

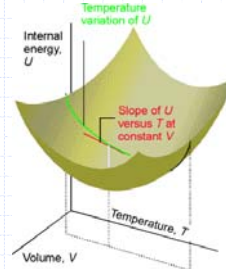
Physical Chemistry

Lecture 6

Equations of State for Condensed Phases

Derivatives in thermodynamics

- ◆ Determine the way variables change with changes in other variables
 - $(\partial V_m / \partial T)_P$ – change of volume with temperature while the pressure is unchanging
 - $(\partial V_m / \partial P)_T$ – change of volume with pressure while the temperature is unchanging
 - Many others, e.g. $(\partial U_m / \partial T)_V$



State functions and non-state functions

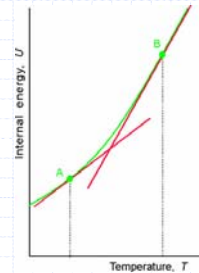
- ◆ Determine variation of functions
- ◆ Property of line integrals
- ◆ State function has integral that is independent of path:

$$U(T_2, V_{m2}) - U(T_1, V_{m1}) = \int dU_{\text{along path}}$$
- ◆ Some functions have integrals that depend on path – not state functions

Partial derivatives and state functions

- ◆ Must know the functional dependence of the derivative to integrate
- ◆ Differential is sum of two parts:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV_m$$
- ◆ Integral independent of path, so choose simple path



Variation of volume for condensed phases

- ◆ Small variation with both T and P
- ◆ Treat derivatives as approximately constant
 - $(1/V_m)(\partial V_m / \partial T)_P = \alpha$, thermal expansion coefficient
 - $-(1/V_m)(\partial V_m / \partial P)_T = \kappa_T$, isothermal compressibility
- ◆ Differential equation of state

$$dV_m = \left(\frac{\partial V_m}{\partial T}\right)_P dT + \left(\frac{\partial V_m}{\partial P}\right)_T dP$$

Equations of state of condensed phases

- ◆ Treat the derivatives as if not functions of P and T
- ◆ The differential equation can be integrated to give an approximate equation of state

$$V_m(T, P) \cong V_m(T_0, P_0) [1 + \alpha(T - T_0) - \kappa_T(P - P_0)]$$
- ◆ Condensed phases are often not very compressible and do not expand much on heating

Material	$\alpha \times 10^6 \text{ (K}^{-1}\text{)}$	$\kappa_T \times 10^6 \text{ (bar}^{-1}\text{)}$
Aluminum	25	
Acetone	1587	112
Benzene	1237	96.7
Silver	56.7	1.0
Water (25°C)	257	45.2

Condensed phases summary

- ◆ Use a differential approach to determine the equation of state
- ◆ Treats the thermal expansion coefficient and isothermal compressibility as constants
- ◆ The variation of volume with temperature and pressure of many condensed phase is small
- ◆ Must check to ensure that approximations are valid for any system; the use of an equation is predicated on the knowledge that assumptions underlying it are valid