

### 1.3 Saturation vapor pressure

Increasing temperature of liquid (or any substance) enhances its evaporation that results in the increase of *vapor pressure* over the liquid. By lowering temperature of the vapor we can make it condense back to the liquid. These two phase transitions, *evaporation* and *condensation*, are accompanied by consuming/evolving enthalpy of transition and by a change in entropy of the material. Below we will consider water vapor as an example of the vapor phase. All conclusions we will get for water vapor are true also for any vapor. We will use water vapor not only for the reason that it is the most familiar vapor phase but also that it plays a major role in the cloud formation and precipitations.

#### 1.3.1 Vapor pressure

Above the surface of liquid water there always exists some amount of gaseous water and consequently there exists a *vapor pressure*. When a container containing water is open then the number of the escaping molecules is larger than the number of molecules coming back from the gaseous phase (Fig. 5.1). In this case vapor pressure is small and far from saturation. When the container is closed then the water vapor pressure above the surface increases (concentration of molecules increases) and therefore the number of molecules coming back increases too (Fig. 5.2). After some time, the number of molecules escaping the liquid and that coming back becomes equal. Such situation is called by *dynamic equilibrium* between the escaping and returning molecules (Fig. 5.3). In this case, it is said that the water vapor pressure over the liquid water is *saturated*.

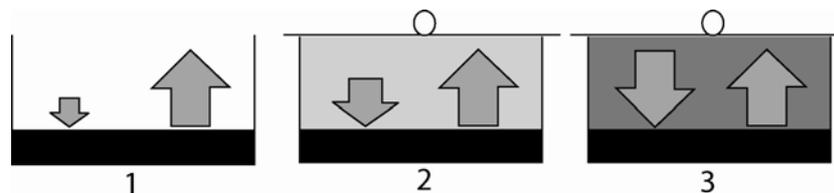


Fig.5. Evaporation and condensation of water molecules in open and closed container. (1) In the open container, when gas is under-saturated, number of the evaporating molecules is larger than the number of molecules coming back from the gaseous phase. In this case water vapor is unsaturated. (2) When the container is closed then the number of the returning molecules increases. (3) After some time, when dynamical equilibrium between the escaping and returning molecules is established, the water vapor pressure becomes *saturated*.

Saturated water vapor pressure is a *function of temperature only* and independent on the presence of other gases. The temperature dependence is exponential. For water vapor the semi empirical dependence reads as

$$p_{w,s} = e^{A + \frac{B}{T} + C \ln T + Dt}, \quad (1.49)$$

where temperature is in *Kelvin* and  $A = 77.34$ ,  $B = -7235$ ,  $C = -8.2$ ,  $D = 0.005711$ .

Evaporation and condensation are the first order phase transitions which are accompanied by a change in the degree of molecular arrangement of water. The change in the degree of molecular arrangement is necessarily accompanied by a change in entropy,  $\Delta S$ . In the atmosphere, condensation (formation) of cloud and rain drops and their evaporation occur at constant pressure. Therefore speaking about the latent heat of evaporation/condensation we should remember that we deal with enthalpy change,  $\Delta H_{vap/cond}$ , because  $\Delta Q = \Delta H$  at constant pressure. Evaporation is an *endothermic* process because heat (enthalpy change) is consumed i.e.,  $\Delta H_{vap} > 0$ . Condensation is an *exothermal* process because heat is evolved i.e.  $\Delta H_{cond} < 0$ . The entropy change during the evaporation can be calculated as  $\Delta S_{vap} = \Delta H_{vap}/T_{tr}$ , where  $T_{tr}$  is temperature of transition (evaporation). Because  $\Delta H_{vap} > 0$ , we obtain that the  $\Delta S_{vap} > 0$ . This means that during evaporation the entropy increases, because the degree of molecular order decreases when liquid water transforms to gaseous phase. During condensation, the entropy decreases,  $\Delta S_{vap} < 0$ , because the degree of molecular order increases.

For any liquid, vapor pressure  $p$  and enthalpy of evaporation  $\Delta H_{vap}$  at temperature  $T_{tr}$  are connected by the *Claperyron* equation,

$$\frac{dp}{dT} = \frac{\Delta S_{vap}}{\Delta V_{vap}} = \frac{\Delta H_{vap}}{T_{tr} \Delta V_{vap}}, \quad (1.50)$$

where we used the definition of the entropy change of  $\Delta S_{vap} = \Delta H_{vap}/T_{tr}$  (see above). Because molar volume of a vapor  $V_m(v)$  is much larger than that of a liquid  $V_m(l)$ , we can assume that volume change during evaporation  $\Delta V_{vap} = V_m(v) - V_m(l)$  is mainly due to the change of volume of the vapor itself i.e.,  $\Delta V_{vap} \approx V_m(v)$ . Moreover, if the vapor behaves perfectly, then for one mole of the vapor we can write  $V = RT/p$  (here we omitted a subscript  $m$  and  $tr$ ). Substituting in (1.48) the volume change  $\Delta V_{vap}$  by  $RT/p$  and assuming that the enthalpy of evaporation  $\Delta H_{vap}$  is independent of temperature, the exact Clapeyron equation (1.50) can be rearranged into the *Clausius-Claperyron equation*

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}. \quad (1.51)$$

The equation (1.51) integrates to give

$$p = p^* e^{-\frac{\Delta H_{vap}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)}, \quad (1.52)$$

where  $p^*$  is vapor pressure at temperature  $T^*$  and  $p$  vapor pressure at temperature  $T$ .

For water, the assumption that the enthalpy of evaporation  $\Delta H_{vap}$  is independent of temperature is not true. For pure water the  $\Delta H_{vap}$  depends on  $T$  exponentially and instead of (1.50) we have the equation (1.47).

### 1.3.2 Air humidity

Amount of water vapor in the air can be expressed by several different ways:

*Specific humidity*: Mass of water vapor in unit mass of humid air:  $\frac{m_{H_2O}}{m_{air}}$

*Absolute humidity*: Mass of water vapor per unit volume of humid air ( $\text{kg}/\text{m}^3$ )

*Relative humidity (RH)*: Ratio of water vapor pressure  $p_w$  to the saturated water vapor pressure at that temperature multiplied by 100%,

$$RH = \frac{p_w}{p_{s,w}^{pure}(T)} \times 100\% . \quad (1.53)$$

*Saturation ratio, S*: Ratio

$$S = \frac{p_w}{p_{s,w}^{pure}(T)} . \quad (1.54)$$

From the last two definitions we see that  $RH = S \cdot 100\%$  i.e., their physical meanings are almost the same.

*Supersaturation*:  $S - 1 > 0$ .

*Dew point (kastepoiste)* is temperature at which relative humidity of cooling air becomes 100% (Fig. 2.3).

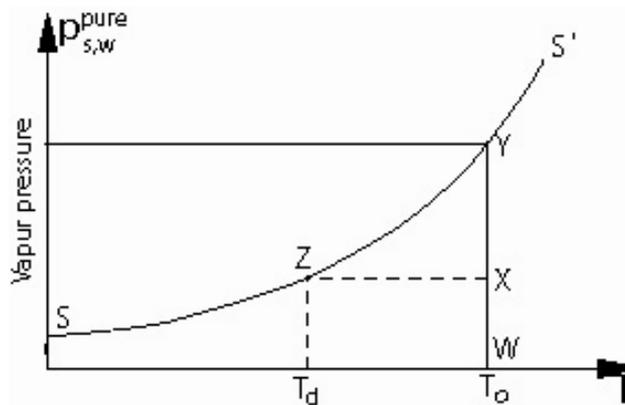


Fig. 2.3 Curve  $SS'$  depicts the saturation pure water vapor pressure  $p_{w,s}^{pure}$  as a function of temperature  $T$ . If we take an air sample at temperature  $T_0$  with vapor pressure corresponding to

point  $X$  then its dew point is  $T_d$ . Relative humidity at point  $X$  is  $\frac{XW}{YW} \times 100\%$ . The value of pressure depicted by  $XY$  is called by *saturation vapor pressure deficit*.

When a warm humid air and a cold dry air parcels are mixed then the vapor pressure  $p_w$  and temperature of the resulting air parcel can be represented as a linear combination of their initial values. Since the saturation water vapor pressure  $p_{w,s}^{pure}$  varies exponentially with temperature, the mixed air may have humidity above 100%, although the initial parcels were under-saturated, Fig. 2.4. As a result a *mixing cloud* is formed. This explains the formation of a cloud of a fog after breathing in cold air. Exhaled air may reach RH up to 200 %.

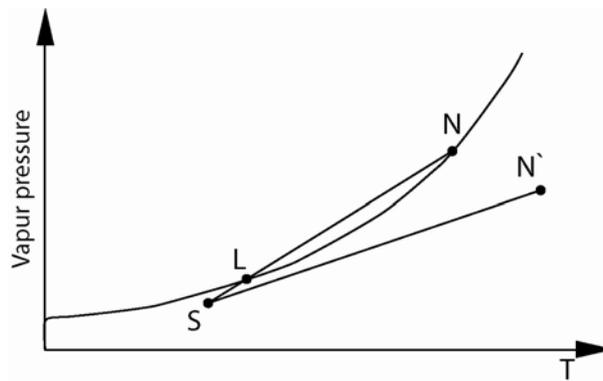


Fig. 2.4 When two air parcels, warm humid N and cold dry S, are mixed then so called mixing cloud is formed in the region NL, where water vapor pressure is above the saturation curve. When two air parcels S and N' are mixed there is not mixing clouds.

## 1.4 Vapor pressure over solutions

Besides the laboratory samples, pure liquids are rarely encountered in nature. Usually liquids are mixed (if they do not react together) or contain some dissolved substances, for example, salts. A dissolved substance is called *solute* and the liquid *solvent*. The mixture itself is called *solution*. Vapor pressure of a component of the solution (for example, solvent) over the surface of the solution is smaller than that over the pure component. This is due to the fact that the solute molecules at the surface of the solution prevent escaping solvent molecules into the vapor phase, but do not hinder their return. Below we will consider the solution that is in equilibrium with its vapor. This means that *chemical potentials* of the liquids and vapors are similar i.e,

$$\mu_{\text{vapor}} = \mu_{\text{liquid}}. \quad (1.55)$$

We will consider a two component (binary) solution of a liquid A and a liquid B. The chemical potentials of the pure liquids will be denoted by  $\mu_A^*$  and  $\mu_B^*$ , and the chemical potentials of liquids in the solution by  $\mu_A$  and  $\mu_B$ . The vapor pressures over the

pure liquid will be denoted by  $p_A^*$  and  $p_B^*$  and the partial vapor pressures over the solution by  $p_A$  and  $p_B$ . Since at equilibrium, the chemical potentials of the liquid and its vapor are similar we can write (see Eq. 1.40) for the chemical potential  $\mu_A^*$  of the pure liquid A,

$$\mu_A^* = \mu_A^\circ + RT \ln \frac{p_A^*}{p_A^\circ}, \quad (1.56)$$

and for the chemical potential  $\mu_A$  of the liquid A in the solution,

$$\mu_A = \mu_A^\circ + RT \ln \frac{p_A}{p_A^\circ}. \quad (1.57)$$

In the Eqs. (1.56) and (1.57), the pressure  $p_A^\circ$  is the standard pressure of 1 bar over the pure liquid A (see 1.41 and 1.42). Combining (1.56) and (1.57) to eliminate the standard chemical potential  $\mu_A^\circ$  and  $p_A^\circ$  we can write that the chemical potential  $\mu_A$  of the liquid A in the solution is

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}. \quad (1.58)$$

Similar result can be written for the chemical potential  $\mu_B$  of the liquid B in the solution,

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*}. \quad (1.59)$$

### 1.4.1 Raoult's law and solvent activity

*a) Ideal solution:* The expression (1.58) shows that the chemical potential of the liquid A in the solution increases with increasing the partial vapor pressure  $p_A$  and becomes equal to the chemical potential of pure liquid when  $p_A = p_A^*$ . The French chemist F. Raoult experimentally found that the ratio of the partial vapor pressure of each component to its vapor pressure as a pure liquid is approximately equal to the mole fraction  $X_A$  in the solution i.e.,

$$\frac{p_A}{p_A^*} = X_A \quad \text{or} \quad p_A = X_A p_A^*. \quad (1.60)$$

The Eq. (1.60) is known as the *Raoult's law*. Linear dependence of the partial vapor pressures  $p_A$  and  $p_B$  are shown by the dashed lines in Fig. 6.

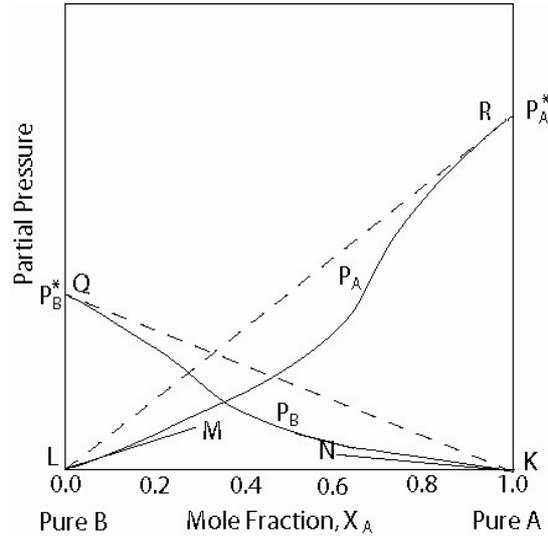


Fig. 6. Equilibrium partial pressures of the components of ideal and nonideal binary solution as a function of the mole fraction  $X_A$ . For the real solution, relationships between the  $p_A$ ,  $p_B$ , and the mole fractions  $X_A$ ,  $X_B$  are not linear as it is in the case of ideal solution where the relationships are linear what is shown by the straight dashed lines LR and KQ. When  $X_A \rightarrow 1$ , then we have a dilute solution of B in A. In this region the Raoult's law  $p_A = X_A p_A^*$  is applied for the component A. For the component B the Henry's law  $p_B = K_B X_B$  is applied (see below). In the region where  $X_A \rightarrow 0$ , we have the Raoult's law  $p_B = X_B p_B^*$  for B component and the Henry's law  $p_A = K_A X_A$  for A component. The straight lines LM and KN depict the Henry's law (Seinfeld and Pandis, 1998).

Using (1.60) we can write for the chemical potential  $\mu_A$  of the liquid A in the solution (instead of 1.59) the expression

$$\mu_A = \mu_A^* + RT \ln X_A. \quad (1.61)$$

The solutions, which obey the Raoult's law (1.60) throughout the whole composition range from pure A to pure B, are called *ideal solutions*.

The solutions, which components are *structurally similar*, obey the Raoult's law very well. In Fig. 6, the equilibrium partial pressures of the components A and B in the ideal solution are shown by the straight dashed lines LR and KQ. This shows that solution is only ideal if (1.61) is satisfied for each component. Dissimilar liquids (large difference in the liquid structures) significantly depart from the Raoult's law. Nevertheless, even for these mixtures, the law is obeyed closely for the component in excess as it approaches purity i.e., when  $X_A \rightarrow 1$  or  $X_A \rightarrow 0$  (Fig. 6).

*b) Real solution:* The Eq. (1.61) is the expression for the chemical potential of the solvent in the *ideal* solution. It is reasonable to preserve the form of the Eq. (1.61) also for the *real* solution because then the deviations from the idealized behavior will be seen most simply. Similar to the case of the fugacity introduced for the real gas, the form of

Eq. (1.61) can be preserved also for the solution that do not obey the Raoult's law, if we introduce a new quantity called the solvent *activity*  $a_A$ . and write

$$\mu_A = \mu_A^* + RT \ln a_A. \quad (1.62)$$

In chemistry, activity is a measure of how different molecules in a non-ideal (real) gas or solution interact with each other. The solvent activity is a kind of *effective mole fraction* just as the fugacity is an effective pressure. Activity is the mole fraction, corrected with a coefficient, described with the equation

$$a_A = \gamma_A X_A, \quad (1.63)$$

where  $\gamma_A$  is the *activity coefficient*, which must be measured for different substances, and  $X_A$  is the mole fraction of solvent. The activity coefficient is a factor by which the value of a concentration of a solute must be multiplied to determine its true thermodynamic activity. In solutions, the activity coefficient is a measure of how much the solution differs from an ideal solution. The activity coefficient of ions in *solution* can be estimated, for example, with the Debye-Hückel or the Pitzer equation. Activity effects are the result of interactions between ions both electrostatic and covalent. The activity of an ion is influenced by its surroundings. The reactivity of an ion in a cage of water molecules is different from that in the middle of a counter-ion cloud.

The activity of the solvent approaches the mole fraction as  $X_A \rightarrow 1$  i.e.,

$$a_A \rightarrow X_A \quad \text{as} \quad X_A \rightarrow 1,$$

and the activity coefficient

$$\gamma_A \rightarrow 1 \quad \text{as} \quad X_A \rightarrow 1,$$

at all temperatures and pressures. At this conditions (when  $X_A \rightarrow 1$ ) the solvent activity can be expressed as

$$a_A = \frac{p_A}{p_A^*}, \quad (1.64)$$

i.e., when  $X_A \rightarrow 1$  the solvent activity can be determined experimentally by measuring the partial vapor pressure over the solution and then using Eq. (1.64).

If the values of the  $X_A$ ,  $\gamma_A$ , and  $p_A^*$  are known then one can calculate the partial vapor pressure of the solvent

$$p_A = p_A^* \gamma_A X_A. \quad (1.65)$$

Using (1.63) the chemical potential of the solvent can be written as

$$\mu_A = \mu_A^* + RT \ln X_A + RT \ln \gamma_A. \quad (1.66)$$

## 1.4.2 Henry's law and solute activity

In ideal solutions, both the solvent A and solute B obey the Raoult's law. But it had been found experimentally that for a *real low concentration solution* ( $X_B \rightarrow 0$ ), although the partial vapor pressure of the solute  $p_B$  is proportional to its mole fraction  $X_B$  the constant of proportionality is not the vapor pressure of the pure solute  $p_B^*$  as it is in the case of the Raoult law but a some constant  $K_B$  i.e.,

$$p_B = K_B X_B. \quad (1.67)$$

This expression is known as the *Henry's law*. The coefficient of proportionality  $K_B$  is called by the *Henry's constant*. The Henry's constant is empirical with the dimension of pressure. Value of the  $K_B$  is chosen so that the straight line depicted by (1.67) is tangent to the experimental curve at  $X_B = 0$ . In Fig. 6, the straight lines LM and KN depict the Henry's law.

The Henry's constant is a *material characteristic* and depends only on temperature. Because amount of solute is very small the distance between the molecules is very large and, therefore, interaction between the solute molecules can be neglected. Vapor pressure of solute above the solution is determined mainly by the interaction of the solvent molecules with solute molecules. From (1.64) one can obtain molar fraction of solute in solution if vapor pressure and Henry's constant are known,

$$X_B = \frac{p_B}{K_B}. \quad (1.68)$$

The expression (1.68) can be considered as definition of *solubility* of solute B. It can be treated as follows: If we somehow increase the partial vapor pressure of solute over the solution then amount of solute in the solution increases too i.e., increases its solubility.

Dimension of the Henry's law constant can be *different*. One has to be careful with this. For example, from the Eq. (1.67), its dimension is  $[K_B] = [Pa]$ . Dimensionless Henry's law constant is obtained when we, instead of values used in (1.67), will do a replacement:  $p_B \rightarrow c_g$  (concentration of solute vapor in gaseous phase,  $[mole/m^3]$ ),  $X_B \rightarrow c_l$  (concentration of solute in solution,  $[mole/m^3]$ , or molar concentration  $[mole/l]$ ). When  $p_B$  is in  $Pa$  and  $X_B \rightarrow c_l$  with  $[mole/m^3]$  then  $[K_B] = [mol/m^3 Pa]$ .

Liquid mixtures in which the solvent A obeys the Raoult's law and the solute B obeys the Henry's law are called *ideal-dilute solutions*. Physically the different behavior of the solvent and solute is explained by their different environment. Environment of the solvent A is only slightly modified by the very small number of solute molecules. In contrast, the environment of the solute B is very strongly perturbed because the solute molecules are very far from each another. Therefore, the solvent behaves like a slightly modified pure liquid, whereas the solute behaves totally differently from its pure state.

Only when the structure of solute molecules is similar to that of the solvent then the solute also obeys the Raoult's law.

*The solute activity:* In contrast to the solvent activity  $a_A$  which is defined when  $X_A \rightarrow 1$ , the *solute activity*  $a_B$  is defined when  $X_B \rightarrow 0$  i.e, when the solution approaches *ideal-dilute behavior*. The chemical potential of B in the dilute solution obeying the Henry's law  $p_B = K_B X_B$  can be written as

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln X_B. \quad (1.69)$$

Since both  $p_B^*$  and  $K_B$  are characteristics of the solute, the first two terms can be combined to get a new standard chemical potential,

$$\mu_B^\circ = \mu_B^* + RT \ln \frac{K_B}{p_B^*}. \quad (1.70)$$

Then the expression (1.69) can be written as

$$\mu_B = \mu_B^\circ + RT \ln X_B. \quad (1.71)$$

As in the case of the solvent, all deviations from the ideal-dilute behavior of the real solute is most simply expressed by introducing the solute activity  $a_B$  instead of  $X_B$  in the Eq. (1.71) i.e.,

$$\mu_B = \mu_B^\circ + RT \ln a_B. \quad (1.72)$$

But in contrast to the solvent activity, which can be expressed as  $a_A = \frac{p_A}{p_A^*}$  when  $X_A \rightarrow 1$ , instead of  $p_A^*$  we should use the Henry's constant  $K_B$ ,

$$a_B = \frac{p_B}{K_B}. \quad (1.73)$$

The *solute activity coefficient* is introduced in the same way as in the case of solvent activity i.e.,

$$a_B = \gamma_B X_B. \quad (1.74)$$

Because the solute obeys the Henry's law,  $p_B = K_B X_B$ , when  $X_B \rightarrow 0$  we have

$$a_B \rightarrow X_B \quad \text{and} \quad \gamma_B \rightarrow 1 \quad \text{as} \quad X_B \rightarrow 0 \quad (1.75)$$

at all temperatures and pressures. Combining (1.73) and (1.74) we get an expression

$$p_B = \gamma_B K_B X_B, \quad (1.76)$$

which allows to calculate the vapor pressure of the solute,  $p_B$ , if the values on the right hand side are known. (Compare with (1.65)).

*Electrolyte solution:* The above consideration has been performed for the substances that do not dissociate into ions during the dissolution. When strong acid, base or salt ( $HM$ ) dissolve in water they dissociate into ions,  $H^+$  and  $M^-$ . Such solution is called *electrolyte solution*. For example, in water, salt  $NaCl$  dissociates in  $Na^+$  and  $Cl^-$ , whereas sugar does not. Fig. 7 shows how dissociation affects water vapor pressure over salt and sugar solutions.

In order for the dissociated substance could escape from the electrolyte solution into the gaseous phase, the ions should link together to form the initial substance because evaporation of the ions is of little probability (due to additional attractive electrical force). If in the electrolyte solution, the components totally dissociate into ions, then the expression for vapor pressure can be written as

$$p_s \propto X(H^+) X(M^-) f_{\pm}^2, \quad (1.77)$$

where  $f_{\pm}^2$  is mean rational activity coefficient,  $X(H^+)$  and  $X(M^-)$  molar concentration of the totally dissociated substance.

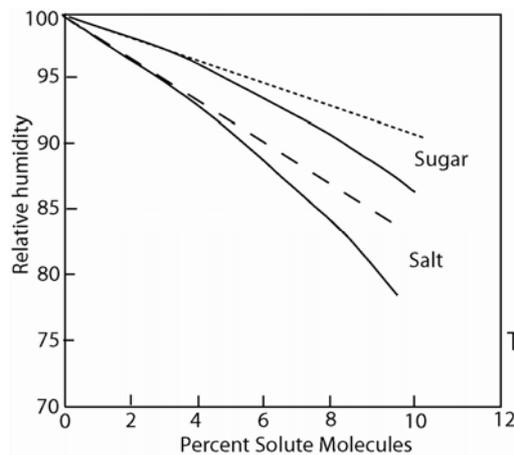


Fig. 7. Equilibrium RH above the mixture (sugar in water) and salt solution as a function of Percent Solute Molecules. If the Raoult's law were true then the decreasing of RH would have followed the straight lines (dotted and dashed). Interaction between water and solute molecules decreases the RH even more (solid lines). Salt reduces RH in larger extent than sugar, because it dissociates into ions but sugar does not.

