

# STATISTICAL MOLECULAR THERMODYNAMICS

*Christopher J. Cramer*

Video 2.8

Review of Week 2

## CRITICAL CONCEPTS FROM WEEK 2

- The ideal gas equation of state is  $PV=nRT$
- The compressibility  $Z$  is defined as  $PV / \bar{R}T$
- Gases are rarely ideal (only at very low pressure)
- The van der Waals equation of state better predicts non-ideal gas behavior, as do the Redlich-Kwong and Peng-Robinson equations
- All cubic equations of state are capable of describing the liquid and gaseous regions of  $PV$  isotherms
- At the critical point, the vdW EOS has only one root, which permits the direct relation of the critical volume, pressure and temperature in terms of the vdW constants  $a$  and  $b$ . This is how  $a$  and  $b$  are determined experimentally

## CRITICAL CONCEPTS FROM WEEK 2

- The Law of Corresponding States says that all gases have the same properties if compared at “corresponding conditions”
- “Corresponding conditions” means relative to their respective critical properties
- The virial expansion is an equation of state whose coefficients relate directly to intermolecular interactions
- The second virial coefficient  $B_{2v}$  measures the deviation of the volume of a real gas compared to an ideal one under the same temperature and pressure conditions

## CRITICAL CONCEPTS FROM WEEK 2

- Lennard-Jones proposed an expression for the intermolecular potential  $u(r)$  in terms of the strength of molecular interactions ( $\epsilon$ ) and the size of the molecules ( $\sigma$ )
- The Lennard-Jones potential has an  $r^{-6}$  attractive term and an  $r^{-12}$  repulsive term
- Lennard-Jones parameters ( $\epsilon, \sigma$ ) can be determined from experimental  $B_{2v}$  values
- London developed a quantum mechanical explanation for dispersion and derived an equation predicting its magnitude based on atomic (or molecular) ionization potentials and polarizabilities

## CRITICAL CONCEPTS FROM WEEK 2

- A square-well potential permits analytic solution of the integral that determines  $B_{2V}(T)$  as does a hard-sphere potential
- The hard-sphere potential is appropriate only for gases at high temperatures (where  $B_{2V}(T)$  is positive and effectively constant)
- The square-well potential, with its additional free parameter  $\lambda$  that dictates the length over which a constant potential  $-\varepsilon$  is attractive, leads to fairly good estimates for values over a broader range of temperatures and pressures