

VAPOUR PRESSURE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.41.

Two systems in diffusive equilibrium have equal chemical potentials. We can use this fact to solve the following problem.

We begin with a closed system consisting of a liquid such as water in diffusive equilibrium with its vapour. At the start, only the liquid and its vapour are present. Then we pump in an inert gas (that is, a gas that doesn't react chemically with the liquid or vapour) to increase the pressure in the container (we're also assuming that everything is at the same temperature, so no heat flow occurs). Assuming that the inert gas doesn't dissolve in the liquid, and that the liquid and its vapour remain in diffusive equilibrium, the chemical potentials of the liquid and vapour must change by the same amount: $d\mu_\ell = d\mu_v$. What happens to the partial pressure P_v of the vapour?

For the vapour, which we'll assume is an ideal gas, the chemical potential is given by

$$\mu_v(T, P_v) = \mu_v^\circ(T) + kT \ln \frac{P_v}{P^\circ} \quad (1)$$

where the superscript 'o' indicates the value at a reference pressure, usually taken to be 1 bar. If the pressure changes by dP_v , we have

$$d\mu_v = \frac{kT}{P_v} dP_v \quad (2)$$

For the liquid, we can use the relation between the Gibbs energy and chemical potential

$$G = N\mu_\ell \quad (3)$$

If we combine this with the derivative

$$\left(\frac{\partial G}{\partial P} \right)_{T,N} = V \quad (4)$$

we get

$$dG = Nd\mu_\ell = V dP \quad (5)$$

$$d\mu_\ell = \frac{V}{N}dP \quad (6)$$

where the pressure P is now the pressure on the liquid, which is the sum of the vapour pressure P_v and the pressure due to the added inert gas. (Note that V and N refer to the liquid, not the vapour.) Equating 2 and 6, we get a differential equation relating the vapour pressure and total pressure:

$$\frac{kT}{P_v}dP_v = \frac{V}{N}dP \quad (7)$$

$$\frac{dP_v}{dP} = \frac{V}{NkT}P_v \quad (8)$$

We can solve this as follows:

$$\frac{dP_v}{P_v} = \frac{V}{NkT}dP \quad (9)$$

$$\ln P_v + A = \frac{V}{NkT}P + B \quad (10)$$

where A and B are constants of integration. To determine these constants, we use the fact that when there is no inert gas present, $P = P_v$. We'll call this pressure P_{v0} to distinguish it from P_v , the latter of which is actually a function of P . [Schroeder uses the confusing notation $P_v(P_v)$ to indicate the vapour pressure when there is no inert gas present, which makes it look like a function of a function.] That is, we must have

$$\ln P_{v0} + A = \frac{V}{NkT}P_{v0} + B \quad (11)$$

We can choose A and B so that both sides are zero, giving

$$A = -\ln P_{v0} \quad (12)$$

$$B = -\frac{V}{NkT}P_{v0} \quad (13)$$

Substituting these back into 10 we get

$$\ln \frac{P_v}{P_{v0}} = \frac{V}{NkT}(P - P_{v0}) \quad (14)$$

$$P_v(P) = P_{v0}e^{(P-P_{v0})V/NkT} \quad (15)$$

Thus if $P > P_{v0}$, the vapour pressure increases.

As an example, the vapour pressure of water at $T = 25^\circ \text{C}$ is $3.169 \times 10^3 \text{ Pa}$. Suppose we introduce an inert gas at atmospheric pressure ($= 1.01 \times 10^5 \text{ Pa}$) into the container. For one mole of water, $V = 18.068 \times 10^{-6} \text{ m}^3$, so we have for the new vapour pressure

$$P_v \left(1.01 \times 10^5 \right) = 3.169 \times 10^3 e^{(1.01 \times 10^5 - 3.169 \times 10^3)(18.068 \times 10^{-6})/NkT} \quad (16)$$

Using $N = 6.02 \times 10^{23}$, $k = 1.38 \times 10^{-23}$ and $T = 298$, we have

$$P_v \left(1.01 \times 10^5 \right) = 3.169 \times 10^3 e^{7.14 \times 10^{-4}} \quad (17)$$

The exponential is very close to 1, so we can expand in a Taylor series:

$$e^{7.14 \times 10^{-4}} \approx 1 + 7.14 \times 10^{-4} \quad (18)$$

Thus the change in vapour pressure is only about 0.07%.