

# Lecture 9

## Phase diagrams of simple systems

## Stability of phases - free energy condition

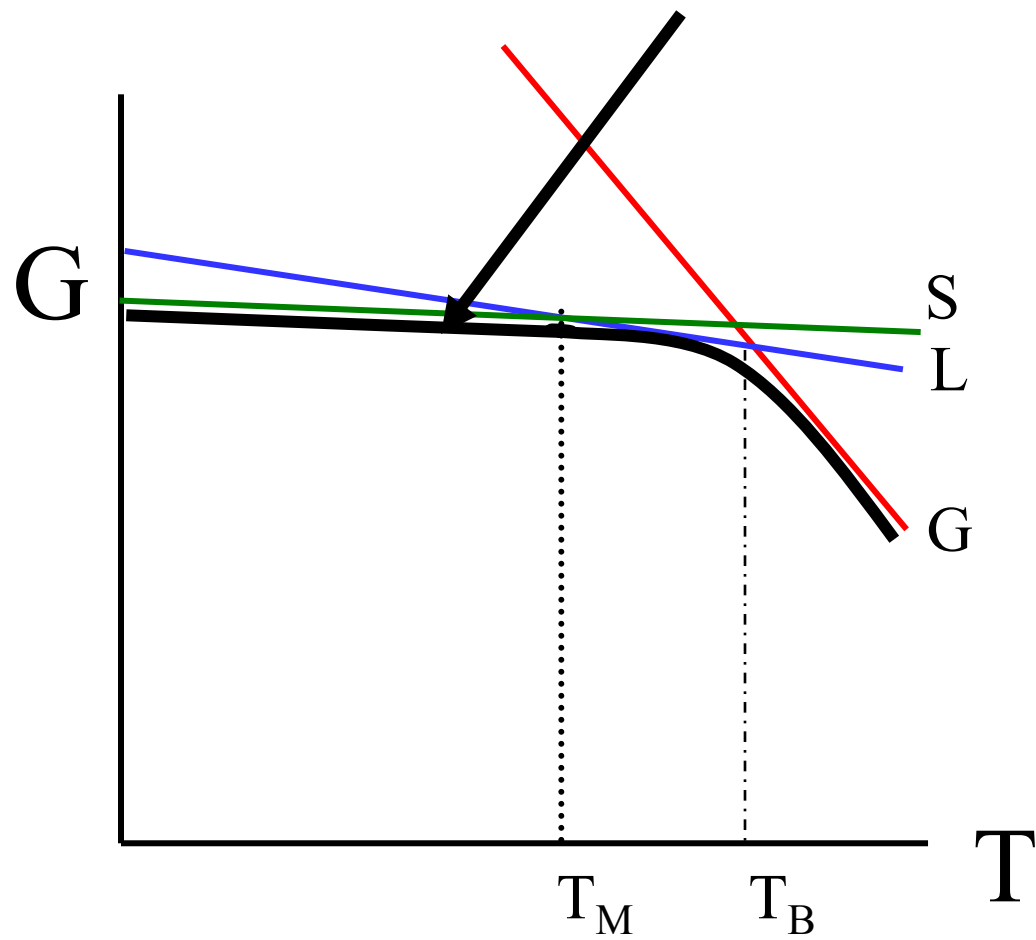
In the following diagram for all temperatures below  $T_B$  the liquid is stable and for all temperatures below  $T_M$  the solid is stable. For all temperatures above  $T_B$ , gas is stable.

Is a G vs. T diagram enough?

Phase diagram represents state of the system.

Any point in the phase diagram tells about the system completely. The phase diagram is far more informative than the simple free energy vs. temperature diagram.

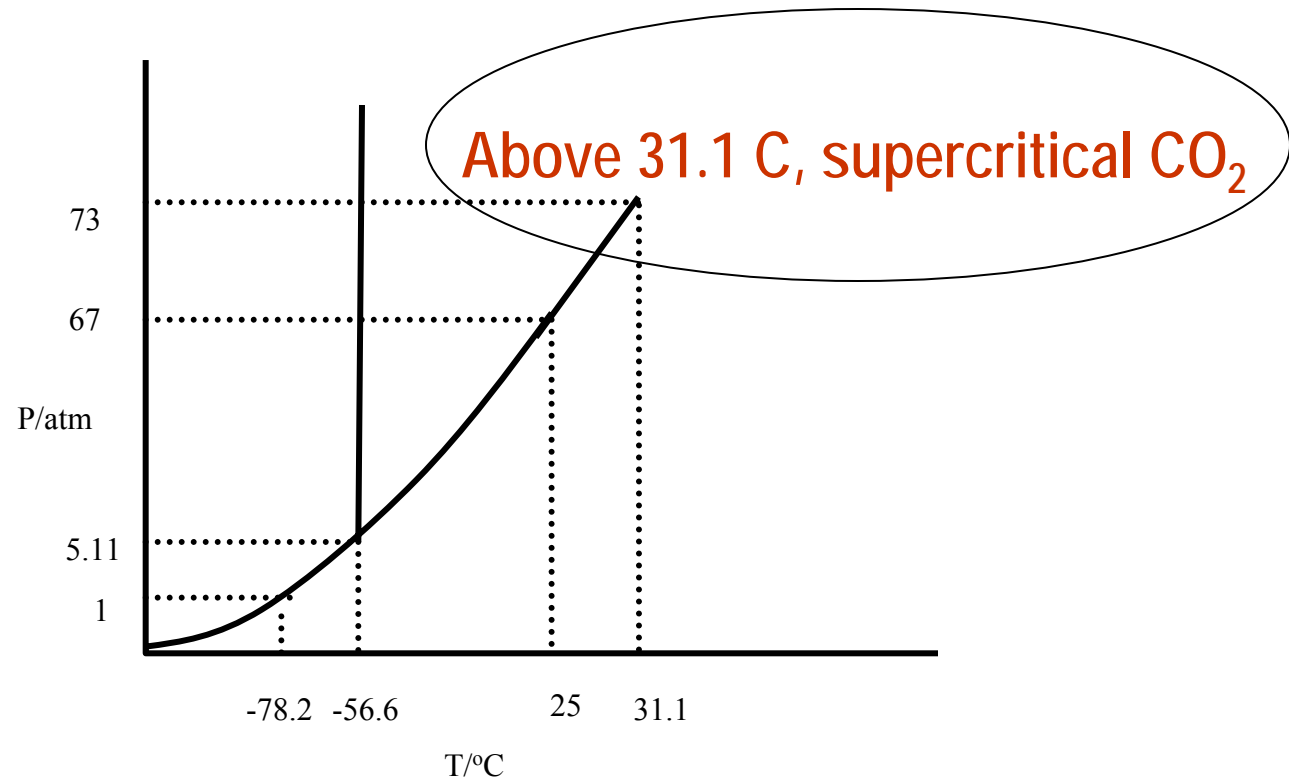
Which path will the system take?



# CARBON DIOXIDE

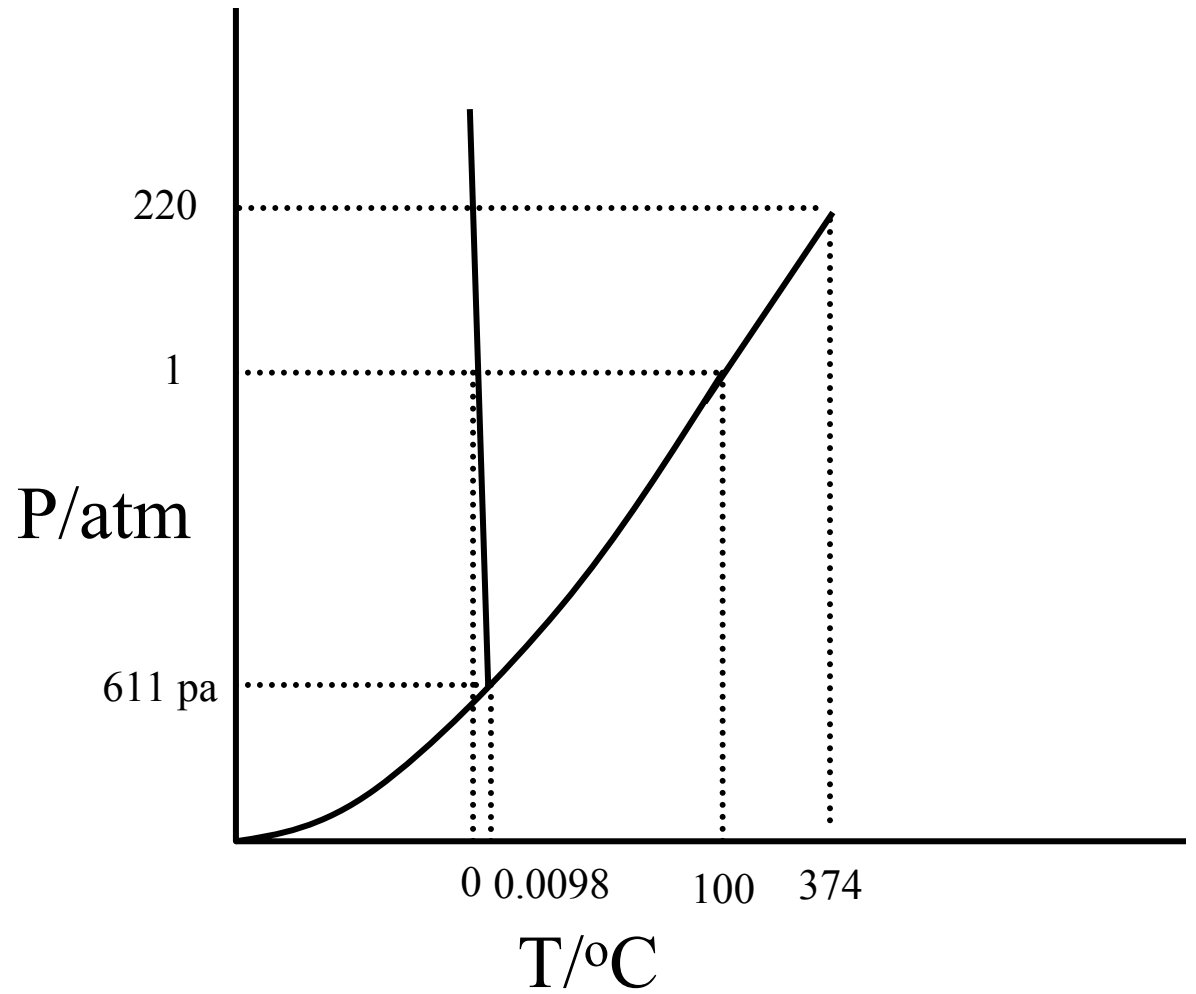
$$\bar{V}_{\text{liq}} > \bar{V}_{\text{solid}}$$

Dry ice – No stable liquid phase at 1 atm and therefore, ice evaporates directly and thus dry. In a CO<sub>2</sub> cylinder, the critical point is above RT and in CO<sub>2</sub> cylinders at 25 C, gas will be in equilibrium with liquid and the pressure will be at 67 atm.

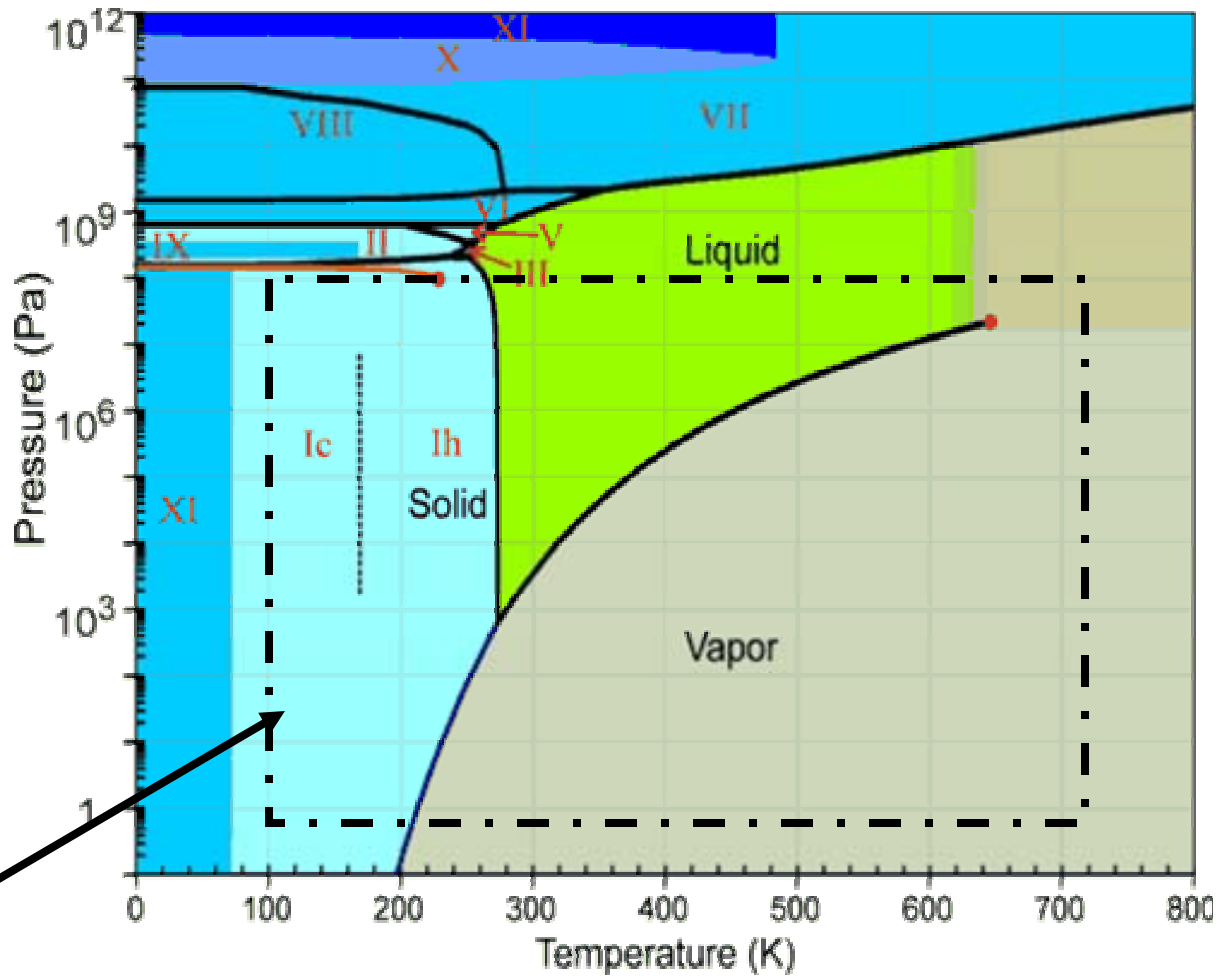


# WATER

$$\bar{V}_{\text{liq}} < \bar{V}_{\text{solid}}$$

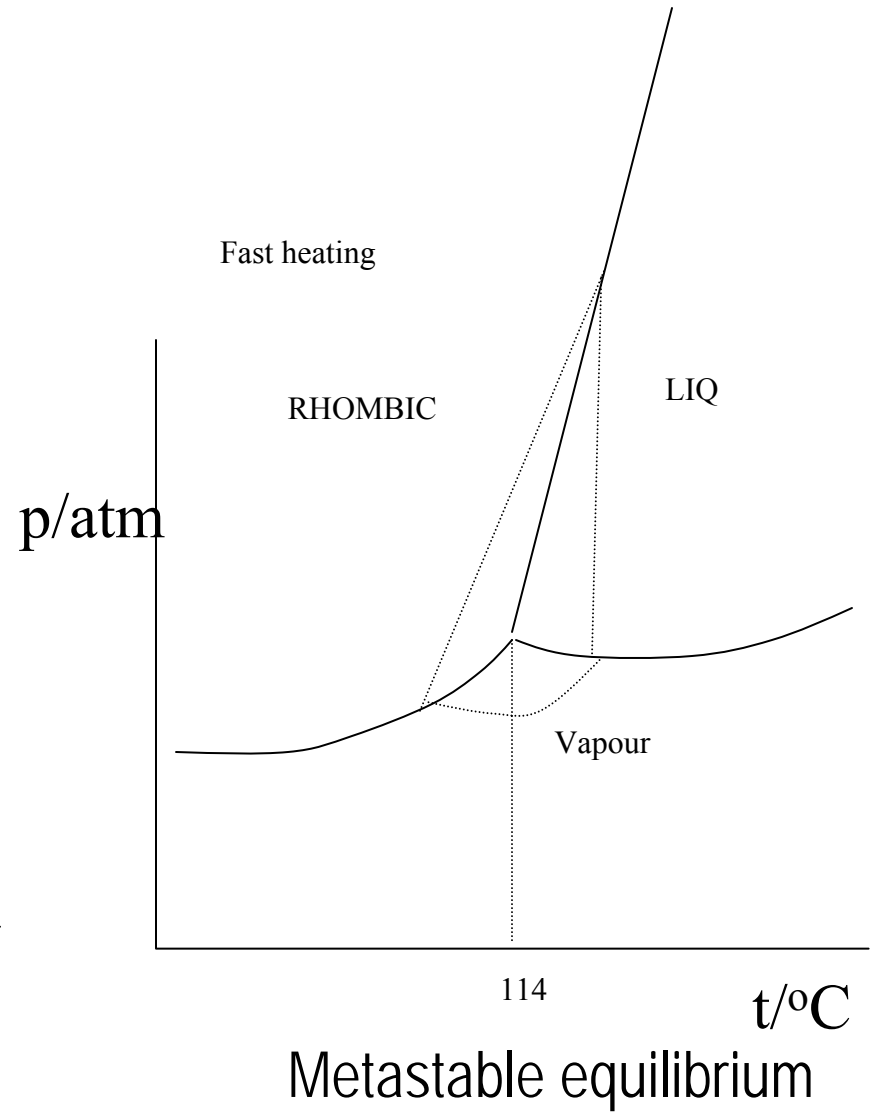
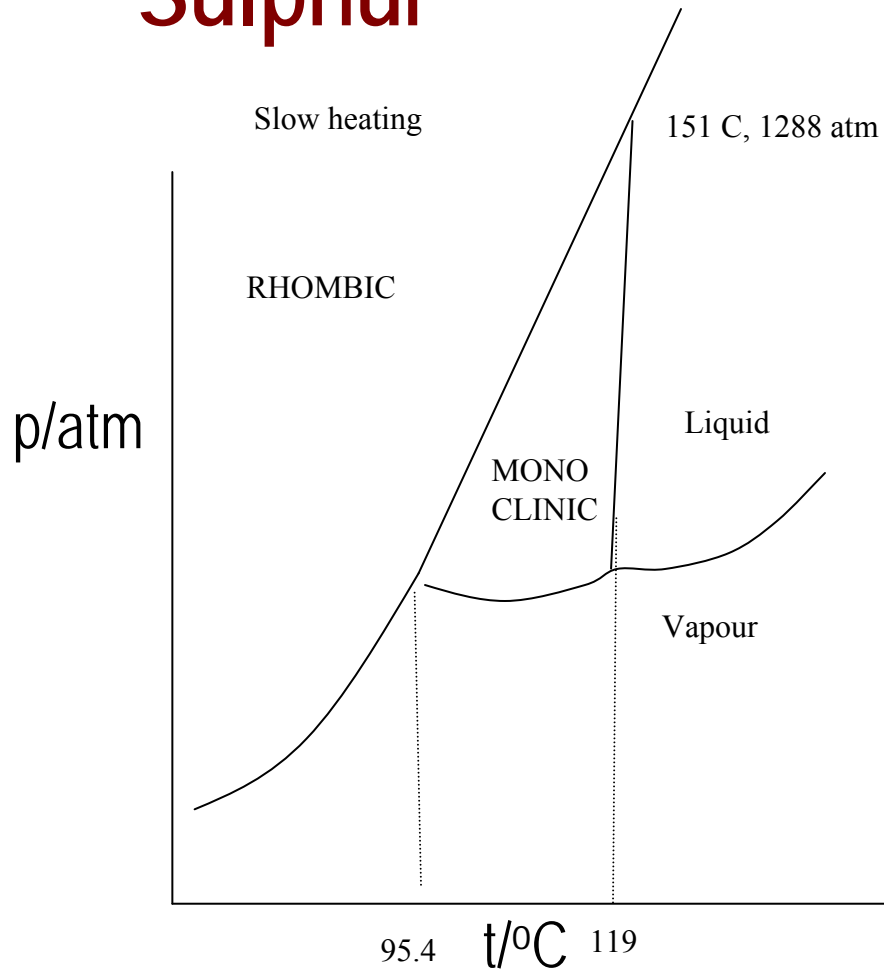


The region you saw earlier



Phase Diagram of Ice

# Sulphur



At 95.4°C

$$\mu_{RH} = \mu_{MONO} = \mu_{GAS}$$

At 119°C

$$\mu_{MONO} = \mu_{LIQ} = \mu_{GAS}$$

At 151°C

$$\mu_{RH} = \mu_{MONO} = \mu_{LIQ}$$



# INTEGRATION OF CLAPEYRON EQUATION

$$dp/dT = \Delta S_{\text{liq}}/\Delta V_{\text{fus}} \leftarrow \text{CLAPEYRON EQUATION (Melting)}$$

$$\int_{P_1}^{P_2} dp = \int_{T_M}^{T_{M'}} [\Delta H_{\text{fu}}/\Delta V_{\text{fu}}] dT/T$$

$\Delta H$  and  $\Delta V$  are nearly independent of temperature

$$P_2 - P_1 = [\Delta H_{\text{fu}}/\Delta V_{\text{fu}}] \ln T_{M'}/T_M$$

$T_{M'} - T_M$  is quite small.

$$\ln T_{M'}/T_M = \ln [(T_M + T_{M'} - T_M)/T_M] = \ln [1 + (T_{M'} - T_M)/T_M]$$

$$\approx (T_{M'} - T_M)/T_M$$

$$\Delta P = \Delta H_{\text{fu}}/\Delta V_{\text{fu}} \Delta T/T_M$$

# SOLID – GAS OR LIQUID – GAS EQUILIBRIUM

$$dP/dT = \Delta \bar{S} / \Delta \bar{V} = \Delta H / T (V_g - \bar{V}_{s/l})$$

$$\bar{V}_g \gg \bar{V}_{s/l}$$

$$d \ln P / dT = \Delta H / RT^2 \quad \bar{V}_g = RT/P$$

$$\int_{P_0}^P d \ln P = \int_{T_0}^T \Delta H / RT^2 dT$$

$$\ln P / P_0 = -\Delta H / T (1/T - 1/T_0)$$

$$= -\Delta H / RT + \Delta H / RT_0$$

$P_0 = 1 \text{ atm}$   $T_0 = T$ , the normal boiling point

$$\ln P = \Delta H / RT_0 - \Delta H / RT$$

$$\log_{10} P = \Delta H / 2.303RT_0 - \Delta H / 2.303RT$$

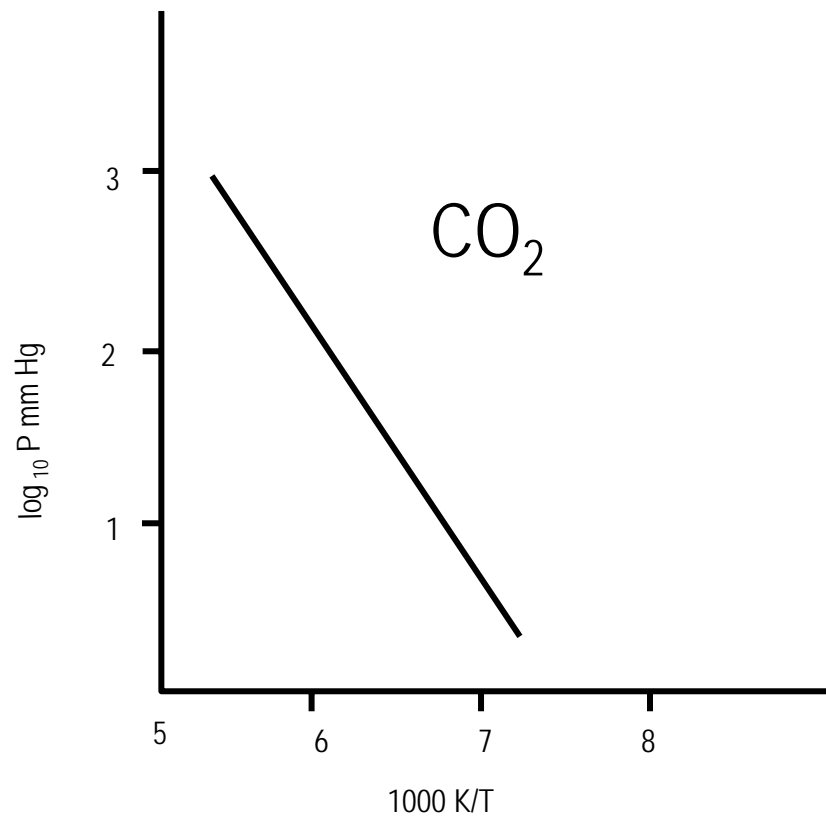
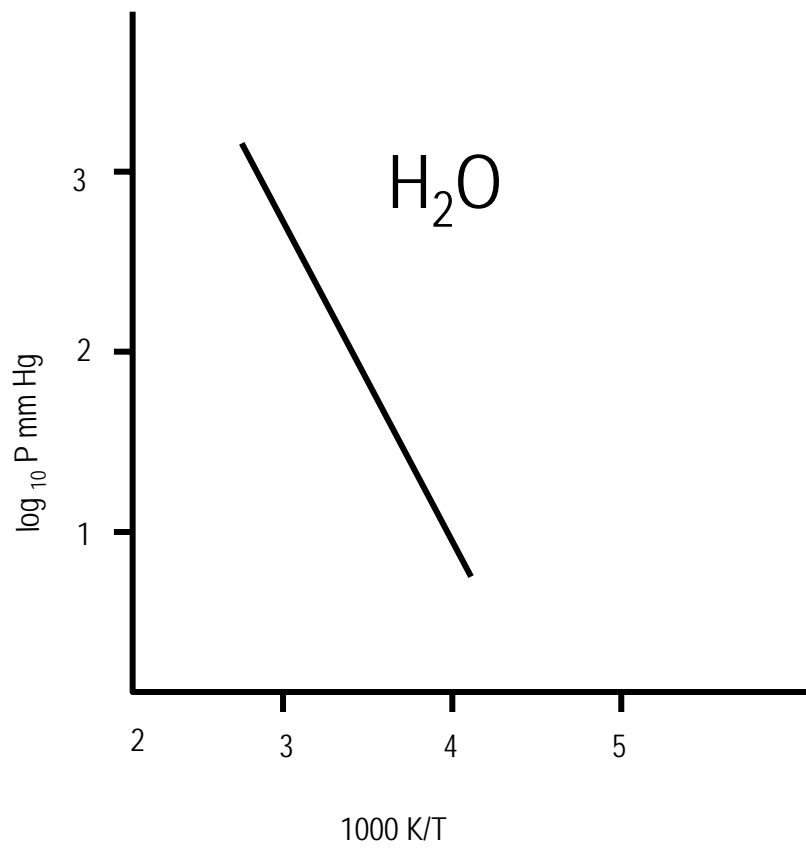
$\ln P$  or  $\log_{10} P$  vs.  $1/T$

Slope  $-\Delta H / R$  or  $-\Delta H / 2.303R$

Intercept  $\Delta H / RT_0$  or  $\Delta H / 2.303RT_0$

This equation is the same as,  $\log_{10} P = A + BT$

A and B are tabulated for substances



# PHASE RULE

Coexistence of two phases, condition:

$$\mu_{\alpha}(T,P) = \mu_{\beta}(T,P)$$

The two intensive variables are related.

Only one true variable - univariant

Three phases,

$$\mu_{\alpha}(T,P) = \mu_{\beta}(T,P)$$

$$\mu_{\beta}(T,P) = \mu_{\gamma}(T,P)$$

There are two relations and therefore the system is invariant

So for one component, number of variables,

$F = 3 - P$ , is the **Phase Rule**.

## How about a general rule?

There are several components and several relations between components. At equilibrium, there are relations between chemical potentials.

How many relations exist?

1. PC - Composition variables for P phases

(In each phase, mole fraction of each component has to be specified. C mole fractions for one phase, PC for P phases.)

2. 2 – Variables corresponding to T and P

Total variables to be known = PC + 2

We have also some relations existing.

1. P - P relations of mole fractions

Why: Each phase, there is a relation,  $x_1 + x_2 + x_3 + \dots + x_C = 1$   
P phases, P equations

2. C(P-1) - C(P - 1) equations of  $\mu$ 's.

Why: For each component, there are a set of equations:

$$\mu_i^\alpha + \mu_i^\beta = \mu_i^\gamma = \dots = \mu_i^P$$

(there are P-1 relations in each set, C(P-1) for C components)

Finally the number of variables,

$$F = PC + 2 - P - C(P - 1)$$

or

$$F = C - P + 2$$

This is the Gibbs phase rule. Can we find out F for a given system?