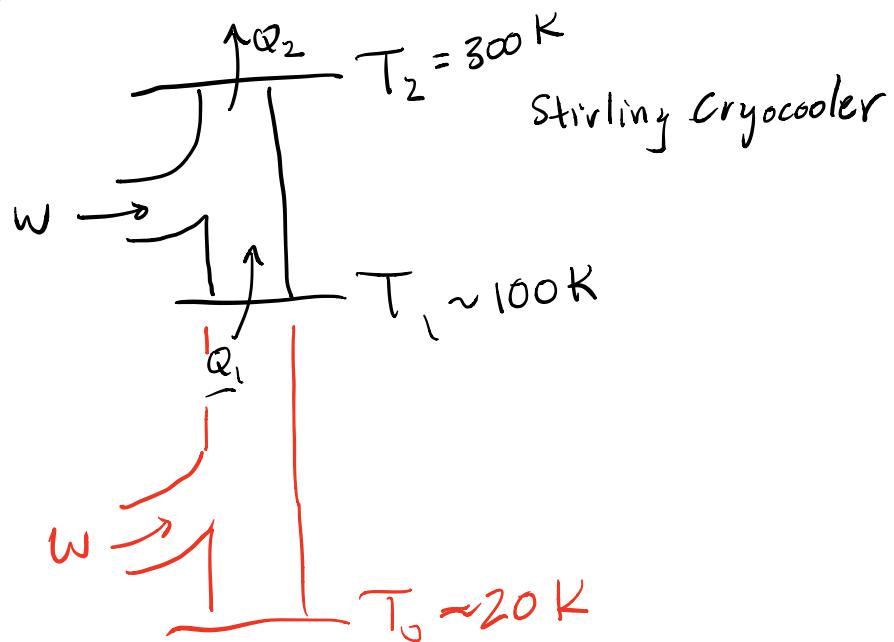
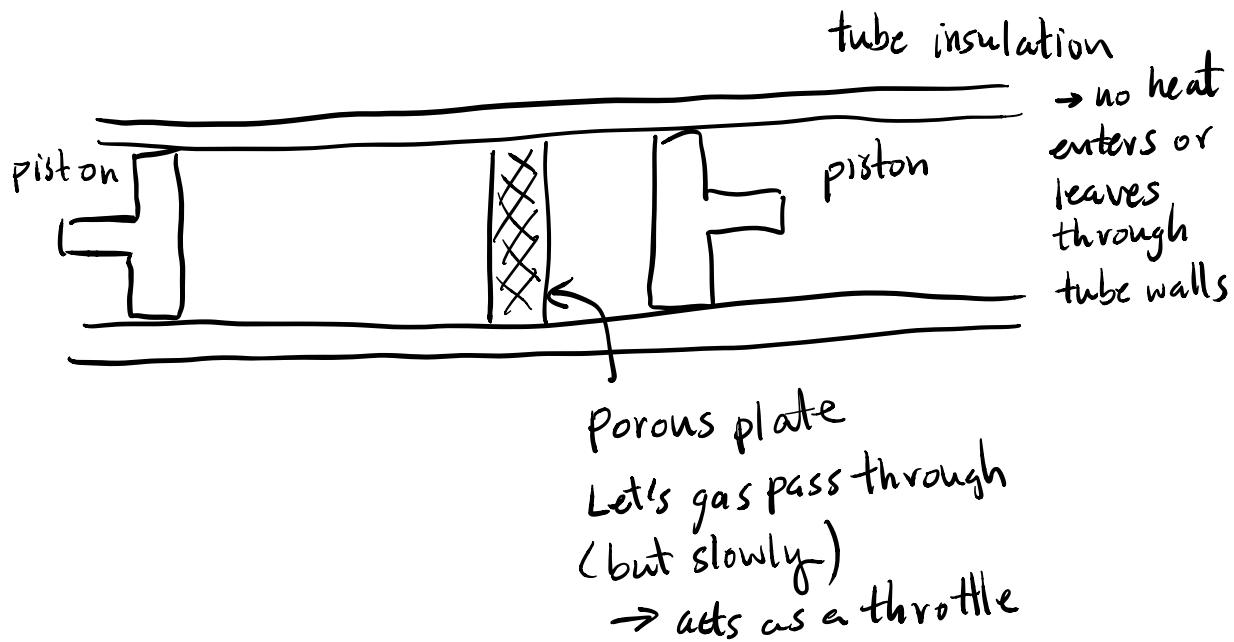


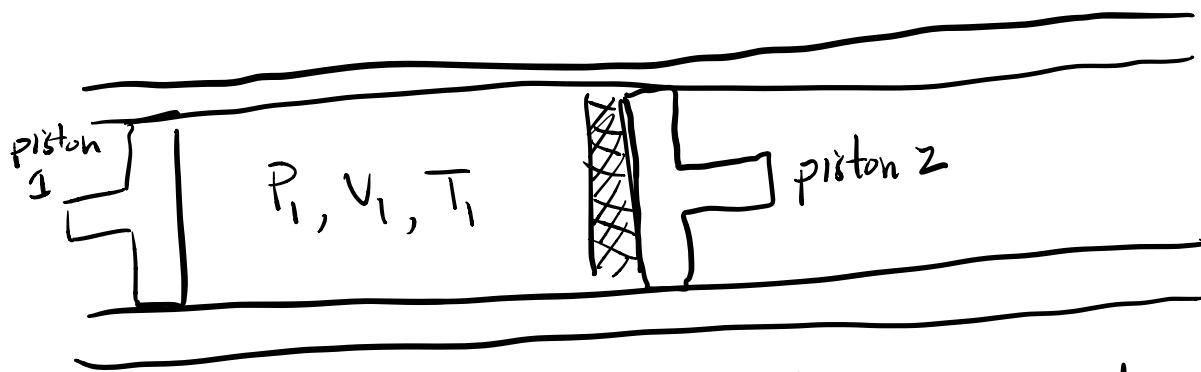
PHYS 425 W13



Joule - Thomson Exp<sup>4</sup>



Start w/ all gas on side 1 (left) & with piston 2 (right) flush against porous plug.

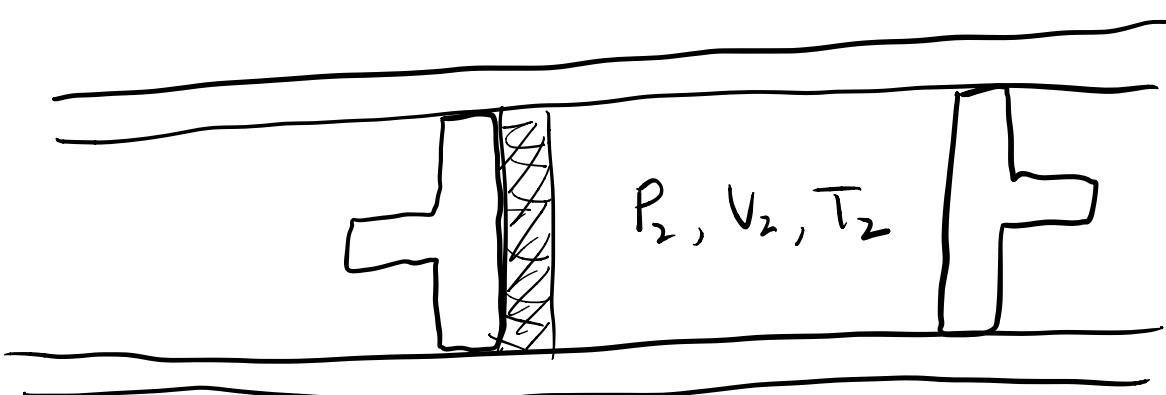


Imagine an experiment in which piston 1 used to push gas through plug s.t.  $P_1$  remains constant.

Simultaneously, piston 2 pulled to right s.t.

pressure on side 2 remains constant  $\Rightarrow P_2 < P_1$   
called a Joule-Thomson (J-T) expansion.

At end of the process  $V_1 = 0$  if all gas is on right side w/ :  $V_2, P_2, T_2$



result of experiment :  $T_1 \neq T_2$

under some conditions  $T_2 < T_1$   
" other "  $T_2 > T_1$

want to be able to understand this result.

### Initial Analysis

External work on side 1.

$$dW_1 = -P_1 dV_1 \Rightarrow W_1 = -P_1 (0 - V_1)$$

$\uparrow$

$$= P_1 V_1$$

pos. b/c we did  
external work on  
gas to compress it.

On side 2

$$dW_2 = -P_2 dV_2 \Rightarrow W_2 = -P_2 (V_2 - 0)$$
$$= -P_2 V_2$$

neg. b/c gas does work  
to push piston.

Total work  $W = P_1 V_1 - P_2 V_2$

Process is adiabatic since tube is insulating

$$dU = \cancel{dQ} + dW$$

$\uparrow$   
work on the gas.

$$dU = dW$$

$$U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$U_1 + P_1 V_1 = U_2 - P_2 V_2$$

$\underbrace{\phantom{0}}$

$$H_1 = H_2$$

$$\underbrace{U + PV}_\text{enthalpy} \equiv H$$

J-T expansion process is isenthalpic.

J-T expansion for an ideal gas

$$H_1 = H_2$$

$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

For an ideal gas we know  $U = \frac{f}{\alpha} N k_B T$

$$PV = N k_B T$$

$$\therefore \text{we have } H = U + PV = \left(\frac{f}{2} + 1\right) N k_B T \\ = \left(\frac{f+2}{2}\right) N k_B T$$

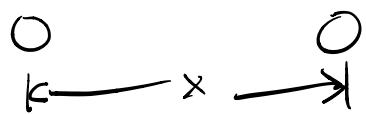
$$\text{If } U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$\text{then } \left(\frac{f+2}{2}\right) N k_B T_1 = \left(\frac{f+2}{2}\right) N k_B T_2 \quad (N_1 = N_2 = N)$$

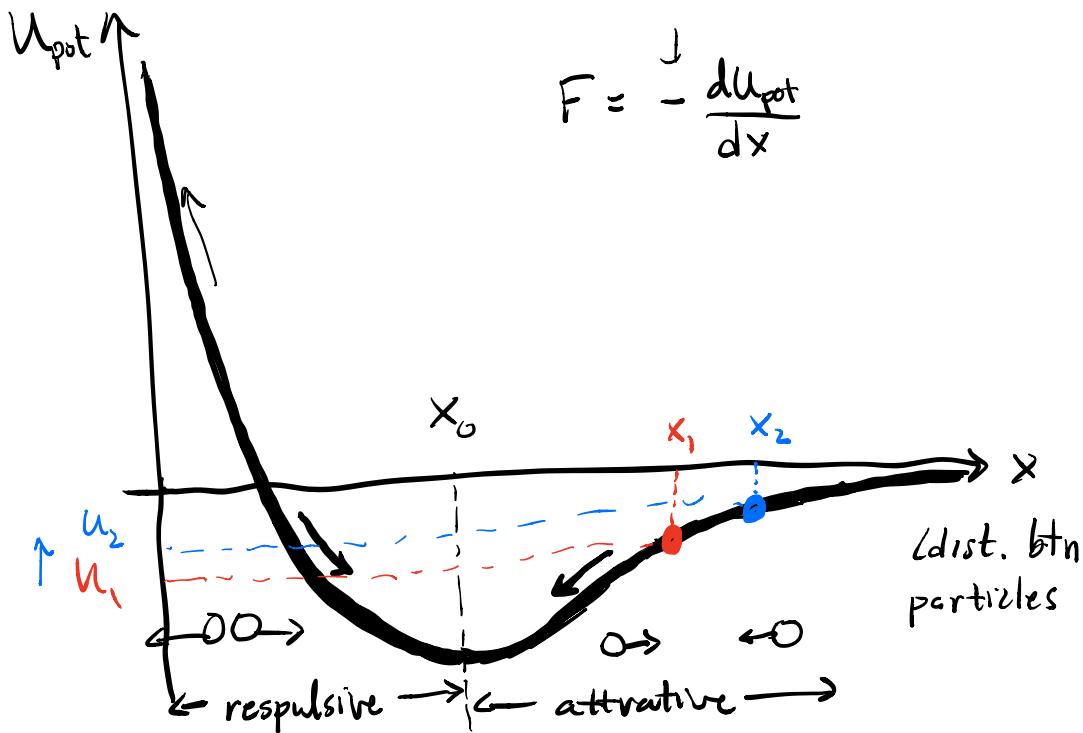
$$\Rightarrow \boxed{T_1 = T_2} \Rightarrow \text{no change in temperature!}$$

The J-T effect relies critically on the non-ideal behaviour of real gases. i.e. the interactions between gas particles are important.

Consider the potential energy between a pair of particles separated by dist.  $x$ .



The P.E. typically has a shape like:



In a real gas, can write internal energy as

$$U = U_{\text{pot}} + U_{\text{kin}}$$

$\left[ \begin{array}{l} \text{ideal gas, } U_{\text{pot}} = 0 \\ \{ \text{internal energy} \\ \text{is all kin. Energy} \end{array} \right]$

Suppose have a gas at

$P_1, V_1, T_1$  } avg. sep. between  
particles is  $x_1$ .

① Then gas is expanded via T-T process s.t.  
avg. sep. becomes  $x_2$ .

$$\Delta U_{\text{pot}} > 0 \quad (\text{became less neg.})$$

$\therefore$  expect  $\Delta U_{\text{kin}} < 0$  by cons. of energy  
{ hence  $\Delta T < 0$  (gas cools.)}

② However, there is a second mechanism to consider. During a collision between two gas particles



If the gas is expanded, expect rate of collisions to decrease.  $\therefore$  would expect a net reduction in avg. P.E. in system  $\rightarrow$  avg. K.E. increases  
{ expect  $\Delta T > 0$ . (gas warms)}

Which of the two processes (① or ②) dominates determines if T-T expansion heats or cools the gas.

In the experiment describe can meas

$$\frac{T_2 - T_1}{P_2 - P_1}$$

define Joule-Thomson coefficient  $\mu_{JT}$

$$\mu_{JT} = \lim_{\Delta P \rightarrow 0} \frac{\overline{T_2 - T_1}}{P_2 - P_1} = \left( \frac{\partial T}{\partial P} \right)_H$$

If  $\mu_{JT} > 0$ , then  $T_2 < T_1$  cooling

If  $\mu_{JT} < 0$ , then  $T_2 > T_1$  heating.

↑  
const. enthalpy.

See if we can analyze  $\mu_{JT}$  in more detail...

If  $H = H(T, P)$ , then

$$\underbrace{dH}_0 = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

But for isoenthalpic process  $dH = 0$ .

$$\therefore \text{O} = \left( \frac{\partial H}{\partial T} \right)_P \underbrace{\left( \frac{\partial T}{\partial P} \right)_H}_{\mu_{JT}} + \left( \frac{\partial H}{\partial P} \right)_T$$

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = - \frac{( \partial H / \partial P )_T}{( \partial H / \partial T )_P}$$

Denominator:

$$H = U + PV$$

$$dH = \underbrace{dU}_{dQ - PV} + PdV + VdP$$

$$dH = dQ - PV + PV + VdP$$

$$= dQ + \underbrace{VdP}_{0 \text{ for const. } P}$$

$$\left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial Q}{\partial T} \right)_P = C_P \quad \begin{array}{l} \text{heat capacity} \\ \text{at const. pressure.} \end{array}$$

Numerator:

Can show that:

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

Finally, we have:

$$u_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = - \frac{(\partial H / \partial P)_T}{(\partial H / \partial T)_P}$$

$$u_{JT} = \frac{T \left(\frac{\partial V}{\partial T}\right)_P - V}{C_P}$$

all variables measurable.

To go further, need a model for the behaviour of real gases:  $\rightarrow$  need eq'n of state.