer placed in the steam will, however, indicate a temperature of 100°C. ... As pointed out above, a thermometer when placed in the steam given off from a boiling aqueous solution of salt, will indicate the boiling point of the water, and not that of the solution. A similar law applies to solutions in general”.

(See also *F. Rudberg*, “Über die Dampfbildung”, *Annalen der Physik*, Vol. 110, 2nd series, Vol. 34, - 1835 -, pp. 257; *J.J. Prechtl*, “Über die Dampfbildung– Aus einem Brief an den Herausgeber”, *Annalen der Physik*, Vol. 111, 2nd series, Vol. 35 – 1835 -, pp. 198; *Ch. Drion/E. Fernet*, *Traite de Physique Elementaire*, 3rd edition, Paris 1869, pp. 275/276; *M.V. Regnault*, “Relation des experiences...”, *Memoires de l'Academie des Sciences de l'Institut Imperiale de France*, Vol. XXVI – 1862 -, pp. 665; *P.A. Daguin*, *Traite Elementaire de Physique Theorique et Experimentale*, Toulouse/Paris 1861, § 962, p. 349/350; *J. Gill*, “On the temperature of the vapours of boiling saline solutions”, *The London, Edinburgh, and Dublin Philosophical Magazine*, 4th series, Vol. 32 – 1866 -, pp. 481; *G. Magnus*, “Über die Temperatur der aus kochenden Salzlösungen und gemischten Flüssigkeiten entweichenden Dämpfe”, *Annalen der Physik*, Band 188, 2nd series, Vol. 112 – 1861 -, pp. 408; see also the

result of an experiment with a saturated salt solution and its vapor in a closed container, compared to pure water and its vapor in the same container, performed at the Fachhochschule Münster – University of Applied Science – .; see also the result of another experiment.)

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