

### 3.D.2. Coexistence Curves: Clausius-Clapyron Equation

Consider two phases I & II of a pure PVT system. In the coexistence region, the equilibrium conditions are

$$T^I = T^{II} = T \quad P^I = P^{II} = P \quad \mu^I = \mu^{II} = \mu \quad (3.12a)$$

Since the chemical potential for a pure phase is just the molar Gibbs energy, we have

$$g^I = g^{II} = g$$

so that

$$dg^I = dg^{II} \quad (3.12b)$$

on the coexistence curve. Using (2.108) of §2.F.4, (3.12b) becomes

$$v^I dP - s^I dT = v^{II} dP - s^{II} dT \quad [\text{On coexistence curve.}] \quad (3.12)$$

where lower case letters represent molar quantities. The slope of the coexistence curve  $P = P_{\text{coex}}(T)$  is therefore

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{s^I - s^{II}}{v^I - v^{II}} = \frac{\Delta s}{\Delta v} \quad (3.13)$$

where

$$\Delta X \equiv X^I - X^{II} \quad \forall X$$

In terms of the molar latent heat

$$\Delta h = T \Delta s \quad (3.13a)$$

(3.13) becomes

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta h}{T \Delta v} \quad (3.14)$$

which is known as the **Clausius-Clapyron equation**.

#### Ex.3.1.

Prove that the latent heat is always positive (heat is absorbed) in the transition from a low, to a high, temperature phase.

#### Answer

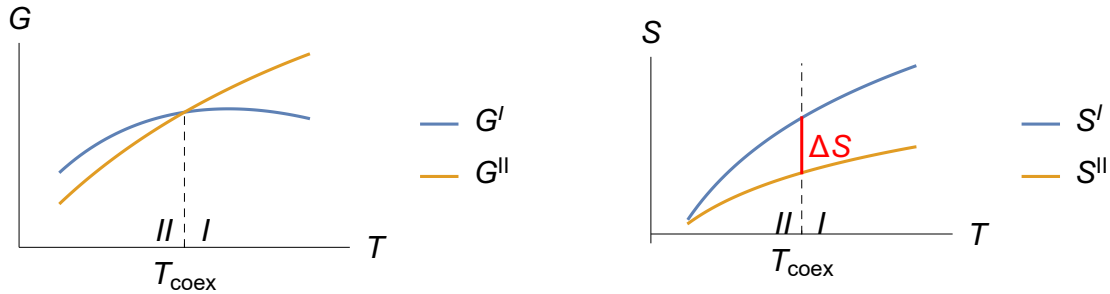
Let I & II be the high & low temperature phases, respectively. Since the stable phase at fixed  $T$  &  $P$  must have the lower Gibbs energy, we have [see figure below],

$$G^I < G^{II} \quad \text{for} \quad T \gtrsim T_{\text{coex}}$$

where  $T_{\text{coex}}$  is the (transition) temperature at a point on the coexistence curve. Since  $G(T)$  is a concave function [see §2.H.3 and figure below], we have

$$\left(\frac{\partial G^{II}}{\partial T}\right)_P > \left(\frac{\partial G^I}{\partial T}\right)_P$$

in the neighborhood of  $T_{\text{coex}}$ .



Using  $S = -\left(\frac{\partial G}{\partial T}\right)_P$ , we have

$$S'' < S' \quad \text{for } T \sim T_{\text{coex}}$$

Thus, in the transition from (low  $T$ ) phase II to (high  $T$ ) phase I, the latent heat (heat absorbed) is

$$\Delta h = T_{\text{coex}} (S' - S'') > 0$$

QED.

## Code

```
In[1]:= G[T_, α_] := T - α T Log[α T]
```

```
In[2]:= Tc = T /. (NSolve[G[T, 1] == G[T, 2], T, Reals] // Flatten)
```

```
Out[2]= 0.25
```

```
In[3]:= Plot[{G[T, 2], G[T, 1]}, {T, .1, .4}, PlotRange -> {{0.05, .45}, {.2, .8}},
  AxesLabel -> {"T", "G"}, Ticks -> {{{Tc, "T_coex"}}, None},
  Epilog -> {Dashed, Line[{{Tc, 0.2}, {Tc, G[Tc, 1]}}],
    Text["I", {1.1 Tc, .25}], Text["II", {.9 Tc, .25}]},
  PlotLegends -> {"GI", "GII"}
]
```

```
In[48]:= sm = -2.5; {s2, s1} = {-∂TG[T, 2], -∂TG[T, 1]} /. T -> Tc;
Plot[{-∂TG[T, 2], -∂TG[T, 1]} // Evaluate, {T, .1, .4},
  PlotRange -> {{0.05, .45}, All}, AxesOrigin -> {0.05, sm},
  AxesLabel -> {"T", "S"}, Ticks -> {{{Tc, "T_coex"}}, None},
  Epilog -> {{Dashed, Line[{{Tc, sm}, {Tc, G[Tc, 1]}}]},
    Text["I", {1.1 Tc, sm + .2}], Text["II", {.9 Tc, sm + .2}],
    Text["ΔS", {1.15 Tc, sm + 1.6}],
    {Red, Thickness[.01], Line[{{Tc, s2}, {Tc, s1}}]}},
  PlotLegends -> {"SI", "SII"}
]
```

### 3.D.2.a. Vaporization Curve

Consider a liquid in a vacuum chamber at some temperature  $T \in (T_A, T_C)$ , where  $T_A$  &  $T_C$  are the temperature at the triple and critical point, respectively. Part of the liquid will evaporate until the vapor pres-

sure is equal to  $P_{\text{coex}}(T)$  [see Fig.3.4]. At which point, equilibrium is established and  $P_{\text{coex}}(T)$  is called the **saturated vapor pressure** at the transition temperature  $T$ .

Now, except for the vicinity of the critical point, the volume of a given amount of substance is much greater in the gas phase than the liquid phase. Hence,

$$\Delta V_{lg} \equiv V_{\text{vapor}} - V_{\text{liquid}} \approx V_{\text{vapor}} \quad \rightarrow \quad \Delta v_{lg} \approx v_{\text{vapor}}$$

In the ideal gas approximation, the vapor molar volume is

$$v_{\text{vapor}} = \frac{V}{n} = \frac{RT}{P}$$

$$\rightarrow \Delta v_{lg} \approx \frac{RT}{P}$$

The Clausius-Clapyron equation (3.14) for the vaporization curve thus becomes

$$\left( \frac{dP}{dT} \right)_{\text{coex}} \approx \frac{P \Delta h_{lg}}{R T^2} \quad [ \text{Far from critical point.} ] \quad (3.15)$$

where  $\Delta h_{lg}$  is the **latent heat of vaporization**.

Since the transition at the critical point is 2nd order,  $\Delta h_{lg}$  necessarily drops rapidly to zero near  $T_c$ . However, except for a small temperature interval near the critical point, one can usually assume  $\Delta h_{lg} \approx \text{constant}$  so that (3.15) can be integrated to give

$$\ln P = -\frac{\Delta h_{lg}}{RT} + \text{const}$$

$$\rightarrow P_{\text{coex}}(T) = P_{\infty} \exp\left(-\frac{\Delta h_{lg}}{RT}\right) \quad (3.16)$$

where  $P_{\infty} = P(\infty)$ .

### Ex.3.2.

Compute the molar heat capacity of a vapor on the vaporization curve.

### Answer

Taking  $P_{\text{coex}}$  as a function defined over the  $T$ - $P$  plane, we have

$$\begin{aligned} c_{\text{coex}} &= T \left( \frac{\partial s}{\partial T} \right)_{\text{coex}} = T \left( \frac{\partial s}{\partial T} \right)_{P_{\text{coex}}} \\ &= T \left[ \left( \frac{\partial s}{\partial T} \right)_P + \left( \frac{\partial s}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_{P_{\text{coex}}} \right] \quad [ (2.8) \text{ of } \S 2.B \text{ used.} ] \\ &= T \left[ \left( \frac{\partial s}{\partial T} \right)_P + \left( \frac{\partial s}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_{\text{coex}} \right] \\ &= c_P + T \left( \frac{\partial s}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_{\text{coex}} \\ &= c_P - T \left( \frac{\partial v}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_{\text{coex}} \quad [ \text{Maxwell relation (2.112) for } G(T, P) \text{ used.} ] \quad (1) \\ &\approx c_P - \left( \frac{\partial v}{\partial T} \right)_P \frac{P \Delta h_{lg}}{RT} \quad [ (3.15) \text{ used.} ] \quad (1a) \end{aligned}$$

Using the ideal gas approximation for the vapor phase, we have

$$\left( \frac{\partial v}{\partial T} \right)_P \approx \left( \frac{\partial v_{\text{vapor}}}{\partial T} \right)_P \approx \frac{R}{P}$$

so that (1a) becomes

$$c_{\text{coex}} \approx c_p - \frac{\Delta h_{lg}}{T} \quad (2)$$

Stability requires

$$c_{\text{coex}} > 0$$

$$\rightarrow c_p > \frac{\Delta h_{lg}}{T}$$

### 3.D.2.b. Fusion Curve

The Clausius-Clapyron equation (3.14) for the fusion curve is [see Fig.3.4],

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta h_{sl}}{T\Delta v_{sl}} \quad \text{for} \quad \begin{cases} T > T_A & \text{if } \left(\frac{dP}{dT}\right)_{\text{coex}} > 0 \\ T < T_A & \text{if } \left(\frac{dP}{dT}\right)_{\text{coex}} < 0 \end{cases} \quad (3.17)$$

For most substances,  $\left(\frac{dP}{dT}\right)_{\text{coex}} > 0$ , so that raising  $P$  at fixed  $T$  will drive a system point in liquid phase

into the solid phase [see fusion curve (solid line with arrow) in Fig.3.4]. However, for  $H_2O$ ,  $\left(\frac{dP}{dT}\right)_{\text{coex}} < 0$ ,

so that raising  $P$  at fixed  $T$  will drive a system point in solid phase into the liquid phase [see fusion curve (dashed line with arrow) in Fig.3.4]. This is what makes skating on ice possible. The pressure exerted by the skate blades turns the ice beneath into water, which acts as lubricant for speedy horizontal movement.

### 3.D.2.c. Sublimation Curve

As in the case of the vaporization curve, a solid in a vacuum chamber at some temperature  $T < T_A$  will sublime until the vapor pressure is equal to  $P_{\text{coex}}(T)$  [see Fig.3.4]. At which point, equilibrium is established and  $P_{\text{coex}}(T)$  is called the **saturated vapor pressure** at the transition temperature  $T$ .

The Clausius-Clapyron equation (3.14) for the sublimation curve is

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta h_{sg}}{T\Delta v_{sg}} \quad (3.18)$$

$$\approx \frac{\Delta h_{sg}}{T\Delta v_g} \quad [v_g \gg v_s] \quad (3.18a)$$

where  $\Delta h_{sg}$  is the **latent heat of vaporization**.

Using the ideal gas approximation for the vapor phase, we have [see (3.15)]

$$\left(\frac{dP}{dT}\right)_{\text{coex}} \approx \frac{P\Delta h_{sg}}{RT^2} \quad (3.19)$$

which can be written as

$$\Delta h_{sg} = R \frac{\frac{dP_{\text{coex}}}{P_{\text{coex}}}}{\frac{dT}{T^2}} = -R \frac{d \ln P_{\text{coex}}}{d(1/T)} \quad (3.20)$$

which allows us to obtain the latent heat  $\Delta h_{sg}$  from the slope of the experimentally obtained curve of  $\ln P_{\text{coex}}$  vs  $\frac{1}{T}$ .

Consider the equation of state for solids [see (2.14) of §2.C.4],

$$v = v_0(1 + \alpha_P T - \kappa_T P) \quad (3.20a)$$

where

$$v_0 = v \Big|_{T=P=0} \quad \alpha_P = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = \text{expansivity} \quad \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = \text{compressibility}$$

In the coexistence region, the vapor pressure  $P$  is usually very small for  $T \ll T_A$ . (3.20a) then simplifies to

$$v = v_0(1 + \alpha_P T) \quad \text{for } T \ll T_A \quad (3.20b)$$

On the sublimation curve, the molar enthalpy change for phase  $\alpha = l, II$  is

$$\begin{aligned} dh^\alpha &= T ds^\alpha + v^\alpha dP_{\text{coex}} \\ &= c_P^\alpha dT + v^\alpha \frac{dP_{\text{coex}}}{dT} dT \end{aligned} \quad (3.21)$$

where

$$c_P = \left( \frac{dq}{dT} \right)_P = \left( \frac{\partial h}{\partial T} \right)_P$$

As shown in Fig.3.4, the sublimation curve levels off as  $T \rightarrow 0$  so that

$$\frac{dP_{\text{coex}}}{dT} \rightarrow 0 \quad \text{as } T \rightarrow 0$$

provided no quantum effects intervene. Hence,

$$dh^\alpha \approx c_P^\alpha dT \quad \text{as } T \rightarrow 0$$

so that, on the sublimation curve,

$$d\Delta h_{sg} \equiv dh^g - dh^s \approx (c_P^g - c_P^s) dT \quad \text{as } T \rightarrow 0$$

Integrating, we have

$$\Delta h_{sg}(T) \approx \Delta h_{sg}^0 + \int_{T_0}^T (c_P^g - c_P^s) dT \quad (3.22)$$

where

$$\Delta h_{sg}^0 = \Delta h_{sg}(T_0)$$

Putting (3.22) into (3.19) gives

$$\begin{aligned} \frac{dP_{\text{coex}}}{dT} &\approx \frac{P_{\text{coex}}}{R T^2} \left[ \Delta h_{sg}^0 + \int_{T_0}^T (c_P^g - c_P^s) dT' \right] \\ \rightarrow \frac{dP_{\text{coex}}}{P_{\text{coex}}} &\approx \frac{1}{R T^2} \left[ \Delta h_{sg}^0 + \int_{T_0}^T (c_P^g - c_P^s) dT' \right] dT \\ \therefore \ln \frac{P_{\text{coex}}(T)}{P_{\text{coex}}^0} &= \int_{T_0}^T \frac{1}{R T'^2} \left[ \Delta h_{sg}^0 + \int_{T_0}^{T'} (c_P^g - c_P^s) dT'' \right] dT' \end{aligned}$$

where

$$P_{\text{coex}}^0 = P_{\text{coex}}(T_0)$$

Hence,

$$\ln \frac{P_{\text{coex}}(T)}{P_{\text{coex}}^0} = \frac{\Delta h_{sg}^0}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) + \int_{T_0}^T \frac{1}{RT'^2} \int_{T_0}^{T'} (c_p^g - c_p^s) dT' dT'' \quad (3.23)$$

### Ex.3.3.

In the neighborhood of the triple point of ammonia ( $\text{NH}_3$ ), the equation for the sublimation curve is

$$\ln P = 27.79 - \frac{3726}{T} \quad (1a)$$

while that for the vaporization curve is

$$\ln P = 24.10 - \frac{3005}{T} \quad (1b)$$

where  $P$  &  $T$  are in units of Pa & K, respectively. Thus, each term in (1a) & (1b) are dimensionless. Alternatively, we can say that the constants 3726 & 3005 have dimensions  $[T] = K$ .

- Compute  $T$  &  $P$  of the triple point.
- Find  $\Delta h_{sg}$  &  $\Delta h_{lg}$ .

### Answer (a)

At the triple point  $A$ , all 3 phases coexist at the same  $P$  &  $T$ . Equating (1a) and (1b) gives

$$27.79 - \frac{3726}{T_A} = 24.10 - \frac{3005}{T_A}$$

with solution

$$T_A = 195.4 \text{ K}$$

where we have put back the unit by hand.

Putting this back into (1a) gives

$$\begin{aligned} P_A &= \exp\left(27.79 - \frac{3726}{195.4}\right) \\ &= 6132.9 \text{ Pa} = 6.13 \text{ kPa} \quad [\text{Unit added by hand.}] \end{aligned}$$

### Code

$$\text{NSolve}\left[27.79 - \frac{3726}{T_A} == 24.10 - \frac{3005}{T_A}, T_A\right]$$

{ {  $T_A \rightarrow 195.393$  } }

$$\text{Exp}\left[27.79 - \frac{3726}{195.4}\right]$$

6132.9

### Answer (b)

For the sublimation curve,  $\frac{d(1a)}{dT}$  gives

$$\begin{aligned} \frac{1}{P_{\text{coex}}} \frac{dP_{\text{coex}}}{dT} &= \frac{3726}{T^2} \\ \rightarrow \left( \frac{\partial P}{\partial T} \right)_{\text{coex}} &= \frac{dP_{\text{coex}}}{dT} = P_{\text{coex}} \frac{3726}{T^2} \\ &\approx \frac{P_{\text{coex}} \Delta h_{sg}}{RT^2} \quad [ (3.19) \text{ used.} ] \end{aligned} \quad (1)$$

Since 3726 has dimensions  $[T] = K$ , we have

$$\begin{aligned} \Delta h_{sg} &\approx 3726 R \cdot [T] \\ &\approx 3726 \times 8.314 \text{ J/mol} \\ &\approx 31 \text{ kJ/mol} \end{aligned}$$

$$3726 \times 8.314$$

$$30978.$$

For the vaporization curve,  $\frac{d(1b)}{dT}$  gives

$$\frac{1}{P_{\text{coex}}} \frac{dP_{\text{coex}}}{dT} = \frac{3005}{T^2} \approx \frac{P_{\text{coex}} \Delta h_{lg}}{RT^2} \quad (2)$$

$$\begin{aligned} \rightarrow \Delta h_{lg} &\approx 3005 R \cdot [T] \\ &\approx 25 \text{ kJ/mol} \end{aligned}$$

$$3005 \times 8.314$$

$$24983.6$$