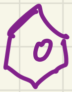
Chemistry 082

Lecture Notes 9

Weliky

Hydrophobic effect ≡ intermolecular free energy associated with low miscibility of water and hydrocarbon

C_p( in H_2O) − C_p( in ) ≈ 350 $\frac{J}{mol\text{-}K}$

≈295K ⇒ chosen for $\Delta h = 0$

$$\Delta h(T) = \Delta h(T_1) + \Delta c_p (T - T_1)$$

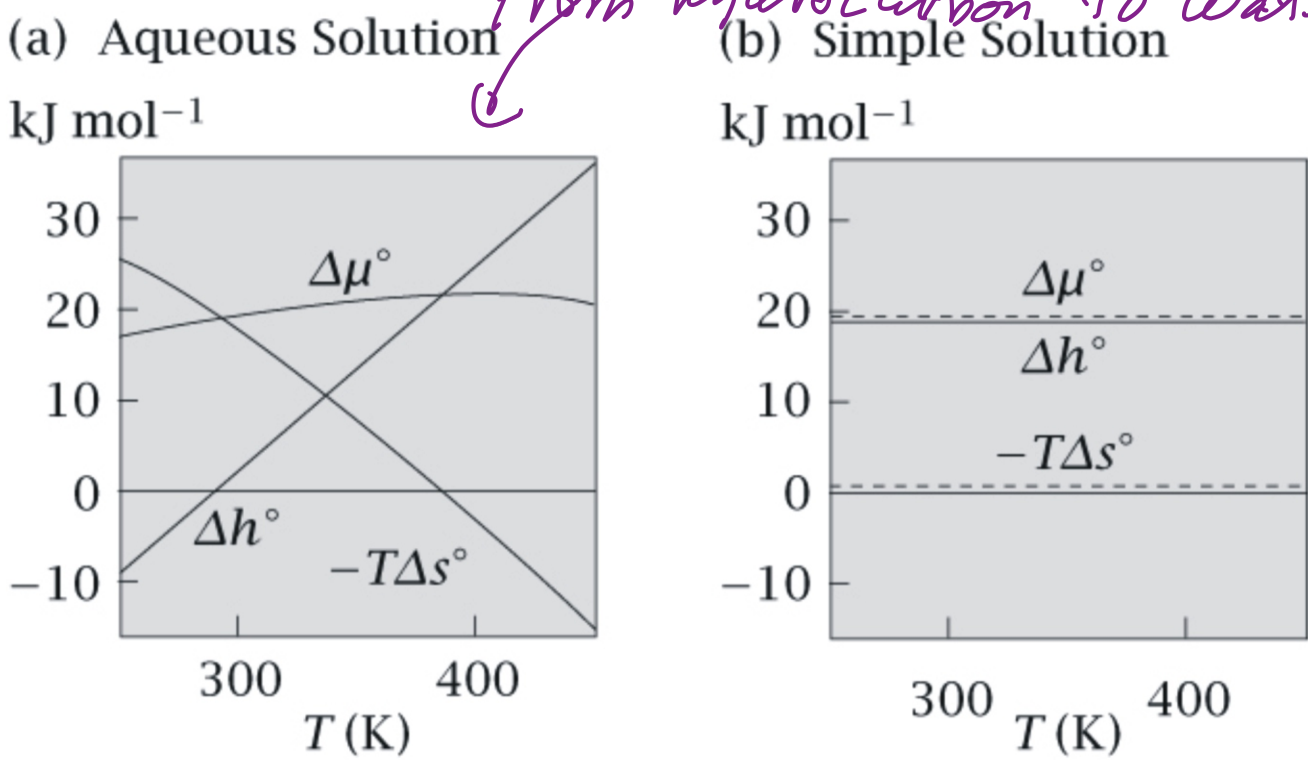
$$\Delta s(T) = \Delta s(T_2) + \Delta c_p \ln(T/T_2)$$

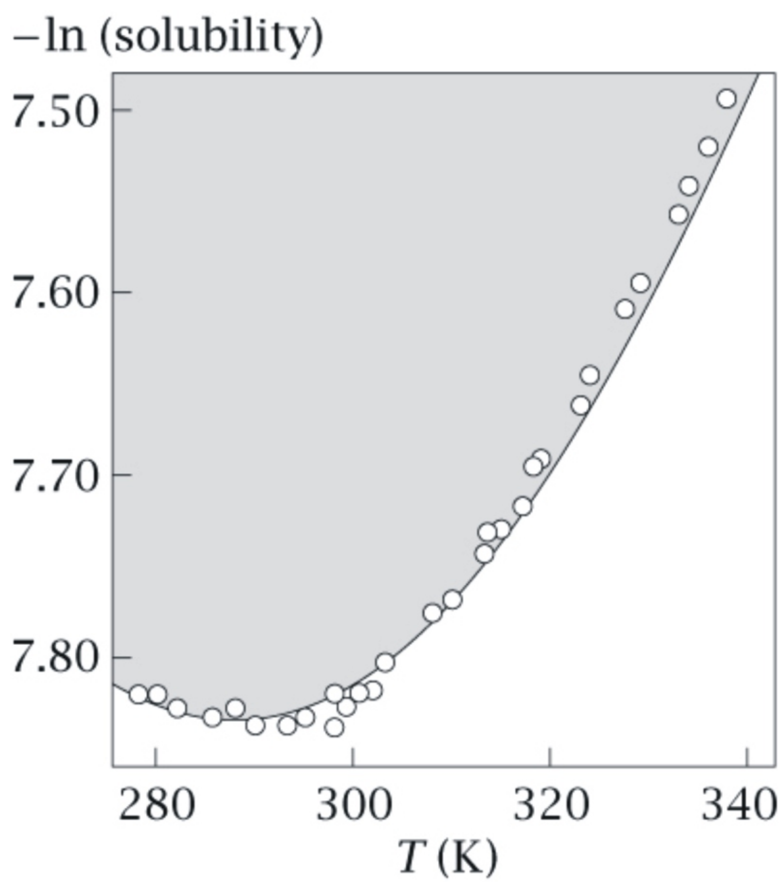
~390 K ⇒ chosen for $\Delta s(T_2) = 0$

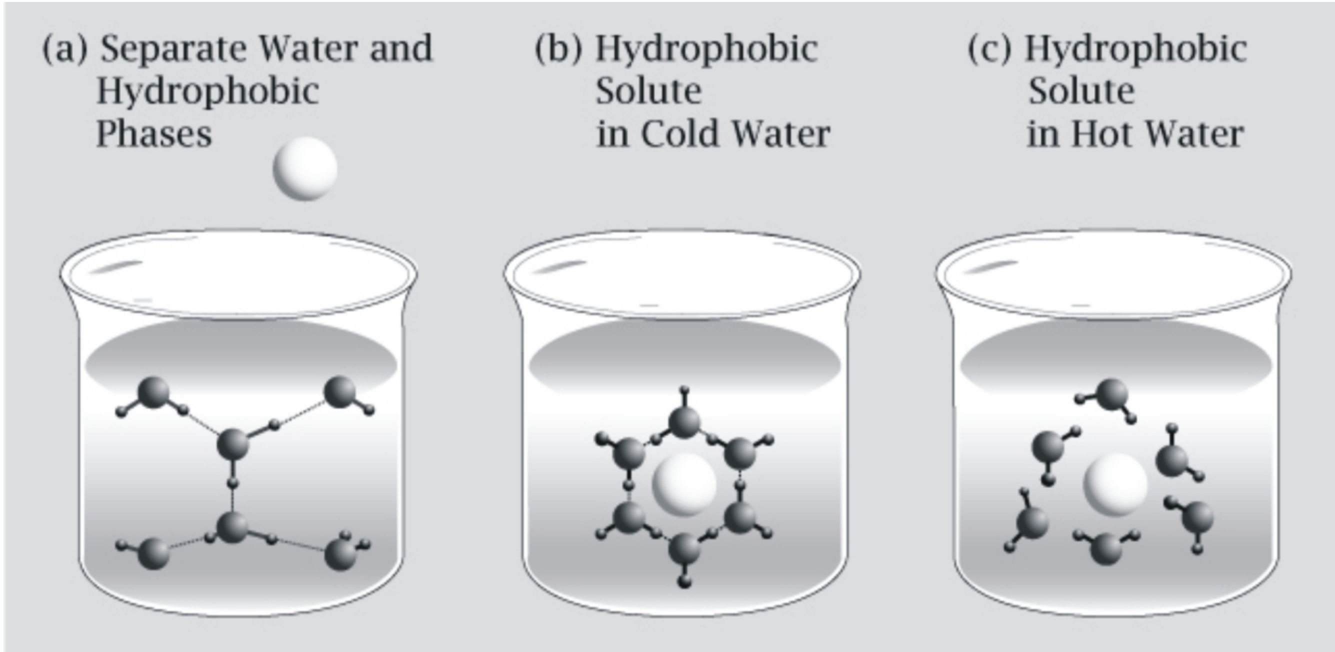
$$\Delta \mu(T) = \Delta h(T_1) - T\Delta s(T_2) + \Delta c_p (T - T_1) - T\Delta c_p \ln(T/T_2)$$

$$= \Delta c_p (T - T_1) - T\Delta c_p \ln(T/T_2)$$

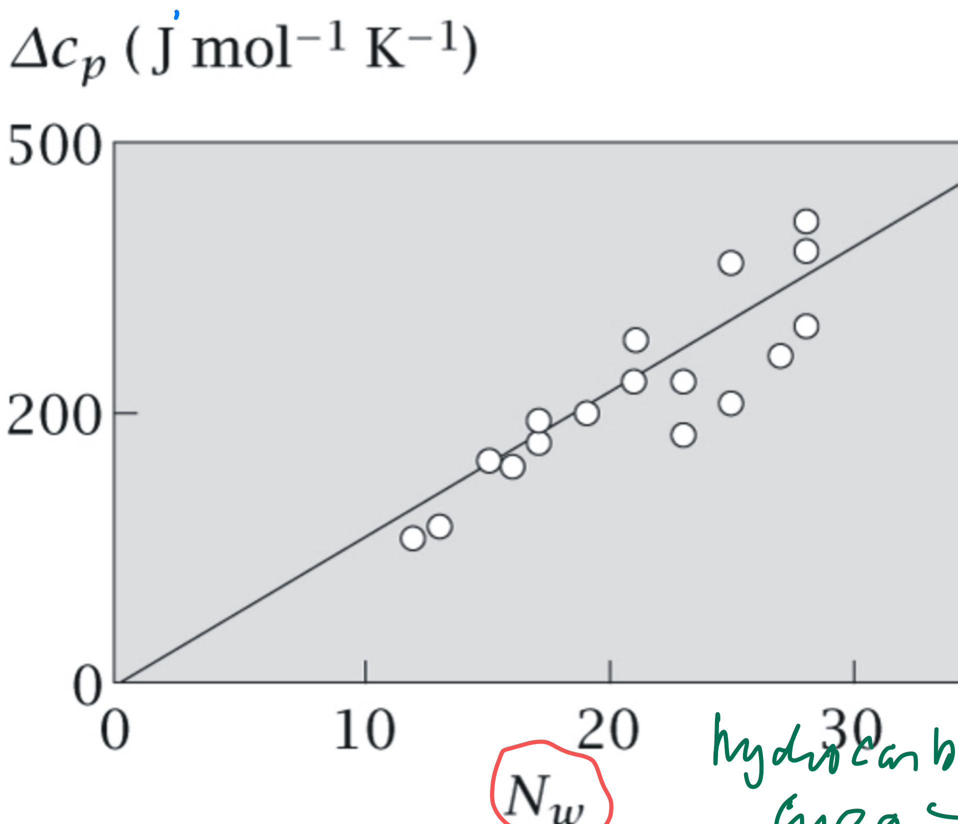
transfer of benzene from hydrocarbon to water







water ordering around hydrocarbon ("ice")



hydrocarbon surface area →

number of water molecules contacting hydrocarbon

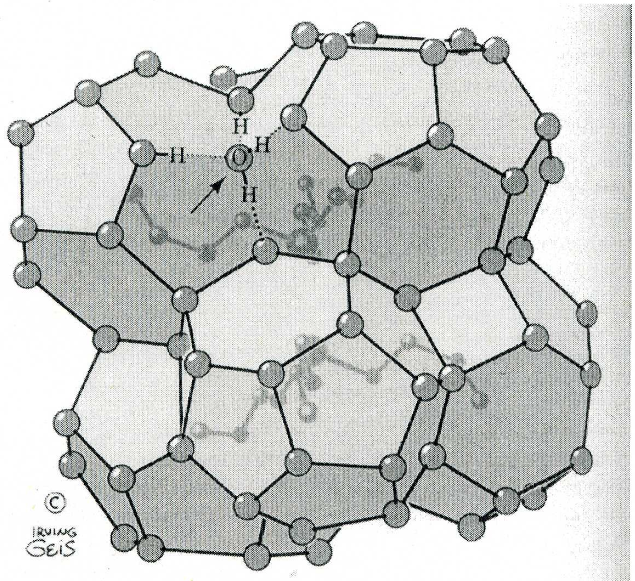


FIGURE 8-59 Structure of the clathrate $(n\text{-}C_4H_9)_3S^+F^- \cdot 23H_2O$. Clathrates are crystalline complexes of nonpolar compounds with water (usually formed at low temperatures and high pressures) in which the nonpolar molecules are enclosed, as shown, by a polyhedral cage of tetrahedrally H bonded water molecules (here represented by only their oxygen atoms). The H bonding interactions of one such water molecule (*arrow*) are shown in detail. [Illustration, Irving Geis/Geis Archives Trust. Copyright Howard Hughes Medical Institute. Reproduced with permission.]

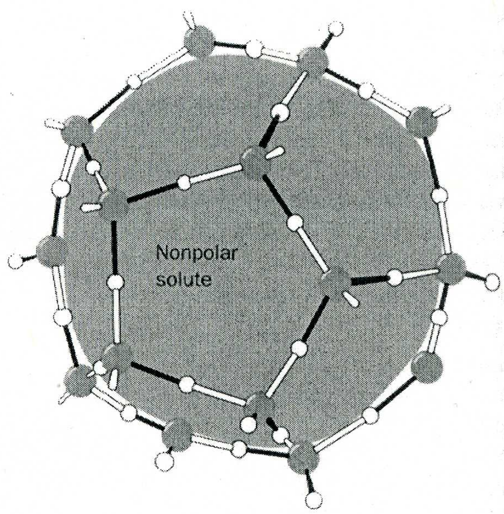
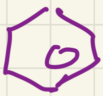


FIGURE 8-58 The orientational preference of water molecules next to a nonpolar solute. In order to maximize their H bonding energy, these water molecules tend to straddle the inert solute such that two or three of their tetrahedral directions are tangential to its surface. This permits them to form H bonds (*black*) with neighboring water molecules lining the nonpolar surface. This ordering of water molecules extends several layers of water molecules beyond the first hydration shell of the nonpolar solute. [Illustration, Irving Geis/Geis Archives Trust. Copyright Howard Hughes Medical Institute. Reproduced with permission.]

Consider that 15 water molecules have half of their orientational multiplicity when they contact

 vs. H_2O

$$\Delta S = R \ln\left(\frac{1}{2}\right)^{15} = 15 R \ln\left(\frac{1}{2}\right)$$

$$\approx \left(120 \frac{J}{mole\text{-}K}\right)(-0.7) \approx -85 \frac{J}{mole\text{-}K}$$

Near 0°C

$$T\Delta S \approx -25000 \frac{J}{mole\text{-}K}$$

$$\Delta S \approx -90 \frac{J}{mole\text{-}K}$$