

# KK ch. 10 Phase transformations

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We finally get to the interesting stuff.

Some information you will never need:

Phase transitions are purely thermodynamic phenomena based solely on the free-energy.

Phase transformations include kinetics

Diamond vs coal

Coal vs hot air

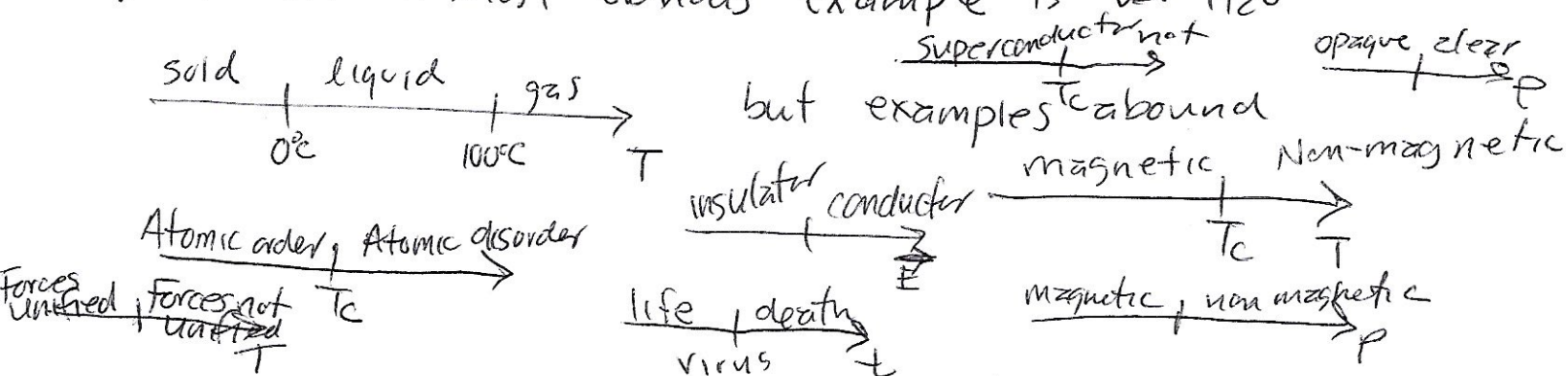
The two terms are pretty much used interchangeably, but at least now you can secretly judge people when they use the incorrect term.

Vapor is the term used for a gas that is in equilibrium with its solid or liquid form. Phase transitions are discontinuities in the free energy and

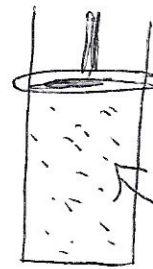
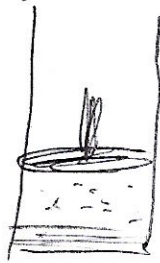
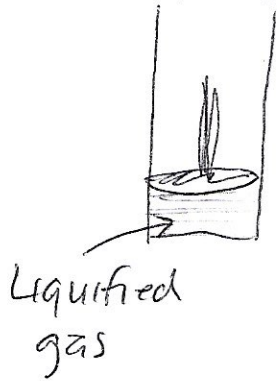
$F = -T \ln Z$ , so they are discontinuities in the partition function,  $Z = \sum e^{-\epsilon_i/kT}$

A "phase" is an arrangement of matter, so the crystal structure, or lack of (body-centered cubic, glass, liquid, gas, pasta)

In real life, it means that you change a parameter by a little bit,  $T, p$ , etc. and you get an important, qualitatively distinct system. Most obvious example is  $H_2O$



Consider a gas in a tank at really high pressure, but you start using it

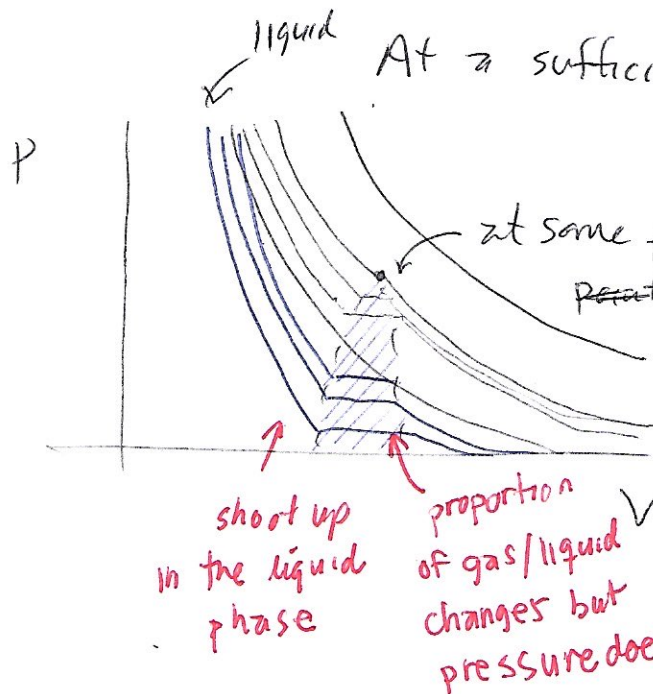
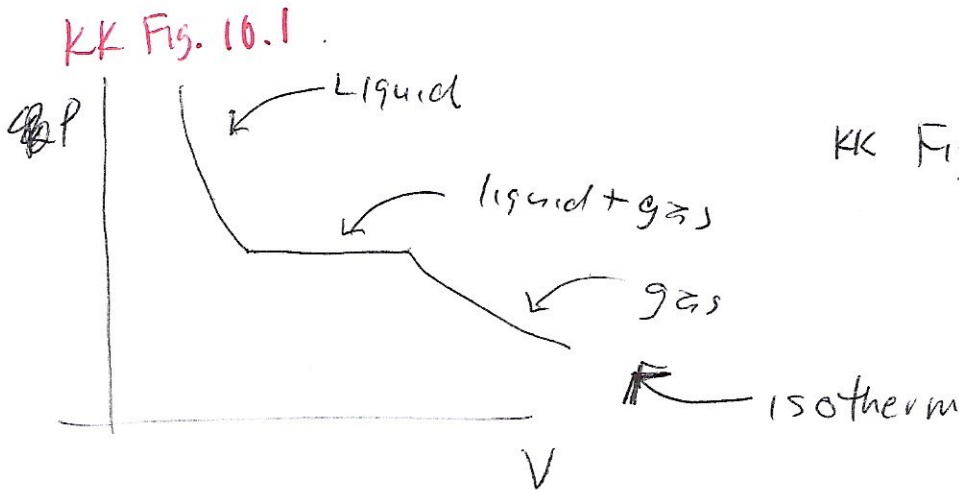


liquid and gas are in thermal, diffusive, and mech. contact

WHAT HAPPENS IN BETWEEN

WHAT IS THE DIFFERENCE BETWEEN GAS AND LIQUID  
Liquids interact

KK Fig. 10.1



At a sufficiently high  $\tau$ ,

it is always a gas

at some point, ~~there is a~~ point the derivative is zero, below this  $\tau$

there is a region of

coexistence, not

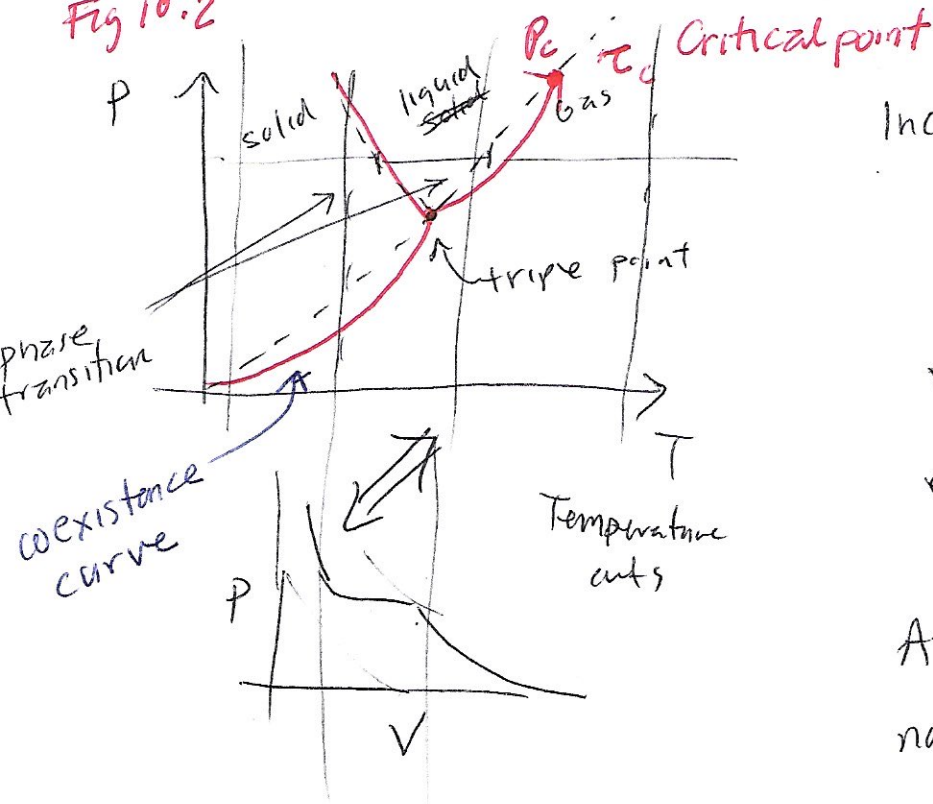
just a point.

At a sufficiently low  $\tau$ , it is always a liquid

proportion of gas/liquid changes but pressure does not

How does this look in the PT plane? Consider  $H_2O$

Fig 10.2



Increase pressure,  $T$  range for solid and liquid increases, gas decreases (although it goes to  $\infty$ )

You can imagine that at low enough pressure, solid would sublimate.

At zero  $P$ , everything goes to gas no matter how low  $T$ .

Let's get more quantitative. The system is in thermal, diffusive, and mechanical eq.

so  $T_l = T_g$  thermal equilibrium  
same  $T$  even though they are in different phases

$\mu_l = \mu_g$  diffusive equilibrium

KK Eq. 10.1  $P_l = P_g$  mechanical equilibrium

Coexistence curve  
Given by:  
 $\mu_l(T_c, P_c) = \mu_g(T_c, P_c)$

KK Eq. 10.3

Consider a small change  $c$ , they still have to match.

$$\mu_g(P_0 + dp, T_0 + dT) = \mu_l(P_0 + dp, T_0 + dT) \quad \text{KK Eq. 10.4}$$

~~$$\left(\frac{\partial \mu_g}{\partial P}\right)_T dp + \left(\frac{\partial \mu_g}{\partial T}\right)_P dT = \left(\frac{\partial \mu_l}{\partial P}\right)_T dp + \left(\frac{\partial \mu_l}{\partial T}\right)_P dT$$

$$\left(\frac{\partial \mu_g}{\partial T}\right)_P dT - \left(\frac{\partial \mu_l}{\partial T}\right)_P dT = \left(\frac{\partial \mu_l}{\partial P}\right)_T dp - \left(\frac{\partial \mu_g}{\partial P}\right)_T dp$$~~



$$\mu_g(p_0 + dp, \tau_0 + d\tau) = \mu_l(p_0 + dp, \tau_0 + d\tau)$$

Taylor expansion  $f(x) = f(a) + f'(a)(x-a) + \dots$  first order  
evaluated at  $a = p_0, \tau_0$

$$\begin{aligned} \mu_g(p_0 + dp, \tau_0 + d\tau) &= \cancel{\mu_g(p_0, \tau_0)} + \left( \frac{\partial \mu_g(p_0, \tau_0)}{\partial p} \right)_{\tau} (\cancel{p_0 + dp} - \cancel{p_0}) \\ &\quad + \left( \frac{\partial \mu_g(p_0, \tau_0)}{\partial \tau} \right)_{p} (\cancel{\tau_0 + d\tau} - \cancel{\tau_0}) \end{aligned}$$

$$\begin{aligned} \mu_l(p_0 + dp, \tau_0 + d\tau) &= \cancel{\mu_l(p_0, \tau_0)} + \left( \frac{\partial \mu_l(p_0, \tau_0)}{\partial p} \right)_{\tau} (\cancel{p_0 + dp} - \cancel{p_0}) \\ &\quad + \left( \frac{\partial \mu_l(p_0, \tau_0)}{\partial \tau} \right)_{p} (\cancel{\tau_0 + d\tau} - \cancel{\tau_0}) \end{aligned}$$

since  $\mu_g(p_0, \tau_0) = \mu_l(p_0, \tau_0)$ ,

$$\left( \frac{\partial \mu_g}{\partial p} \right)_{\tau} dp + \left( \frac{\partial \mu_g}{\partial \tau} \right)_{p} d\tau = \left( \frac{\partial \mu_l}{\partial p} \right)_{\tau} dp + \left( \frac{\partial \mu_l}{\partial \tau} \right)_{p} d\tau \quad \text{KK Eq. 10.6}$$

$$\left[ \left( \frac{\partial \mu_g}{\partial p} \right)_{\tau} - \left( \frac{\partial \mu_l}{\partial p} \right)_{\tau} \right] dp = \left[ \left( \frac{\partial \mu_l}{\partial \tau} \right)_{p} - \left( \frac{\partial \mu_g}{\partial \tau} \right)_{p} \right] d\tau$$

$$\frac{dp}{dT} = \frac{\left(\frac{\partial \mu_l}{\partial T}\right)_p - \left(\frac{\partial \mu_g}{\partial T}\right)_p}{\left(\frac{\partial \mu_g}{\partial p}\right)_T - \left(\frac{\partial \mu_l}{\partial p}\right)_T}$$

KK Eq. 10.7

Differential equation of the coexistence curve

Remember that  $G = N\mu(p, T) \Rightarrow \mu(p, T) = \frac{G(N, p, T)}{N}$

$$\frac{1}{N} \left(\frac{\partial G}{\partial p}\right)_{N, T} = \frac{V}{N} = \left(\frac{\partial \mu}{\partial p}\right)_T = v \quad \text{specific volume}$$

$$\frac{1}{N} \left(\frac{\partial G}{\partial T}\right)_{N, p} = -\frac{S}{N} = \left(\frac{\partial \mu}{\partial T}\right)_p = -s \quad \text{specific entropy}$$

then

$$\frac{dp}{dT} = \frac{-s_l - (-s_g)}{v_g - v_l} = \frac{s_g - s_l}{v_g - v_l}$$

← change in entropy when a molecule moves from liquid to gas

KK Eq. 10.11

← change in ~~ent~~ volume when a molecule moves from liquid to gas

Entropy times temperature is heat, ~~the~~ the quantity  $T(s_g - s_l) \equiv L$  is called the latent heat of vaporization, which is easily measured in the lab.  $\Delta v$  also easily measured.

$$T \frac{dp}{dT} = \frac{T(s_g - s_l)}{v_g - v_l} = \frac{L}{\Delta v}$$

$$\boxed{\frac{dp}{dT} = \frac{L}{T \Delta v}}$$

Clausius - Clapeyron Equation

KK Eq. 10.15

Completely agnostic of the atomistic details.

A useful simplification of the Clausius-Clapeyron Eq.

involves  $\Delta v \approx v_g$ , since  $v_l$  is typically much smaller.

Also, assuming ideal gas behavior,  $pV = N\tau$

$$v_g = \frac{V_g}{N} \Rightarrow V_g = Nv_g \Rightarrow \frac{N\tau}{p} = Nv_g$$

$$\text{so } \frac{dp}{d\tau} \approx \frac{L}{\tau(\tau/p)} = \frac{Lp}{\tau^2}$$

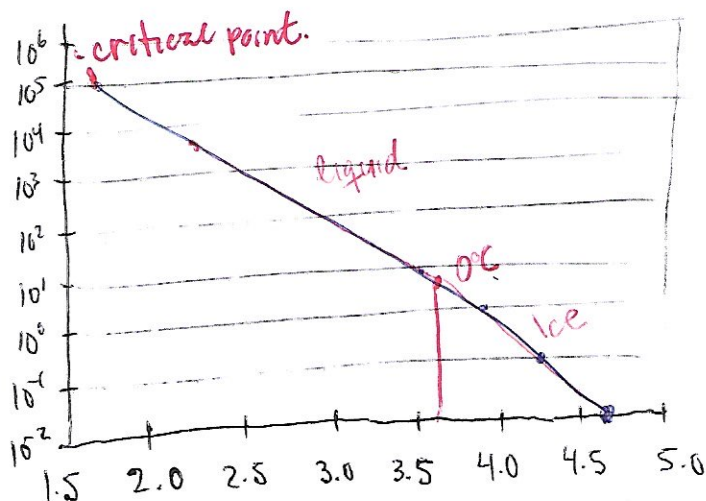
$$\frac{1}{p} \frac{dp}{d\tau} = \frac{d}{d\tau} \ln p = \frac{L}{\tau^2} \quad \text{KK Eq. 10.18}$$

we can also integrate. Assuming  $L$  independent of  $\tau$ ,  $L_0$ ,

$$\int \frac{dp}{p} = L_0 \int \frac{d\tau}{\tau^2} \Rightarrow \ln p = -\frac{L_0}{\tau} + \text{Constant}$$

$\exp(\ln p) = \exp\left(-\frac{L_0}{\tau}\right) \exp(\text{constant})$ . Let  $\exp(\text{constant}) = p_0$

$$p(\tau) = p_0 e^{-L_0/\tau} \quad \text{KK Eq. 10.20}$$



Vapor pressure of water

KK Fig. 10.3