

Answer on Question #73628 - Chemistry - Physical Chemistry

Question:

Derive the integrated form of Clausius-Clapeyron equation

Solution:

The condition for the coexistence of two phases of a substance with the simultaneous change in pressure and temperature

is described by the Clausius equation - Clapeyron:

$$dP / dT = \Delta H_{f.p} / T_{f.p} \cdot \Delta V_{f.p}.$$

where dP / dT is the change in pressure at temperature change, $\Delta H_{f.p}$ is the molar enthalpy of the phase transition (melting, evaporation, sublimation, the transition between allotropic modifications), $T_{f.p}$ - the phase transition temperature $\Delta V_{f.p}$ - distribution of phase volumes.

For melting and sublimation processes, assuming that the pairs obey the equation of state

ideal gas, and in temperatures that are far from critical, a change

volume $\Delta V_{f.p} = V_{\text{vapour}} - V_{\text{liquid}} (V_{\text{solid}})$ can be neglected, since the volume of steam is much greater than the volume of liquid or volume of a solid. In this case, the Clausius-Clapeyron equation in the differential form is written:

$$dP / dT = P \cdot \Delta H_{f.p} / RT^2$$

In a small temperature range, when the heat of evaporation (sublimation) $\Delta H_{f.p}$ does not depend on temperature, the integral form of the Clausius-Clapeyron equation

for the process of evaporation or sublimation will be written:

$$\ln (P_2 / P_1) = (\Delta H_{f.p} / R) \cdot (1 / T_1 - 1 / T_2)$$

or

$$\ln (P_2 / P_1) = \Delta H_{f.p} \cdot (T_2 - T_1) / RT_2 T_1$$

According to the equations, one can calculate the heat of evaporation or sublimation, knowing the vapor pressure at two temperatures.

If there are several experimental data on the relationship between vapor pressure and temperature, the full integral form of the Clausius-Clapeyron equation is used:

$\ln P = \Delta H_{f.p} / RT + C$ - where C is the constant of the integration of the differential form. In this case, we plot the dependence of $\ln P = f(1 / T)$. The tangent of the inclination angle of the received straight line is $\Delta H_{f.p} / R$.

For a process of melting a substance, when a volume change can not be neglected, the full form of the Clausius-Clapeyron equation is used. In this case, the temperature coefficient (dP / dT) which in a narrow temperature region is equal to the total differential is experimentally calculated:

$$dP / dT = \Delta P / \Delta T, \text{ and further necessary data are calculated.}$$