

# STATISTICAL MOLECULAR THERMODYNAMICS

*Christopher J. Cramer*

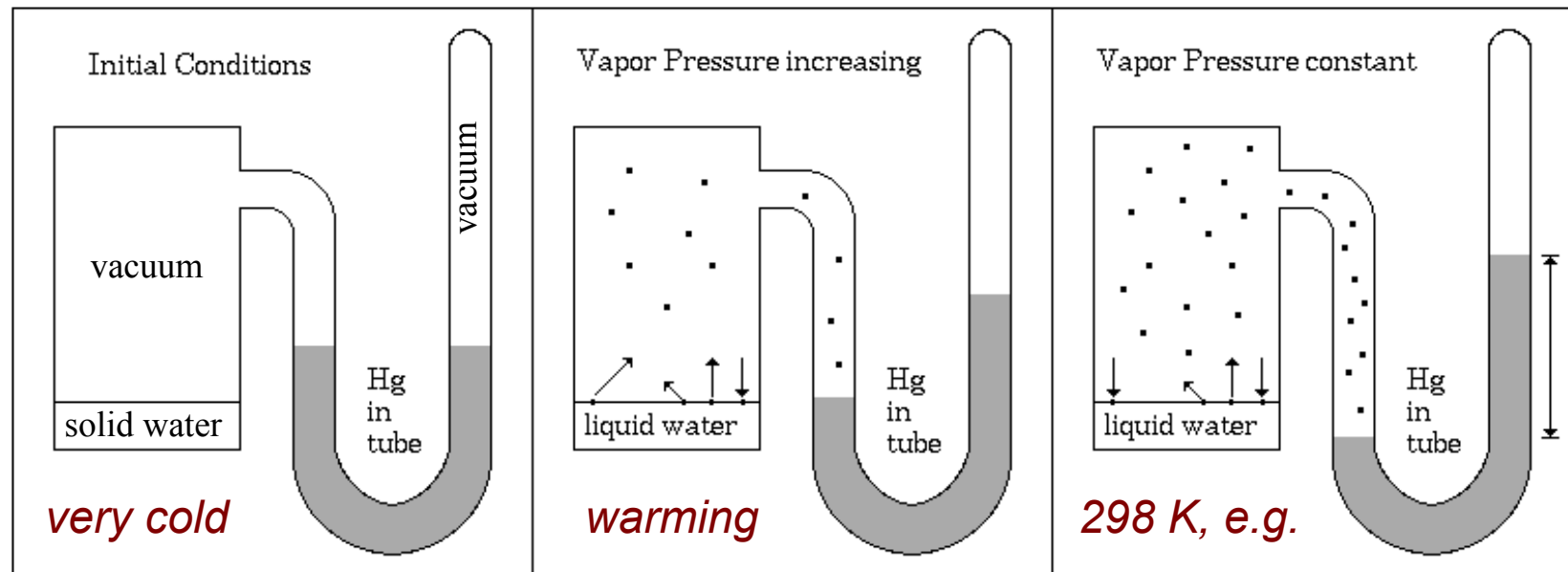
Video 11.3

Determining Solute Activity

# PURE SOLVENT VAPOR PRESSURE

Very hard to measure  $P_2$  directly if solute is not particularly volatile

But, we have a rule that lets us relate the activity of one component to another: the Gibbs-Duhem equation (cf. Video 10.2). So, we can measure the activity of the *solvent* to begin.

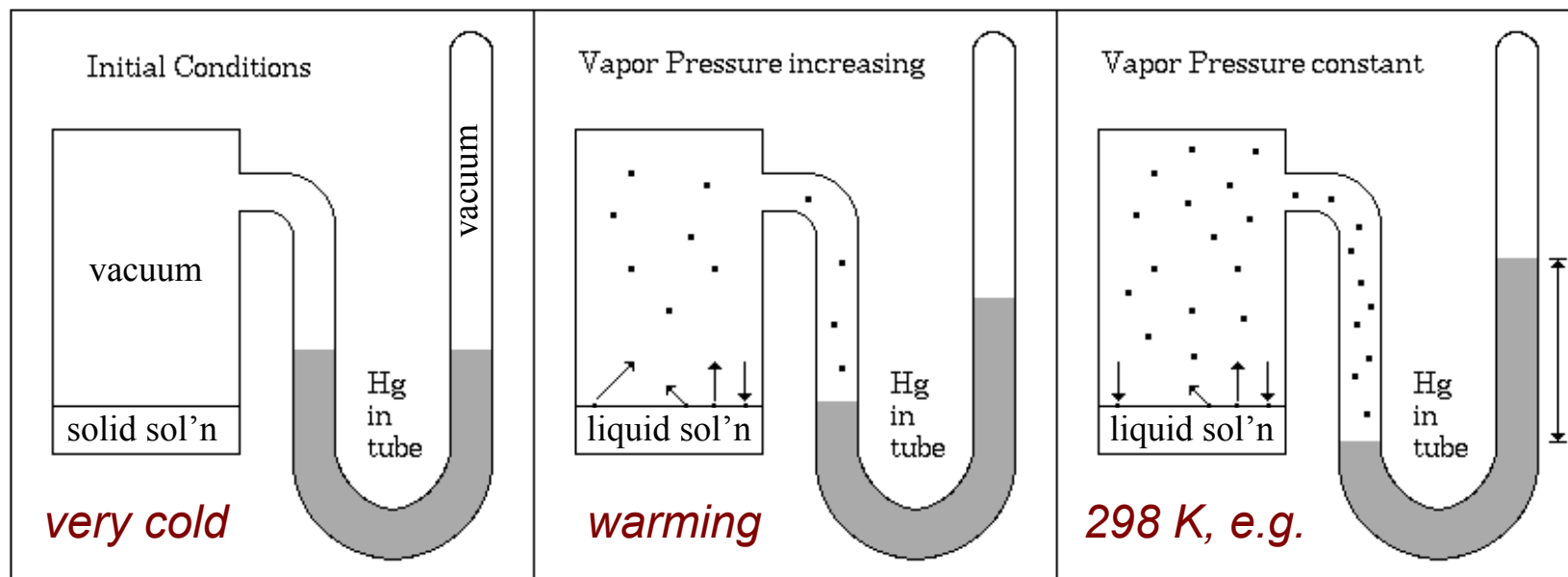


*Now, we can monitor the variation in the vapor pressure over a solution in water (for example) as we change the concentration of a very dilute solute*

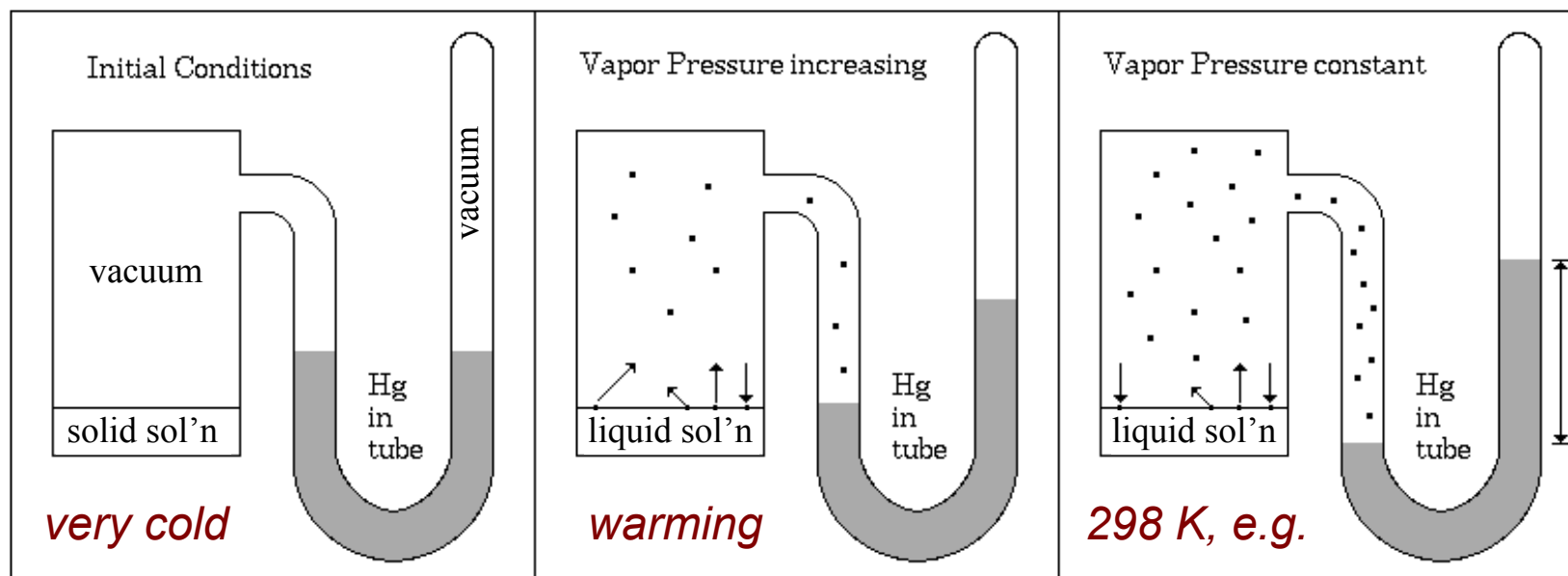
# SOLVENT VAPOR PRESSURE WITH SOLUTE

One now repeats for a dilute solution of solute in solvent

*The mercury level will drop compared to pure solvent, because the solvent vapor pressure must fall as its mole fraction is less than 1; the drop will follow Raoult's Law at first, and then possibly become non-ideal with increasing solute concentration*



# DETERMINING SOLVENT ACTIVITY



$$\ln a_1 \approx \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.51 \text{ mol kg}^{-1} \text{ water}}$$

*Raoult's law behavior*      *x<sub>2</sub> very small*

$$m \ll 55.51 \text{ molal}$$

Define  $\phi$ , whose deviation from unity quantifies non-ideality of solution

$$\ln a_1 = -\frac{m\phi}{55.51 \text{ mol kg}^{-1} \text{ water}}$$

# DETERMINING SOLUTE ACTIVITY 1

$$n_1 d \ln a_1 = -n_2 d \ln a_2 \quad \text{Gibbs-Duhem equation}$$

For dilute (aqueous) solution on a per kilogram basis:

$$55.51 d \ln a_1 = -m d \ln a_2$$

From l.h.s. of eqn on last slide and from definition of  $a_2$ :

$$d(m\phi) = m d \ln(m\gamma_{2m})$$

$$\begin{aligned} \Rightarrow m d\phi + \phi dm &= m d(\ln m) + m d(\ln \gamma_{2m}) \\ &= dm + m d(\ln \gamma_{2m}) \end{aligned}$$

$$\Rightarrow d(\ln \gamma_{2m}) = d\phi + \frac{\phi - 1}{m} dm$$

If we now integrate from  $m' = 0$  (Henry ideal,  $\ln(\gamma_{2m}) = 0$ ) to  $m' = m$ , we can compute any  $\gamma_{2m}$

## DETERMINING SOLUTE ACTIVITY 2

$$\int_{\gamma'_{2m}=1}^{\gamma'_{2m}=\gamma_{2m}} d(\ln \gamma'_{2m}) = \int_1^{\phi(m)} d\phi + \int_0^m \frac{\phi(m') - 1}{m'} dm'$$
$$\Rightarrow \ln \gamma_{2m} = \phi(m) - 1 + \int_0^m \frac{\phi(m') - 1}{m'} dm'$$

### Practical steps:

- 1) Measure solvent vapor pressure  $P_1$  as function of solute molality
- 2) From  $P_1$  and  $P^*$ , determine *solvent* activity
- 3) Determine  $\phi(m)$  from deviation of solvent activity from ideal behavior
- 4) Fit  $\phi(m)$  to a convenient (e.g., polynomial) function of solute molality
- 5) Use that fit in integral above to determine *solute* activity coefficient for any concentration

$$\begin{aligned}\mu_2 &= \mu_2^0 + RT \ln a_2 \\ &= \mu_2^0 + RT \ln m\gamma_{2m} \\ &= \mu_2^0 + RT \ln m + RT \ln \gamma_{2m}\end{aligned}$$

*Dissolution (for example) will continue until  $\mu_2$  is equal to  $\mu$  of the pure solid. Note that  $\mu_2^0$  is the chemical potential of a hypothetical 1 molal solution behaving as though it were infinitely dilute.*

# Self-assessment

If the solute vapor pressure were *not* to be negligible, how could you modify the procedure just outlined in order to determine accurate activity coefficients?

# Self-assessment Explained

If the solute vapor pressure were *not* to be negligible, how could you modify the procedure just outlined in order to determine accurate activity coefficients?

The simplest thing to do would be to iterate. I.e., first proceed assuming negligible solute vapor pressure. From the activity coefficients obtained, it will then be possible to compute expected *solute* vapor pressures (if the vapor pressure of the pure substance is in hand). Subtraction of those pressures from the observed total vapor pressure will provide a new set of *solvent* vapor pressures that can be used to determine new solute activities, and this can be iterated to convergence.



$$dU = \delta q + \delta w$$



*Next: Colligative Properties — Freezing Point Depression*