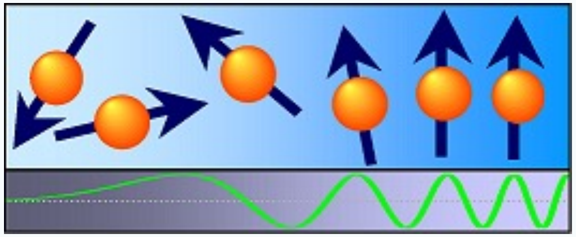
Experimental Physics EP2
Thermodynamics

– Thermodynamic functions –
Application to real gases



https://bloch.physgeo.uni-leipzig.de/amr/

Thermodynamic functions

$$\delta Q = dU + PdV \qquad dS = \frac{\delta Q}{T} \qquad dU = TdS - PdV$$

Enthalpy $\quad I = U + PV \qquad dI = TdS + VdP$

Helmholtz free energy $\quad F = U - TS \qquad dF = -SdT - PdV$

Gibbs free energy $\quad G = I - TS \qquad dG = -SdT + VdP$

$$U = U(S,V) \qquad I = I(S,P) \qquad F = F(T,V) \qquad G = G(T,P)$$

Thermodynamic functions

$U = U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S \qquad dU = TdS - PdV$$

$I = I(S,P)$

$$dI = \left(\frac{\partial I}{\partial S}\right)_P dS + \left(\frac{\partial I}{\partial P}\right)_S dP \qquad T = \left(\frac{\partial I}{\partial S}\right)_P \qquad V = -\left(\frac{\partial I}{\partial P}\right)_S \qquad dI = TdS + VdP$$

$F = F(T,V)$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad dF = -SdT - PdV$$

$G = G(T,P)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T \qquad dG = -SdT + VdP$$

Gibbs-Helmholtz equations

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V \qquad I = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

Thermodynamic functions

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad T = \left(\frac{\partial U}{\partial S}\right)_V = f(S,V) \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S = f'(S,V)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \frac{\partial^2 U}{\partial V \partial S} \qquad \left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\left(-\frac{\partial U}{\partial V}\right)_S\right)_V = -\frac{\partial^2 U}{\partial S \partial V}$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

The Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Internal energy and entropy of VdW gas

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$P = \frac{RT}{V-b} + \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = P + \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

$$U = -\frac{a}{V} + \int C_V(T)dT$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

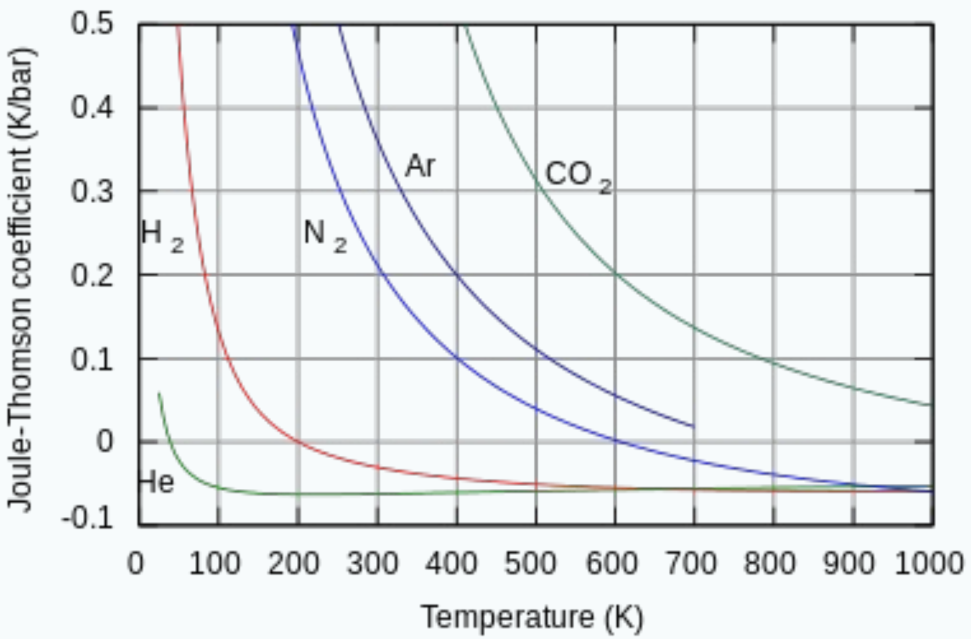
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$dS = \frac{C_V}{T}dT + \frac{R}{V-b}dV$$

$$S = \int \frac{C_V}{T}dT + R\ln\left(V-b\right) + \text{const}$$

Joule-Thomson effect



$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_I \qquad U_2 + P_2V_2 = U_1 + P_1V_1 = const$$

$$dI = \left(\frac{\partial I}{\partial T}\right)_P dT + \left(\frac{\partial I}{\partial P}\right)_T dP = 0$$

$$\left(\frac{\partial I}{\partial T}\right)_P = C_p$$

$$I = I(S,P)$$

$$dI = TdS + VdP$$

$$\left(\frac{\partial I}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial I}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_I = \frac{1}{C_P}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right)$$

Van der Waals gas:

$$\left(\frac{\partial T}{\partial P}\right)_I = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$$

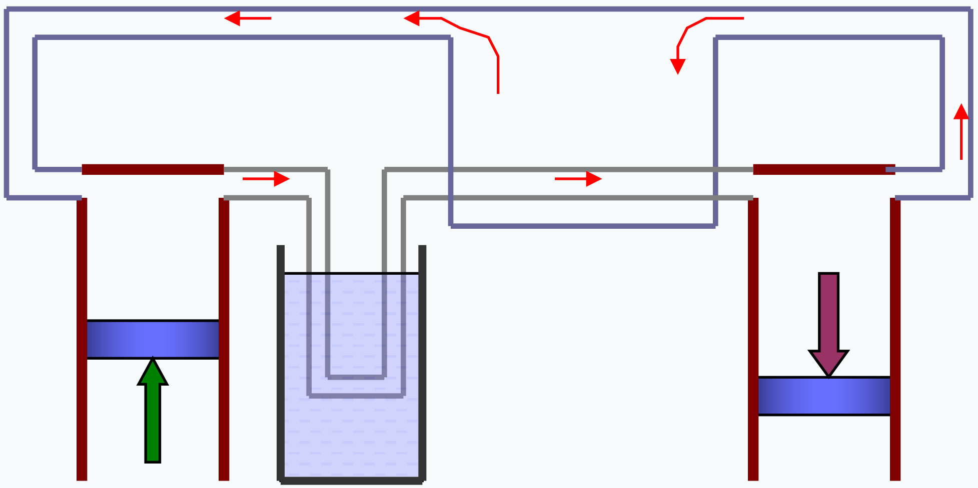
Inversion temperature:

$$T_i = \frac{2a}{Rb} = 2T_B$$

$T > T_i$ **heating**

$T < T_i$ **cooling**

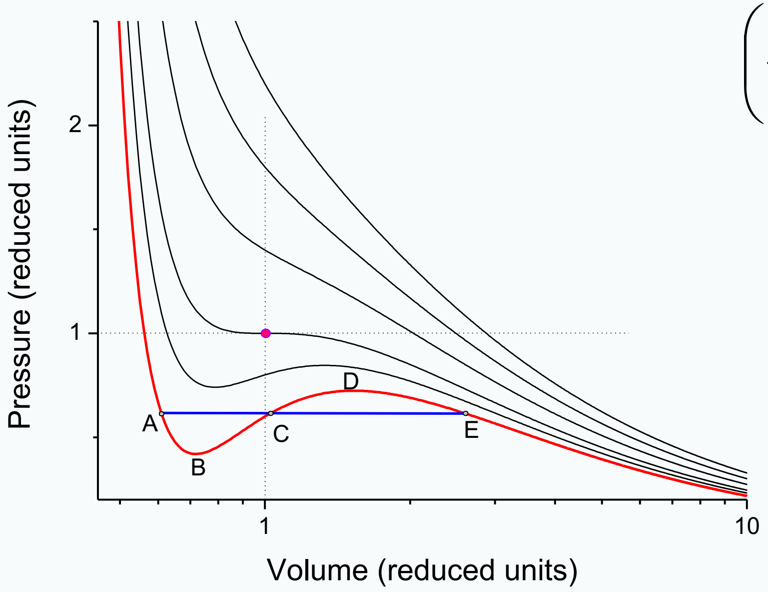
Adiabatic cooling, liquefaction



$$dS = 0$$ - adiabatic process

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{T\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\delta Q}{\partial T}\right)_P = \frac{C_P}{T}$$



$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP = 0$$

$$T_2 - T_1 = \int_{P_1}^{P_2} \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP$$

To remember!

- Four thermodynamic state functions: internal energy, enthalpy, Helmholtz free energy, Gibbs free energy.
- Helmholtz free energy is useful work available in a closed system at constant temperature and volume.
- Gibbs free energy is useful work available in a closed system at constant temperature and pressure.
- The Maxwell relations express relationships between different partial derivatives.
- The approach based on thermodynamic state functions and related equations may substantially simplify calculations.