Chapter 3 ; chap 5 Entropy

October 3 midterm 1

Wed 28 Sept.

$U(T,V)$ internal energy

$H(T,P)$ Enthalpy

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

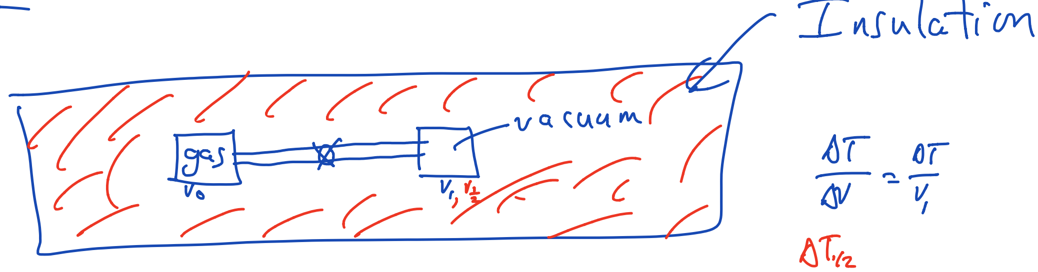
constant volume process, $dV = 0$

$$dU(T,V) = \underline{C_v(T)}\,dT$$

1st "Law" $dU(T,V) = \underline{\underline{đq}} + đW$ $= -P_{ext}\,dV$

$$C_v(T) \equiv \left(\frac{\partial U}{\partial T}\right)_V$$ Thermo. Definition

Joule Free Expansion



$$\frac{\Delta T}{\Delta V} = \frac{\Delta T}{V_1}$$

$$\frac{\Delta T_{1/2}}{V_{1/2}}$$

system: gas

$$dU(T,V) = 0 \qquad \text{constant } U \text{ process}$$

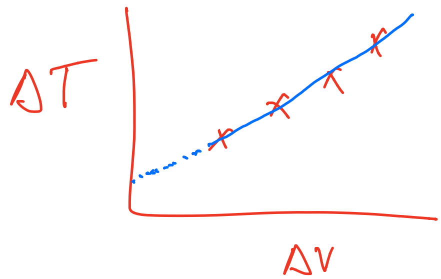
$$dU(T,V) = 0 = C_v(T)\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV = -C_v(T)\,dT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_v(T)\left(\frac{dT}{dV}\right)_U$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = -C_v(T)\left(\frac{\partial T}{\partial V}\right)_U}$$

measurable



$$\left(\frac{\partial T}{\partial V}\right)_U = \lim_{\Delta V \to 0} \left(\frac{\Delta T}{\Delta V}\right)_U$$

$$\left(\frac{\partial T}{\partial V}\right)_U = \text{Joule Coefficient} = \eta_J \leftarrow \text{"eta"}$$

experimentally measured!!

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_v(T)\,\eta_J$$

$$dU(T,V) = C_v(T)\,dT - C_v(T)\,\eta_J\,dV$$

$T_1, V_1 \to T_2, V_2$

$$?\ \Delta U = \int_{T_1}^{T_2} C_v(T)\,dT - \int_{V_1}^{V_2} C_v(T)\,\eta_J\,dV$$

$$= \int_{T_1}^{T_2} C_v(T)\,dT - \int_{V_1}^{V_2} C_v(T(V))\,\eta_J\,dV$$

$T(V)$ from some EOS!!!!

η_J non zero for real gases

$\eta_J = 0$ for Ideal Gas!

$\therefore$ $dU^{ig}(T) = C_v^{ig}(T)\, dT$ ideal gas

only a function of T !! for Ideal Gas

Enthalpy → involve pressure

$dU = đq + đW$

$dU = đq - P_{ext}\, dV$

Reversible ← ① ***

$P_{ext} = P$

$dU = đq - p\,dV$

$đq = dU + p\,dV$

P = constant ***

$p\,dV = d(pV) = Vdp + pdV$
$= pdV$

$đq = dU + d(pV)$

$đq = d(U+pV)$ $U + pV \equiv H$ ← Enthalpy

$$\boxed{dq_p = d(U + pV) = dH}$$

↑ constant Pressure

$$\boxed{q_p = \Delta H}$$

$H(T, P)$

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

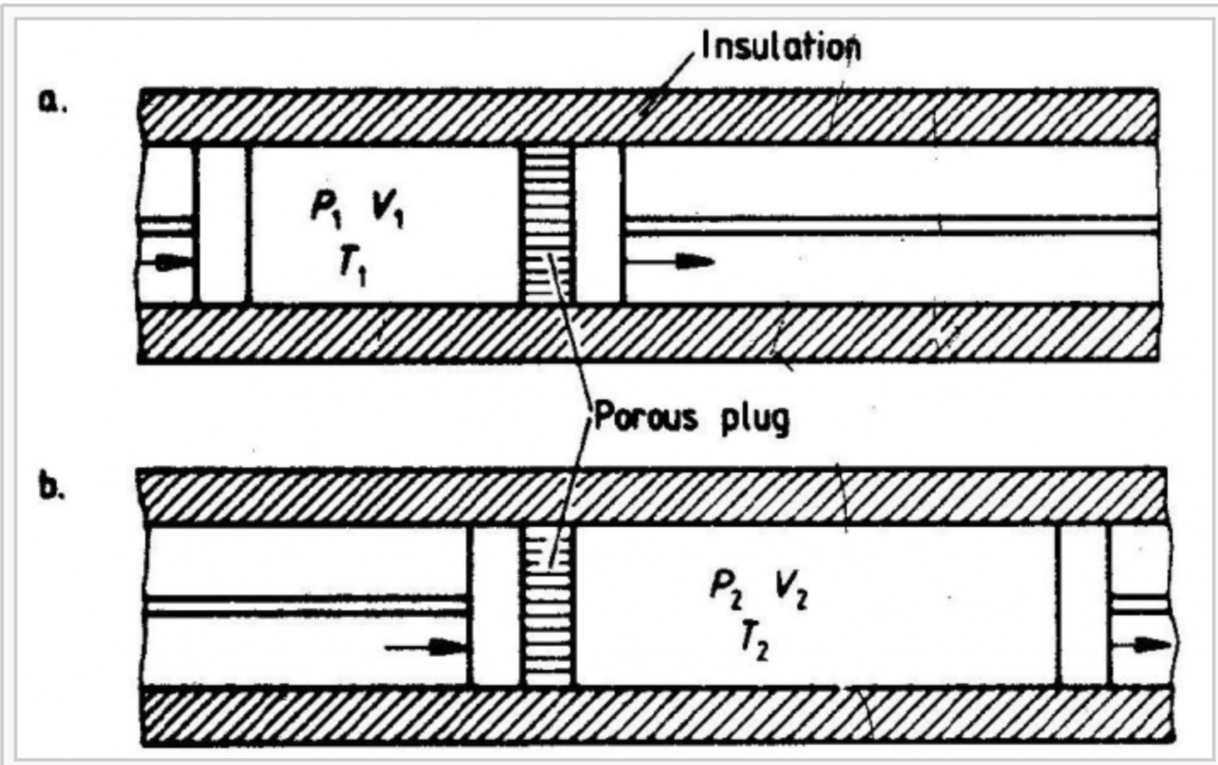
constant pressure case: $dP = 0$

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT = dq_p = C_p(T)\,dT$$

operationally, $dq_p = C_p(T)\,dT$

$$C_p(T) \equiv \left(\frac{\partial H}{\partial T}\right)_P$$ Thermo. definition !!!

$$C_V(T) \equiv \left(\frac{\partial U}{\partial T}\right)_V$$ Thermo. Defn. !!!



Insulation
a.
P_1 V_1
T_1
Porous plug
b.
P_2 V_2
T_2

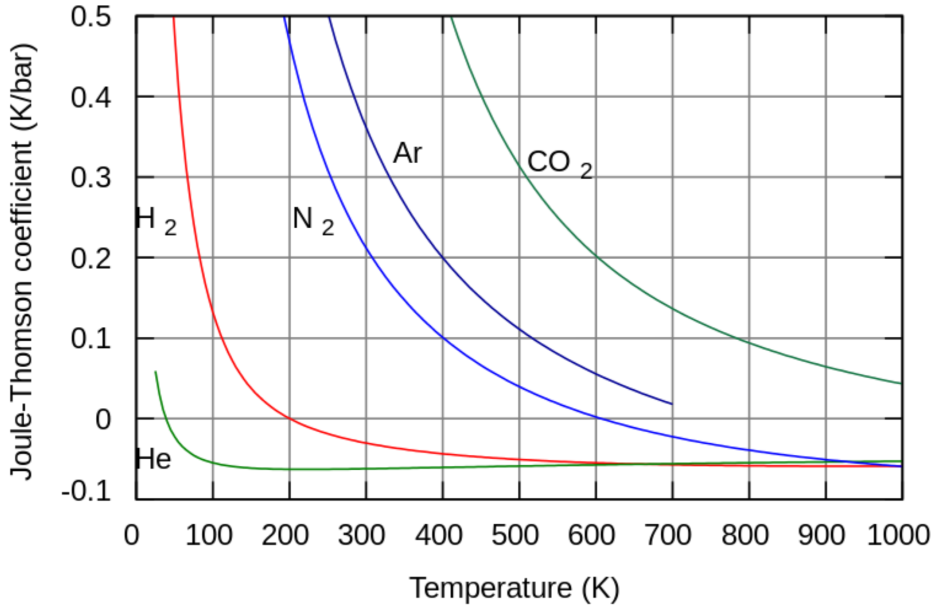
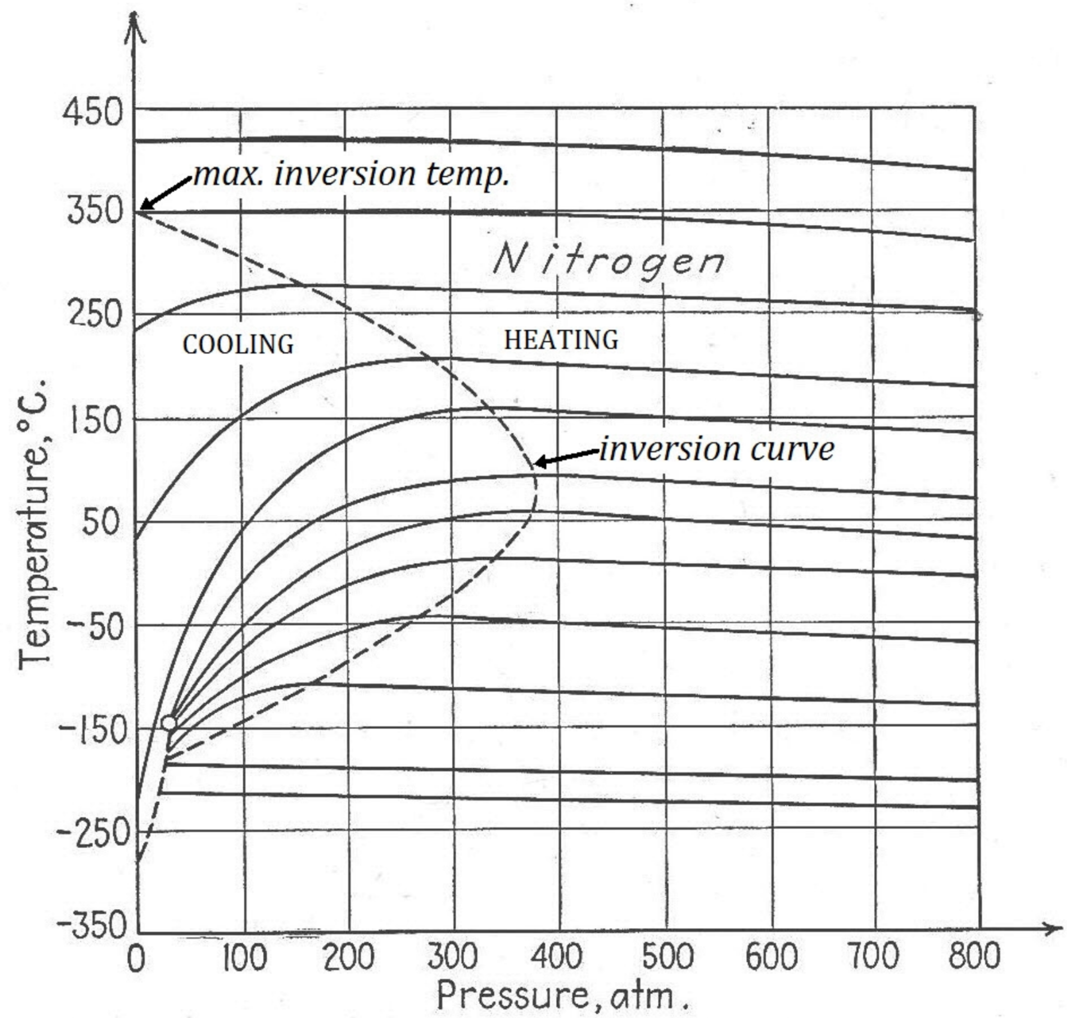


Fig. 1 – Joule-Thomson coefficients for various gases at atmospheric pressure.



Isenthalpic curves and inversion curve for nitrogen