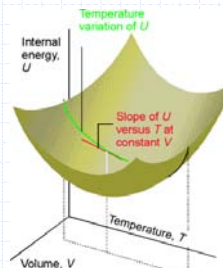


Physical Chemistry

Lecture 6 Derivatives, Differentials, and Integrals

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. $(\partial U_m / \partial T)_V$



Partial derivatives and state functions

- ◆ Generally state functions depend on two independent variables
- ◆ Differential is sum of two parts:
$$dU = \left(\frac{\partial U}{\partial T}\right)_{V_m} dT + \left(\frac{\partial U}{\partial V_m}\right)_T dV_m$$
- ◆ Dependence on third variable is subsumed into these two by the equation of state

State functions

- ◆ State-function differences independent of path
- ◆ Relationship between the two partial derivatives

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial U}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial P}\right)_T\right)_P$$

- ◆ Order of differentiation does not matter
- ◆ Limit on the kinds of functions that represent state parameters

Chain rule

- ◆ Consider the derivative of a function that depends explicitly on a variable, and through it implicitly on a second
- ◆ The partial derivative is a product of derivatives

$$\left(\frac{\partial U}{\partial T}\right)_A = \left(\frac{\partial U}{\partial V_m}\right)_A \left(\frac{\partial V_m}{\partial T}\right)_A$$

Cyclic rule

- ◆ Partial derivatives are related
- ◆ Convert one into a product of two others

$$\left(\frac{\partial U}{\partial T}\right)_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

- ◆ Compare to the chain rule
 - How are they different?

Reciprocal rule

- ◆ A relation between certain derivatives

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial U}\right)_V}$$

- ◆ Note the importance of the subscript in partial derivatives
 - Without the subscript, the symbol is ambiguous

Volume change

- ◆ A differential change in volume is induced by differential changes in the pressure and temperature

$$\begin{aligned}dV_m &= \left(\frac{\partial V_m}{\partial T}\right)_P dT + \left(\frac{\partial V_m}{\partial P}\right)_T dP \\ &= V_m \alpha dT - V_m \kappa_T dP\end{aligned}$$

Volume change

- ◆ Rearrangement and integration provides a form for an equation of state:

$$\begin{aligned}\frac{dV}{V} &= \alpha dT - \kappa_T dP \\ \ln\left(\frac{V_2}{V_1}\right) &= \int_{T_1}^{T_2} \alpha dT - \int_{P_1}^{P_2} \kappa_T dP \\ V_2 &= V_1 \exp\left[\int_{T_1}^{T_2} \alpha dT - \int_{P_1}^{P_2} \kappa_T dP\right]\end{aligned}$$

Volume change

- ◆ Assuming the isothermal compressibility and thermal expansion are constants gives a simple form for the result
 - Appropriate to many condensed phases
- ◆ Expansion and truncation of the exponential gives an approximate form

$$V_2 \cong V_1 [1 + \alpha(T_2 - T_1) - \kappa_T(P_2 - P_1)]$$

Summary

- ◆ State functions have special properties
 - Integrals independent of path
 - Relationships among partial derivatives
- ◆ Can use differential and integral calculus of state functions to define equations of state
- ◆ Approximations for condensed phases
 - Isothermal compressibility is constant
 - Thermal expansion coefficient is constant