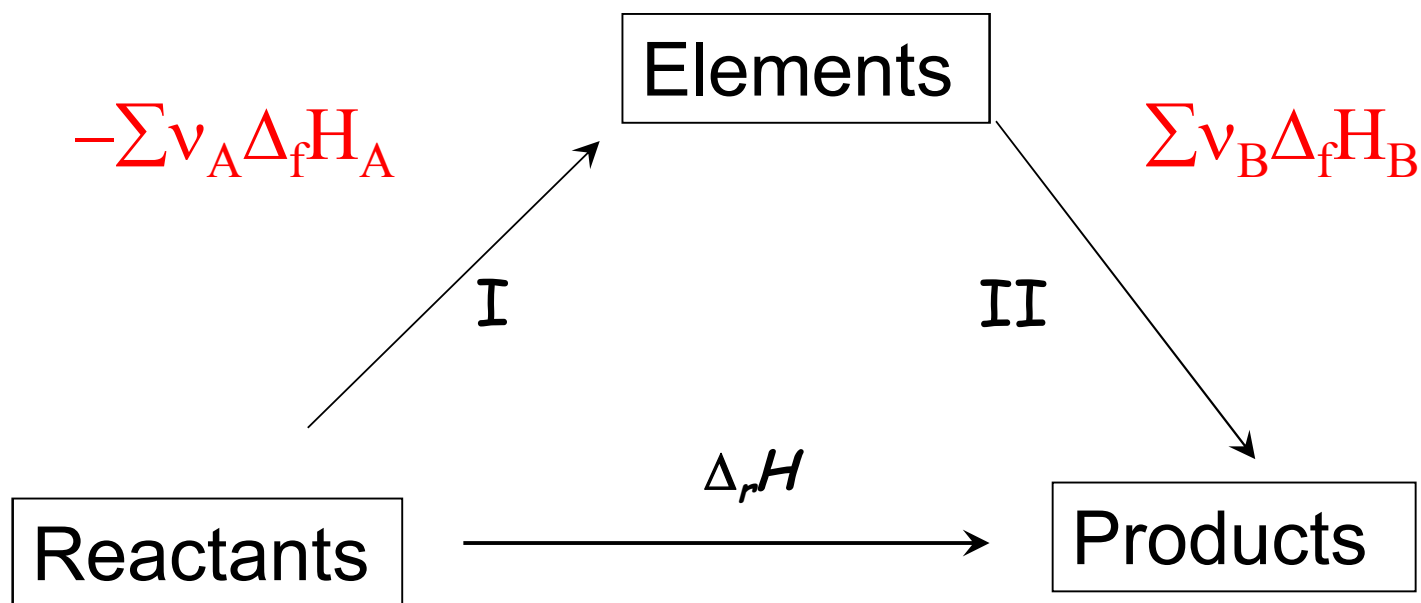
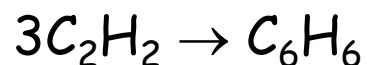


Heat of reaction from heat of formation data

Suppose we first decompose the reactants to their elements (reverse of the formation reaction), then we recombine the products from the elements,



$$\Delta_r H = \Delta_r H(I) + \Delta_r H(II) = \sum v_B \Delta_f H_B - \sum v_A \Delta_f H_A = \Delta_r (\Delta_f H)$$



$$\Delta_r H = \Delta_f H_{\text{C}_6\text{H}_6} - 3 \cdot \Delta_f H_{\text{C}_2\text{H}_2}$$

THE DIRECTION OF PROCESSES IN NATURE

(spontaneity)

- $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$ and not the reverse
- gases uniformly fill the space available (expand)
- a hot object cools down to the temperature of its environment (heat is dissipated)

Ordered \longrightarrow Disordered

In the processes occurring spontaneously energy is dissipating.

We introduce a new state function, which can be used as the measure of the disorder. In *spontaneous* processes in *isolated* systems its change should be *positive*:

S: entropy, the measure of disorder

$$Q_{rev} = T \cdot S$$

$$[S] = \text{J/K}$$

Heat input: the motion becomes more disordered

Work input: makes the system more ordered

Any changes can be characterized by an entropy change.

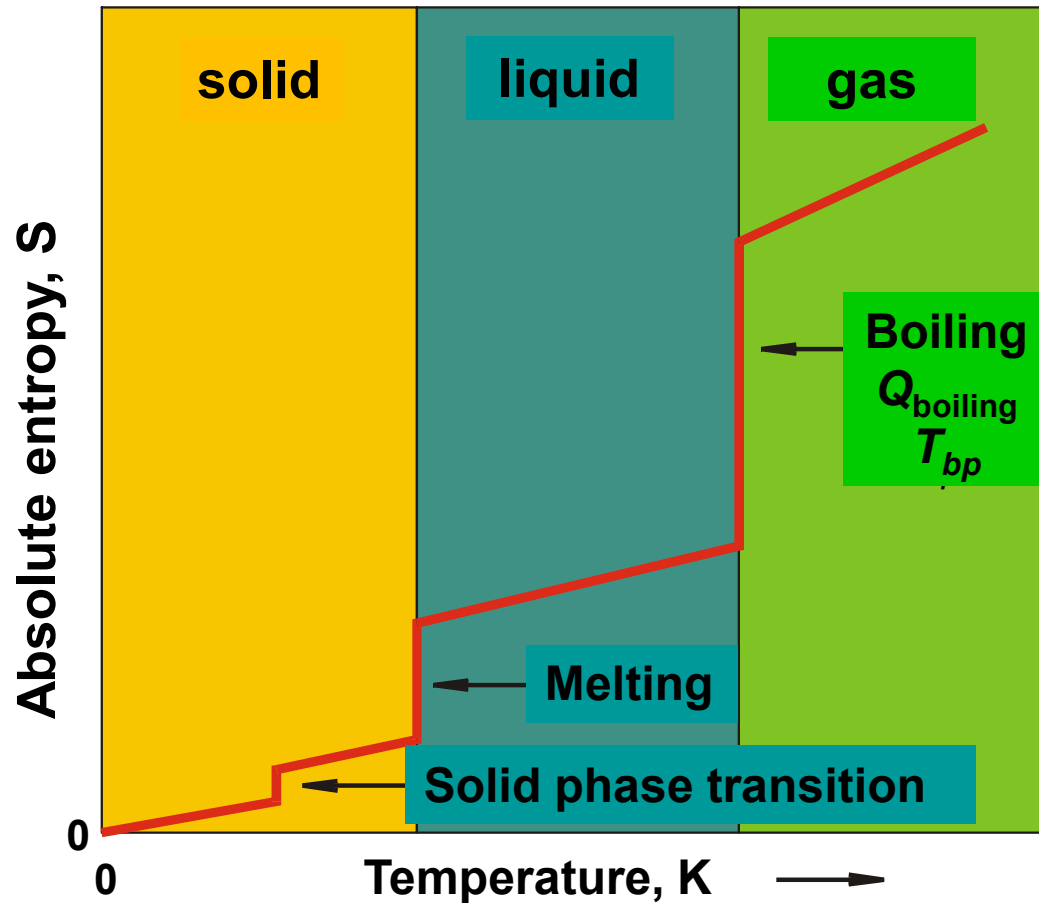
State function, extensive property (depends of the amount)

$$S = nS_m \quad \text{molar entropy}$$

Spontaneous macroscopic processes in isolated systems always increase the entropy. The system gets into equilibrium when its entropy reaches its maximum value.

(This is the 2nd law of thermodynamics.)

T dependence of entropy:



$$\Delta S(\text{phase tr.}) = \frac{Q_{\text{phase tr.}}}{T_{\text{phase tr.}}}$$

at $T=0$ K

- No motion: $S_{\text{thermal}}=0$
- Organisation (configuration) of the atoms might be disordered: $S_{\text{configuration}} > 0$

For pure and perfect crystals at $T \equiv 0$ K $S = 0$. (This is the 3rd law of thermodynamics.)

→ Unlike U and H , the absolute value of entropy is known.³⁵

Entropy at phase transitions (isothermal-isobaric processes)

e.g.

$$\Delta S(\text{melting}) = \frac{\Delta H(\text{melting})}{T_{\text{melting}}}$$

$$\Delta S(\text{evap}) = \frac{\Delta H(\text{evap})}{T_{\text{boiling}}}$$

S increases

heating

melting

evaporation

expansion

Disorder increases

S decreases

cooling

freezing

condensation

compression

Disorder decreases

Entropy of evaporation at the normal boiling point (p=1 atm)

| chemical | $\Delta S(\text{evap})_1, \text{JK}^{-1}\text{mol}^{-1}$ |
|----------------------|--|
| bromine | 88.6 |
| benzene | 87.2 |
| carbon tetrachloride | 85.9 |
| cyclohexane | 85.1 |
| H ₂ S | 87.9 |
| ammonia | 97.4 |
| water | 109.1 |
| mercury | 94.2 |

EXERCISE 1

Problem:

The entropy of evaporation of cyclohexane at its normal boiling point (1 atm, 197.3 °C) is 85.1 J/(molK). Calculate its heat of evaporation at this temperature.

Solution:

EXERCISE 2

Problem:

The melting point of nitrogen is $-196\text{ }^{\circ}\text{C}$.

What will be the change of entropy if 15 liter of liquid nitrogen is evaporated at atmospheric pressure? The density of the liquid nitrogen is 0.81 g/cm^3 ?

What will be the sign of the change and explain why.

Solution:

EXERCISE 3

Problem:

How much heat should be removed from the system if we intend to cool 5 m³ ethane gas from 140 °C to 30 °C ?

The temperature dependence of the molar heat can be neglected.

Solution:

EXERCISE 4

Problem:

The mass of a single cube of sugar ($C_{12}H_{22}O_{11}$) is ca. 1.5 g.
How much heat is evolved when a cube is completely burned in excess oxygen?

Solution:

In spontaneous macroscopic processes the entropy always increases.

In isolated system

$$\Delta S_{system} \geq 0$$

If not isolated

$$\Delta S_{system} + \Delta S_{surrounding} \geq 0$$

The entropy change of an arbitrary process:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$$

if p and T are constant

$$\Delta S_{surrounding} = -\frac{\Delta H_{system}}{T} \quad \begin{array}{l} \text{endothermic} \\ \text{exothermic} \end{array}$$

$$\Delta S_{total} = -\frac{\Delta H_{system}}{T} + \Delta S_{system} \quad / \cdot T$$

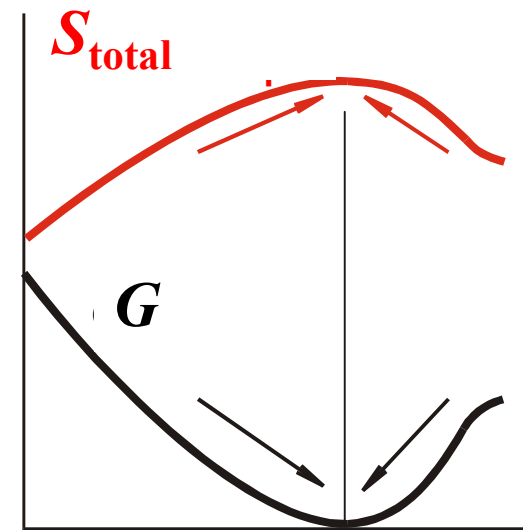
$$T \Delta S_{total} = -\Delta H_{system} + T \Delta S_{system}$$

$$G \equiv H - TS \quad \text{Gibbs free energy}$$

$$-T \Delta S_{total} = \Delta H - T \Delta S \equiv \Delta G$$

In a closed system at constant T and p in spontaneous processes G decreases. When equilibrium is reached, it has a minimum (if no work occurs).

Spontaneity \Leftrightarrow rate $G_{m,graphite} - G_{m,diamond} = -3 \frac{kJ}{mol}$



Direction of changes

Most important properties of G :

1. State function
2. Extensive quantity $G = nG_m$
3. $G = H - TS$

Total energy
stored in the system

Energy stored by the
thermal motion of the atoms/molecules

The spontaneity of a process depends on the sign of ΔG during the transition:

e.g., in phase transition (no chemical changes)

PHASE 1 \longrightarrow PHASE 2

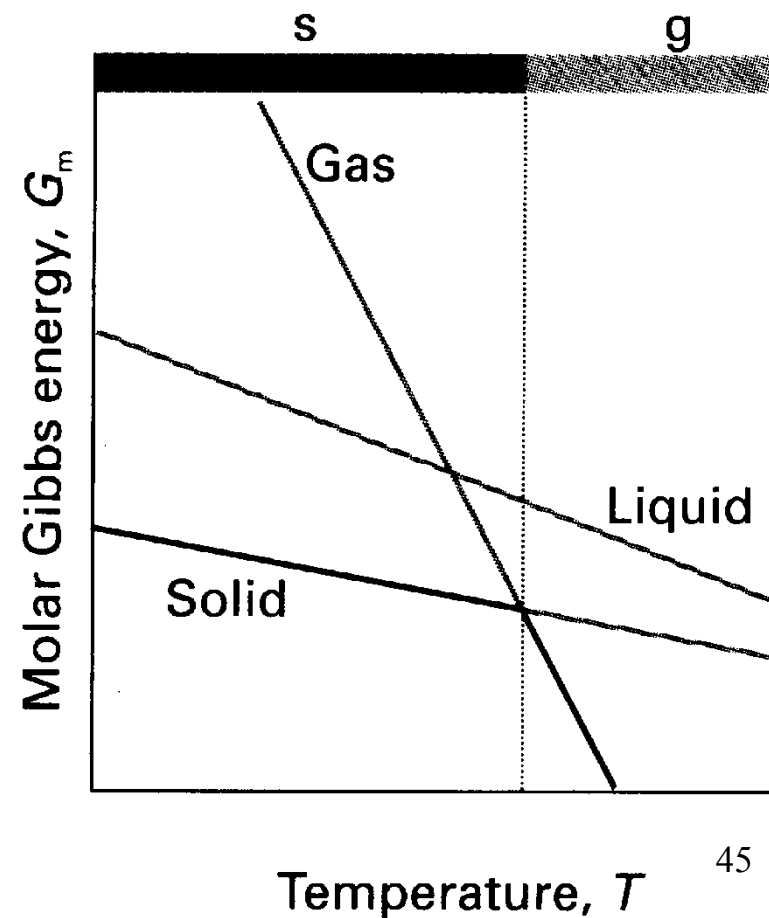
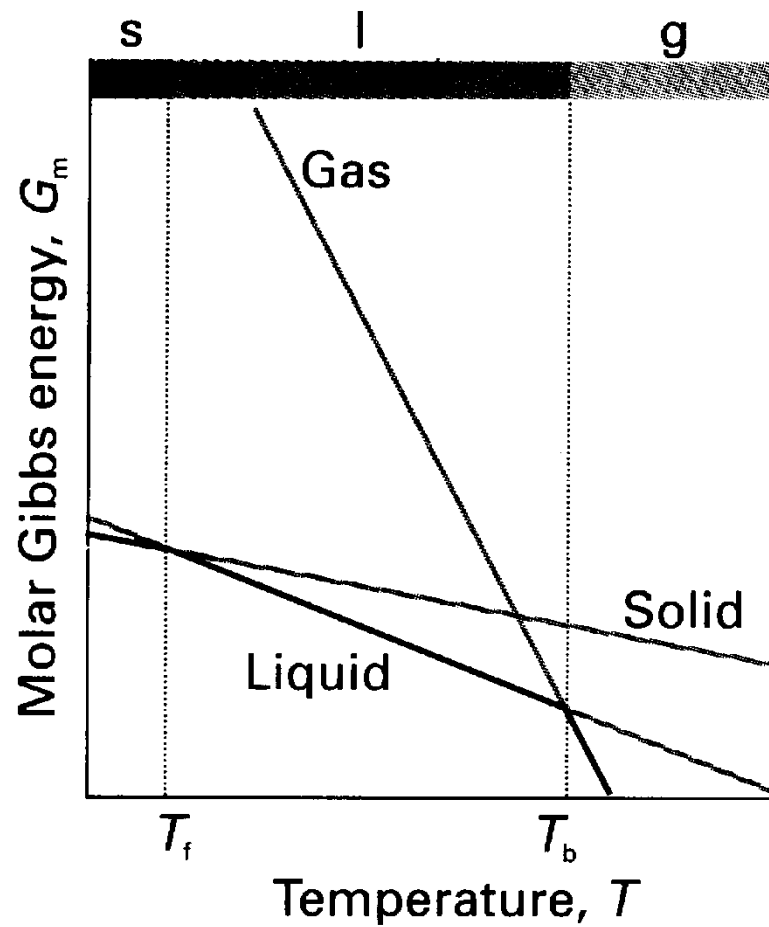
$$G = n \cdot G_m$$

$$n \cdot G_m(2) - n \cdot G_m(1) = n [G_m(2) - G_m(1)] < 0 \quad ?$$

$G(T)$ $p = \text{const.}$ $dG = -SdT$

$G = H - TS$
 $H \equiv U + pV$

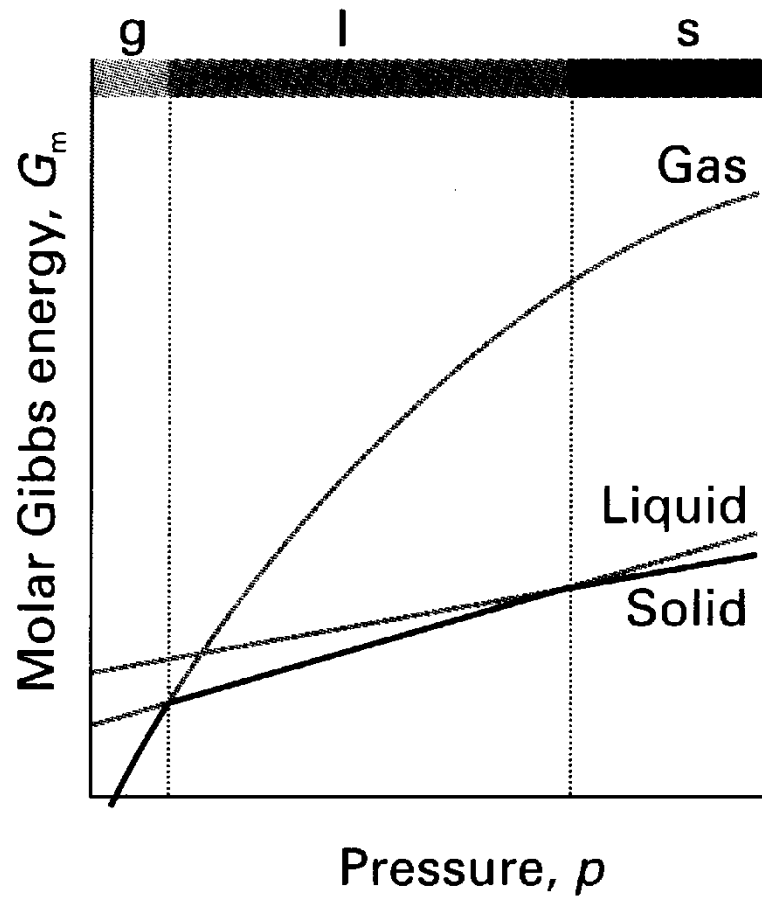
$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$



$G(p)$ $T = \text{const.}$

$$dG = Vdp$$

$$G = H - TS$$
$$H \equiv U + pV$$



$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

$$G_m(1) = G_m(2)$$

$$G_m(1) + dG_m(1) = G_m(2) + dG_m(2)$$

$$dG_m(1) = dG_m(2)$$

$$dG_m = V_m dp - S_m dT$$

$$dG_m(1) = V_m(1) dp - S_m(1) dT$$

$$dG_m(2) = V_m(2) dp - S_m(2) dT$$

$$V_m(1) dp - S_m(1) dT = V_m(2) dp - S_m(2) dT$$

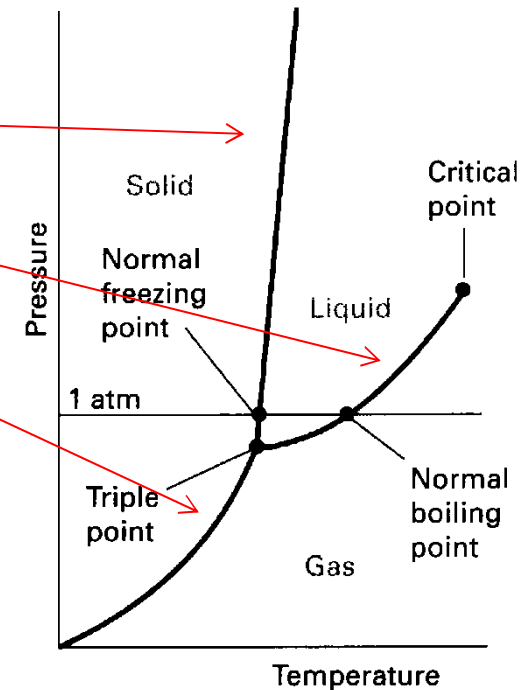
$$[S_m(2) - S_m(1)] dT = [V_m(2) - V_m(1)] dp$$

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

The phase transition is an isothermal and isobaric process:

$$\Delta S_m = \frac{\Delta H_m}{T} \quad \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$$

Clapeyron

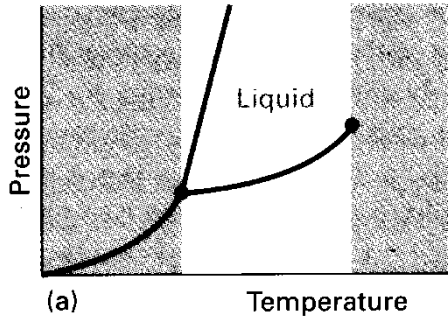


$$\frac{dp}{dT} = \frac{\Delta H_m}{T \cdot \Delta V_m}$$

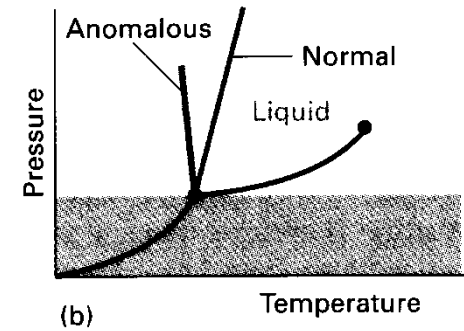
Clapeyron equation (the equation of one component phase equilibrium).

Nothing was neglected in the derivation.

It is valid for: liquid-vapor
solid-liquid
solid-vapor
solid-solid equilibrium



$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

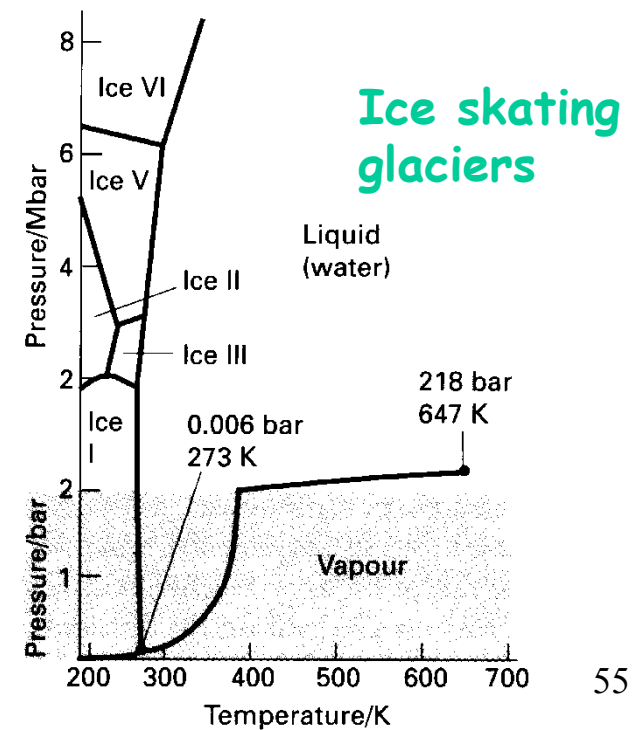
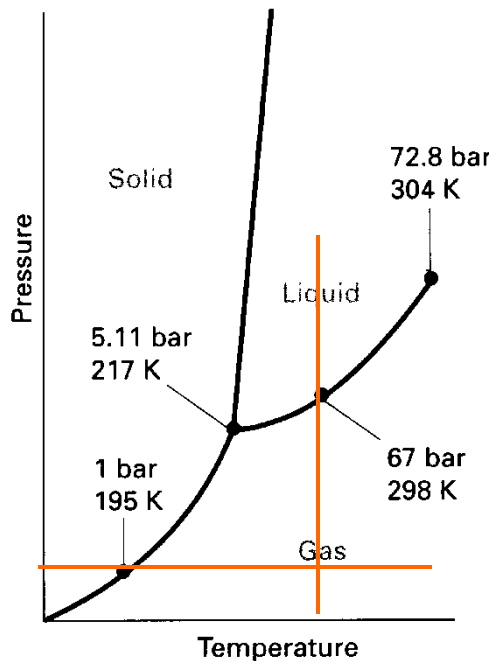


S/L reaction to increasing p $(V_m dp)_S \stackrel{?}{=} (V_m dp)_L$

Water

CO₂

ice: 19,7 cm³/mol water: 18,0 cm³/mol

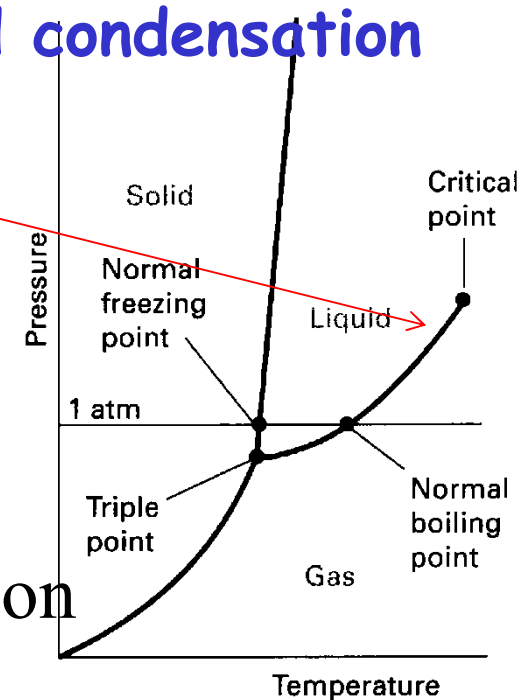


The liquid - gas transition: evaporation and condensation

Let's apply the Clapeyron equation for liquid-vapor equilibrium:

$$\frac{dp}{dT} = \frac{\Delta_{evap} H_m}{T \Delta V_m}$$

molar heat of vaporization
 change of molar volume at vaporization



1. We neglect the molar volume of the liquid (compared to vapor).

$$\Delta V = V_m(\text{gas}) - V_m(\text{liq}) \cong V_m(\text{gas})$$

2. We regard the vapor as ideal gas.

$$V_m(\text{gas}) = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{p \Delta_{evap} H_m}{RT^2}$$

Clausius-Clapeyron

$$\frac{dp}{p} = \frac{p \Delta_{\text{evap}} H'_m}{RT^2} dT$$

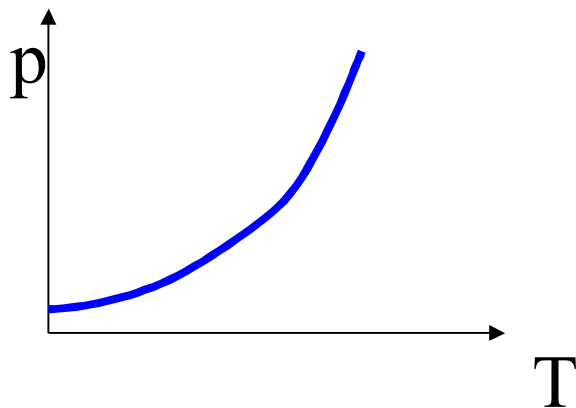
The saturation pressure
of a pure liquid only depends on T .

$$\frac{dp}{p} = d \ln p \quad \frac{dT}{T^2} = -d \frac{1}{T} \quad d(1/T)/dT = -1/T^2$$

$$\ln p = -\frac{\Delta_{\text{evap}} H'_m}{R} \cdot \frac{1}{T} + C$$

$$\int_{p_k}^{p_v} d \ln p = \int_{T_k}^{T_v} \frac{\Delta_{\text{evap}} H'_m}{RT^2} dT$$

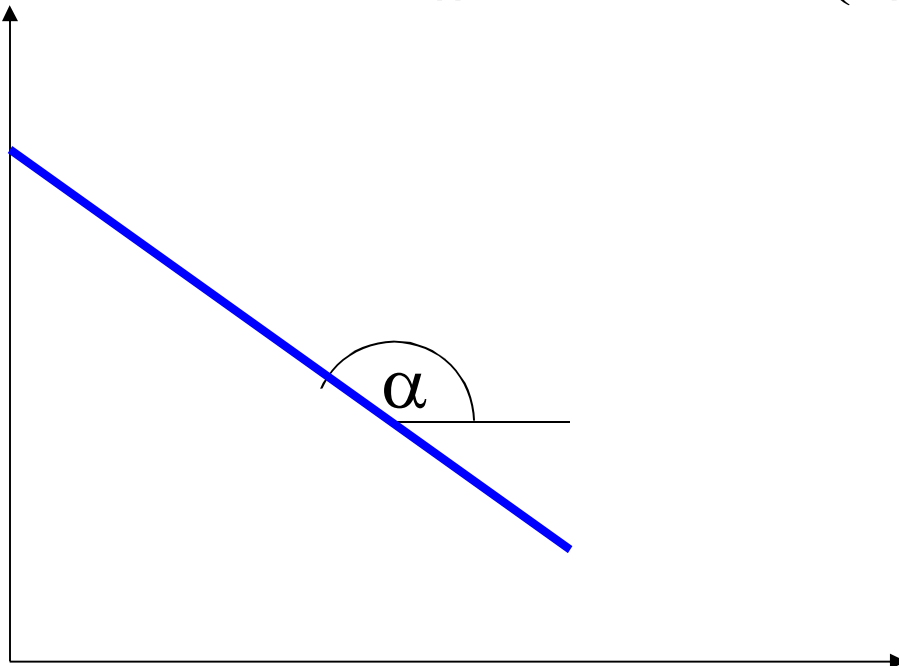
$$\ln \{p\} = -\frac{A}{T} + B \quad \{p\} = \frac{p(\text{Pa})}{1 \text{ Pa}}$$



If the logarithm of the vapor pressure is plotted against the reciprocal of temperature, we obtain a straight line:

$$\ln \frac{p_v}{p_k} = \frac{\Delta_{\text{evap}} H'_m}{R} \left(\frac{1}{T_k} - \frac{1}{T_v} \right)$$

$\lg\{p\}$



$$\lg\{p\} = -\frac{A}{T} + B$$

A, B: constants

$$\tan\alpha = -A$$

$$\{p\} = \frac{p(\text{Pa})}{1 \text{ Pa}}$$