5.60 Thermodynamics & Kinetics
Spring 2008

Clausius-Clapeyron Equation

Let's revisit solid-gas & liquid-gas equilibria. We can make an approximation:

$$\overline{V}^{\,gas} >> \overline{V}^{\,solid}, \ \overline{V}^{\,liquid} \qquad \Delta \overline{V}_{subl}, \ \Delta \overline{V}_{vap} \approx \overline{V}^{\,gas}$$

We can ignore the molar volume of the condensed phase compared to the gas.

Taking the Clapeyron equation (exact), e.g. for solid-gas eq. and using the approximation above:

$$\frac{dp}{dT} = \frac{\Delta \overline{S}_{subl}}{\Delta \overline{V}_{subl}} = \frac{\Delta \overline{H}_{subl}}{T\Delta \overline{V}_{subl}} \approx \frac{\Delta \overline{H}_{subl}}{T\overline{V}^{\,gas}}$$

Assuming an ideal gas, $\overline{V}^{\,gas} = \dfrac{RT}{p}$

$$\Rightarrow \qquad \frac{dp}{dT} = \frac{p\Delta \overline{H}_{subl}}{RT^2} \qquad \frac{dp/p}{dT} = \boxed{\frac{d\ln p}{dT} = \frac{\Delta \overline{H}_{subl}}{RT^2}}$$

This is the Clausius-Clapeyron Equation
for liq-gas, replace $\Delta \overline{H}_{sub}$ with $\Delta \overline{H}_{vap}$

$$\text{i.e. } \frac{dp}{dT} = \frac{p\Delta \overline{H}_{vap}}{RT^2} \qquad \frac{dp/p}{dT} = \frac{d\ln p}{dT} = \frac{\Delta \overline{H}_{vap}}{RT^2}$$

The Clausius-Clapeyron equation relates the temperature dependence of the vapor pressure of a liquid or a solid to $\Delta \overline{H}_{vap}$ or $\Delta \overline{H}_{sub}$ (respectively).

We can make another approximation: Assuming $\Delta \bar{H}_{subl}$ independent of T,

$$\int_{P_1}^{P_2} \frac{dp}{p} = \frac{\Delta \bar{H}_{subl}}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \qquad \boxed{\ln \frac{P_2}{P_1} = -\frac{\Delta \bar{H}_{subl}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta \bar{H}_{subl}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)}$$

<u>This is the Integrated Clausius-Clapeyron Equation</u>
(for liq-gas, replace $\Delta \bar{H}_{sub}$ with $\Delta \bar{H}_{vap}$)

$$\text{i.e. } \ln \frac{P_2}{P_1} = -\frac{\Delta \bar{H}_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{\Delta \bar{H}_{vap}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

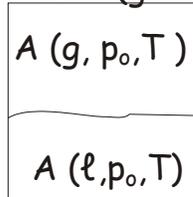In practice this is how you determine vapor pressure over a liquid or solid as a function of T.

Clausius-Clapeyron problems have the two following forms:

1. You know (T_1,p_1) and (T_2,p_2) for s-g or ℓ-g coexistence and want to know $\Delta \bar{H}_{sub}$ or $\Delta \bar{H}_{vap}$
2. You know (T_1,p_1) and $\Delta \bar{H}_{sub}$ or $\Delta \bar{H}_{vap}$ for s-g or ℓ-g coexistence and want to know (T_2,p_2) (coexistence).
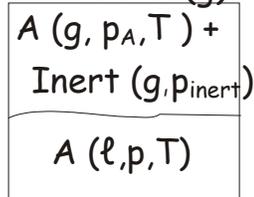
This allows you, for example, to calculate that the boiling point in Denver is 97°C.

Effect of inert gas pressure on vapor pressure over a liquid or solid

Total pressure $p = p_A + p_{Inert}$

Pure A (g + ℓ)

A (g, p_o, T)
A (ℓ, p_o, T)

A + Inert (g)

A (g, p_A, T) + Inert (g, p_{inert})
A (ℓ, p, T)

$p_o \equiv$ equil. vapor pressure of pure A at temperature T

$p_A \equiv$ equil. partial pressure of A in presence of inert gas

What is $p_A(p)$?

At equilibrium, $\mu_A(g, T, p_A) = \mu_A(\ell, T, p)$

Differentiate both sides w.r.t. p

$$d\mu = d\bar{G} = -\bar{S}dT + \bar{V}dp \quad \Rightarrow \quad \left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$$

$$\left(\frac{\partial \mu_A(g, T, p_A)}{\partial p}\right)_T = \left(\frac{\partial \mu_A}{\partial p_A}\right)_T \left(\frac{\partial p_A}{\partial p}\right)_T = \left(\frac{\partial \mu_A(\ell, T, p)}{\partial p}\right)_T$$

$$\bar{V}_g \left(\frac{\partial p_A}{\partial p}\right)_T = \bar{V}_\ell \quad \Rightarrow \quad \left(\frac{\partial p_A}{\partial p}\right)_T = \frac{\bar{V}_\ell}{\bar{V}_g} > 0$$

Presence of inert gas <u>increases</u> p_A. $\bar{V}_\ell \ll \bar{V}_g$ (away from critical point) so the effect is small.

If A is ideal gas $\Rightarrow$

$$\bar{V}_g = \frac{RT}{p_A} \quad \Rightarrow \quad \frac{RT}{p_A} dp_A = \bar{V}_\ell dp$$

$$RT\int_{p_0}^{p_A} \frac{dp_A'}{p_A'} = \bar{V}_\ell \int_{p_0}^{p} dp' \qquad RT\ln\frac{p_A}{p_0} = \bar{V}_\ell(p - p_0)$$

For example, for mercury (Hg)
p_{Hg} = 0.2700 torr at 100°C (pure Hg)
p_{Hg} = 0.2701 torr at 1 bar total pressure
p_{Hg} = 0.2830 torr at 100 bar total pressure

Sample Problem:

A new molecule (a drug), renol, has been synthesized and its phase diagram needs exploring. Near its triple point it is found that the vapor pressure over the liquid (p_ℓ) and over the solid (p_s) are given by
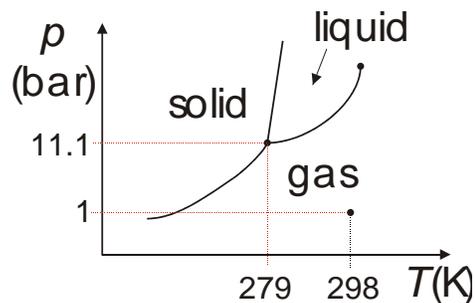
$$\ln p_\ell = -\frac{3,010 \text{ K}}{T} + 13.2 \qquad \ln p_s = -\frac{3,820 \text{ K}}{T} + 16.1$$

(a)   Calculate the triple point temperature T_{tp} and pressure p_{tp}.

Set $\ln p_s = \ln p_\ell$ $\Rightarrow$ $-\frac{3,010 \text{ K}}{T} + 13.2 = -\frac{3,820 \text{ K}}{T} + 16.1$

Solve for T $\Rightarrow$ T_{tp} = 279 K
                 $\Rightarrow$ p_{tp} = 11.1 bar

(b)   Is renol a solid, a gas, or a liquid at (1 bar, 298 K)?

Phase diagram shows it's a gas.

Must be since slopes of (s,g) and (ℓ,g) coexistence curves are always positive.

(c)   What is $\Delta \bar{H}_{subl}$? (approximate)

Use Clausius-Clapeyron equation:

$$\frac{d \ln p_s}{dT} = \frac{3,820 \text{ K}}{T^2} = \frac{\Delta \bar{H}_{subl}}{RT^2}$$

$$\Delta \bar{H}_{subl} = (8.314 \text{ J/K-mol})(3,820 \text{ K}) = 31,760 \text{ J} = 31.8 \text{ kJ}$$

Another example:

RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) is widely used in military applications, including high explosives and rocket and gun propellants. It is also a common ingredient of commercial and military plastic explosives, including C-4 and Semtex, and is often employed for illicit or criminal purposes. It is a white solid with a melting point in the pure state of 204 °C (481 K).

Designing reliable detectors for the presence of RDX requires having an accurate knowledge of its vapor pressure as a function of temperature. Literature data have been reviewed in a recent DOT/TSA report, "Vapor Pressure Data Base for Explosives and Related compounds," by J. C. Wormhoudt (Oct. 2003).

Vapor pressure data for RDX are shown in the diagram. The vapor pressure data are well described by the Clausius-Clapeyron equation to within ±95% confidence limits. Note that the vapor pressure of RDX at 300 K (at which, for example, an explosives detector at an airport security screening station would have to operate is only 10^{-11} bar. Note also that since all reported data are for temperatures less than 450 K the process represented by these data is actually sublimation rather than evaporation from the liquid phase.