

CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

- . Physical Chemistry, [Robert J. Silbey](#), Robert A. Alberty, [Moungi G. Bawendi](#)
- . Physical Chemistry, Ira N. Levine

Physical Transformation of Pure Substance

The slopes of phase boundaries;

At equilibrium,

$$d\mu(\alpha) = d\mu(\beta)$$

$$dG(\alpha) = dG(\beta)$$

$$V_m(\alpha)dp - S_m(\alpha)dT = V_m(\beta)dp - S_m(\beta)dT$$

V_m and S_m : molar volume and entropy. From this equation

$$[S_m(\beta) - S_m(\alpha)]dT = [V_m(\beta) - V_m(\alpha)]dp$$

$$\Delta_{trs}SdT = \Delta_{trs}Vdp$$

Physical Transformation of Pure Substance

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \text{ Clapeyron equation}$$

$$\frac{dT}{dp} = \frac{\Delta_{trs}V}{\Delta_{trs}S}$$

The Clapeyron equation is an exact expression for the slope of tangent to the phase boundary at any point and applies to any phase equilibrium of any pure substance.

Remember $\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$

Physical Transformation of Pure Substance

The liquid-vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \qquad \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{T\Delta_{trs}V} \rightarrow \underbrace{\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}}_{\text{slope of liquid-vapour boundary}}$$

$$\Delta_{vap}V \cong V_m(g) = \frac{RT}{p} \text{ (perfect gas)}$$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T \left(\frac{RT}{p} \right)} = \frac{p\Delta_{vap}H}{RT^2}$$

Physical Transformation of Pure Substance

Remember: $dx/x = d\ln x$; $dp/p = d\ln p$

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} \quad \text{Clasius – Clapeyron equation}$$

$$\int_{p^*}^p d\ln p = \frac{\Delta_{vap}H}{R} \int_{T^*}^T \frac{dT}{T^2}$$

$$\ln \frac{p}{p^*} = - \frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

To start the topic “Chemical equilibrium”:

In this context; The topics to be taught are as follows:

- The equilibrium constant,
- The response of equilibria to conditions,
- Electrochemical cells,
- Electrode potentials