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SIMPLE PROOF OF WÜLLNER'S VAPOR PRESSURE LAW.*

LE ROY D. WELD

It is well known that the vapor pressure of a solvent liquid is lowered by dissolving a nonvolatile solute in it. The experiments of Wüllner (*Pogg. Ann.* **110**, 56. 1860) indicated that if the solute is nonvolatile, nonelectrolytic, and without chemical action on the solvent, the vapor pressure of the solvent is lowered by an amount proportional to the concentration of the solute; *concentration* being in this case defined as the ratio of the mass of the solute to the mass of the whole solution, *i.e.*, the *mass fraction*. Nearly thirty years after Wüllner's work, Raoult (*Zeits. Phys. Chem.* **2**, 353. 1888) gave a more explicit statement of the same law, to the effect that the ratio of the change in vapor pressure to the original vapor pressure of the solvent is *equal* to the mole fraction of the solute.

A theoretical proof of Wüllner's proportion, or rather an argument which leads to it, and which is somewhat simpler than that commonly offered, is based upon the following ideal experiment.

Imagine a vertical, narrow, cylindrical vessel, *infinitely tall*, perfectly nonconducting, and of uniform temperature throughout its length. The vessel is entirely freed of air and contains at the bottom a small quantity of the pure liquid solvent, which has stood evaporating into the infinite tubular vacuum above it until liquid and vapor are in equilibrium at the existing temperature. Under the surface of the liquid is a small, closed, glass capsule containing a little of the pure, nonvolatile, nonelectrolytic solute.

The vapor pressure at the surface of the liquid is that of the pure solvent and is equal to the total weight of vapor in the infinite tube, divided by the cross section of the tube. But let the capsule containing the solute be now broken. The solute dissolves, and this cools the solvent by an amount proportional to the quantity of solute and to its heat of solution. Thereupon the vapor-pressure equilibrium is upset; vapor condenses until the heat of condensation restores the original temperature of the solvent, which is that of the vapor and the enclosing walls, and a new equilibrium pressure is established. To do this, the quan-

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tity of vapor condensing must be sufficient to yield heat equivalent to that absorbed in dissolving the solute. The weight of vapor condensed must therefore be proportional to the mass of solute dissolved. As noted above, the total vapor pressure is proportional to the total weight of vapor; hence the reduction of vapor pressure is proportional to the weight of vapor condensed. It follows at once that the reduction of vapor pressure is proportional to the mass of solute dissolved; which is Wüllner's law.

It should be remarked that neither Raoult's nor Wüllner's form of the law is strictly accurate, and that the above argument ignores certain small corrections. For example, the total thermal capacity of solvent and solute is not quite the same after as it was before solution, so that the heat required to restore their fallen temperature is not quite equal to that abstracted from them. Also their volume is not quite the same; and the condensing vapor contributes further to this change. That is, we have a thermodynamic process in which there are both external work and changes in internal energy, while the system as a whole is adiabatic. But the external work and the *net* change in internal energy, whose chief components are the thermal energies of solution and vaporization, are both very small compared with either of those components.

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