

## ICHO 2021 Preparatory Problem 2. Does water boil or evaporate?

When an ideal gas is isothermally expanded from pressure  $p$  [bar] to  $p'$  [bar] ( $p > p'$ ), the entropy change  $\Delta S$  of the gas is

$$\Delta S \text{ [J K}^{-1} \text{ mol}^{-1}] = -R \ln\left(\frac{p'}{p}\right) \quad (1).$$

The enthalpy change when liquid water evaporates to water vapor at  $p_0$  [bar] is  $\Delta H_v^\circ$  [J mol<sup>-1</sup>], and the entropy change is  $\Delta S_v^\circ$  [J K<sup>-1</sup> mol<sup>-1</sup>]. Let us suppose these values do not depend on temperature, and the gas is an ideal gas. In this case, when liquid water evaporates to water vapor at  $p_1$  [bar], the enthalpy change is  $\Delta H_v$  [J mol<sup>-1</sup>] =  $\Delta H_v^\circ$ , and the entropy change is  $\Delta S_v$  [J K<sup>-1</sup> mol<sup>-1</sup>] = (a).

1. **Write** the appropriate formula for blank (a).

Since we assume that both enthalpy and entropy changes do not depend on temperature, the entropy change from  $p_0$  to  $p_1$ , will only depend on pressure. Since entropy is a state function, we take as reference state the water liquid at a constant temperature, and evaluate the entropy change over pressure from eq. (1):

$$\Delta S = \Delta S_v - \Delta S_v^\circ = -R \ln \frac{p_1}{p_0}$$

Thus we get:

$$\Delta S_v = \Delta S_v^\circ - R \ln \frac{p_1}{p_0}$$

Check. If  $p_1 < p_0$  then  $\Delta S > 0$  so  $\Delta S_v > \Delta S_v^\circ$ , this means that water vapor increases its entropy change if expanded, which is true since it follows eq. (1) that  $\Delta S > 0$  if  $p' < p$ .

For the following questions, assume that  $\Delta H_v^\circ = 4.070 \times 10^4$  J mol<sup>-1</sup> and that,  $\Delta S_v^\circ = 1.091 \times 10^2$  J K<sup>-1</sup> mol<sup>-1</sup> at  $p_0 = 1$  bar.

2. **Calculate** the boiling point of water at 1 bar.

When liquid water evaporates at a fixed pressure  $p_0$ , it reaches thermodynamic equilibrium between the liquid and vapor phases, thus  $\Delta G_v^\circ = 0$ . This means that  $\Delta H_v^\circ - T_v^\circ \Delta S_v^\circ = 0$ , thus:

$$T_v^\circ = \frac{\Delta H_v^\circ}{\Delta S_v^\circ} = 373.1 \text{ K}$$

is the boiling temperature at the specified pressure.

3. **Calculate** the saturated vapor pressure of water at 87 °C.

Let  $T_v = 87$  °C = 360.2 K and  $T_v^\circ = 373.1$  K; from point 2, we know  $p_0$  is 1 bar. Using the entropy relation of point 1 and the thermodynamic equilibrium relation of point 2, we get:

$$\frac{\Delta H_v}{T_v} = \frac{\Delta H_v^0}{T_v^0} - R \ln \frac{p_v}{p_0}$$

which, since  $\Delta H_v = \Delta H_v^0$  from the assumptions, gives:

$$p_v = p_0 \exp \left[ \frac{\Delta H_v^0}{R} \left( \frac{1}{T_v^0} - \frac{1}{T_v} \right) \right] = 0.6 \text{ bar}$$

Check. If  $T_v < T_v^0$  then  $p_v < p_0$ , thus vapor pressure decreases as temperature decreases. The last relation is also called Van't Hoff vapor pressure equation.

4. **Calculate** the Gibbs energy change per mole when water evaporates at 87 °C at a humidity of 50%. The humidity represents the ratio of the actual partial pressure of water vapor relative to the saturated vapor pressure of water.

If the humidity is not 100%, thermodynamic equilibrium is not reached and  $\Delta G'_v = \Delta H_v^0 - T_v \Delta S'_v \neq 0$ . We calculate the entropy change  $\Delta S'_v$  at the actual partial pressure  $p'_1 = 0.5p_v$  as:

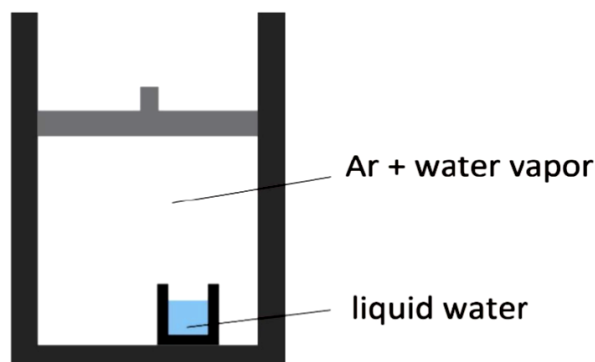
$$\Delta S'_v = \Delta S_v^0 - R \ln \frac{p'_1}{p_0} = 1.191 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$$

Then, we get:

$$\Delta G'_v = \Delta H_v^0 - T_v \Delta S'_v = -2.203 \times 10^3 \text{ J mol}^{-1}$$

Check.  $\Delta G'_v < 0$  thus evaporation is spontaneous until reaching 100% humidity.

A container with a piston like that shown in Figure 1 is filled with 0.10 mol of Ar and 1.00 mol of water (liquid and vapor). The temperature of the entire container is 87 °C and the total pressure is 1 bar. It is assumed that the volume of the liquid or cup is negligible with respect to that of the gas, and that the temperature of water and Ar is always maintained at 87 °C. In this initial situation, the partial pressure of Ar is (b) bar, the partial pressure of water vapor is (c) bar, the volume of the gas is (d) L, and the number of moles of liquid water is (e) mol.



**Figure 1.** A container with a piston containing Ar gas, water vapor and liquid water in a cup.

The piston is then pulled back quickly to fix the gas volume to 15.8 L. At the moment when the piston is pulled, the partial pressure of Ar decreases to (f) bar and the partial pressure of water vapor decreases to (g) bar. In this situation, the water will boil, because the total pressure of the gas is lower than the saturated vapor pressure of water at 87 °C. The partial pressure of water vapor increases due to the boiling until the boiling eventually stops. When the boiling stops, the number of moles of liquid water is (h) mol. After that, evaporation proceeds until equilibrium is reached. At equilibrium, the number of moles of liquid water is (i) mol.

5. **Calculate** the appropriate numerical values for blanks (b) - (i).

For (b), the partial pressure of Ar is given by Dalton's law:

$$p_{Ar} = x_{Ar}p_0 = \frac{n_{Ar}}{n_{Ar} + n_{WV}}p_0$$

however, the moles of water vapor  $n_{WV}$  are not declared. We know that  $n_{WV} + n_W = 1$  mol, and for (c), the partial pressure of water vapor is:

$$p_{WV} = x_{WV}p_0 = \frac{n_{WV}}{n_{Ar} + n_{WV}}p_0$$

such that  $p_{Ar} + p_{WV} = p_0$ . The system is not water saturated (due to the inclusion of Ar), thus the partial pressure of water vapor is equal to its vapor pressure at 87 °C which is known from point 3.

$$p_{WV} = x_{WV}p_0 = p_v = 0.6 \text{ bar}$$

Thus (c) is known,  $p_{WV} = 0.6$  bar, then (b) is known,  $p_{Ar} = p_0 - p_{WV} = 0.4$  bar. Since  $x_{WV} = 0.6$ :

$$0.6 = \frac{n_{WV}}{n_{Ar} + n_{WV}}, \quad n_{WV} = 0.15 \text{ mol}$$

thus (e) is known,  $n_W = 0.85$  mol. For (d), the volume of the gas is obtained by the equation of state:

$$n_0 = n_{Ar} + n_{WV}, \quad V_0 = \frac{n_0RT}{p_0} = 7.48 \text{ L}$$

Then, as the piston is pulled back quickly (not reversible process), we can assume the expansion has a negligible effect on the temperature and on the total number of moles in vapor phase. Thus, from such isothermal expansion, we can calculate the new total pressure  $p_1$  at the moment the piston is pulled:

$$V_0p_0 = V_1p_1, \quad p_1 = p_0 \frac{V_0}{V_1} = 0.5 \text{ bar}$$

For (g) and (f) respectively, the new vapor pressures decrease to:

$$p_{WV,1} = p_{WV} \frac{V_0}{V_1} = 0.3 \text{ bar}, \quad p_{Ar,1} = p_{Ar} \frac{V_0}{V_1} = 0.2 \text{ bar}$$

Since  $p_1 < p_v = 0.6$  bar, water will boil, and the partial pressure of water vapor increases until it stops boiling. For (h), the number of moles of liquid water after boiling are obtained by the equation of state:

$$n_1 = n_{Ar} + n_{WV,1} = \frac{p_v V_1}{RT}, \quad n_{WV,1} = 0.22 \text{ mol}, \quad n_{W,1} = 0.78 \text{ mol}$$

At equilibrium, the total pressure increases to match  $p_v$ , and the partial pressure of water becomes  $p_1$ . Therefore, for (i), the number of moles of liquid water are obtained by the partial pressure relation

$$p_1 = \frac{n'_{WV}}{n_{Ar} + n'_{WV}} p_v, \quad n'_{WV} = 0.50 \text{ mol}, \quad n'_{W} = 0.50 \text{ mol}$$