ChemE 2200 – Chemical Thermodynamics Lecture 3

Today:

Joule-Thomson Expansion.
Calculating Enthalpy Changes.

Defining Question:

How does one choose (or design) a refrigerant?

Reading for Today's Lecture:

McQuarrie & Simon, exercises 19-52 and 22-48.

Reading for Thermodynamics Lecture 4:

McQuarrie & Simon, Chapter 19.9–19.12, 20.1–20.3

Engineering Peer Advisor Job Openings

The paid position offers a chance to grow in professional competencies such as teamwork, oral and written communication, service orientation, reliability, adaptability, and more by:

- Co-planning an ENGRG 1050 seminar
- Co-presenting and facilitating class discussions with Engineering Faculty
- Assisting students transitioning from high school to college by sharing your Cornell experiences
- Communicating academic opportunities and co-curricular activities to students
- Referring students to appropriate academic, personal, and campus resources

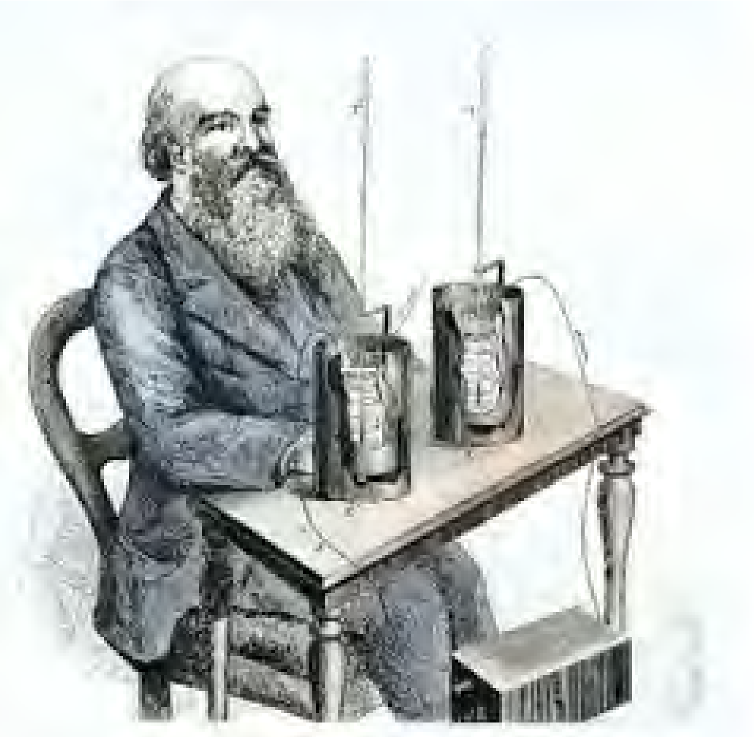
Visit Peer Advisor Position FA25 The application deadline is February 26.
Questions email eng-peeradvising@cornell.edu.

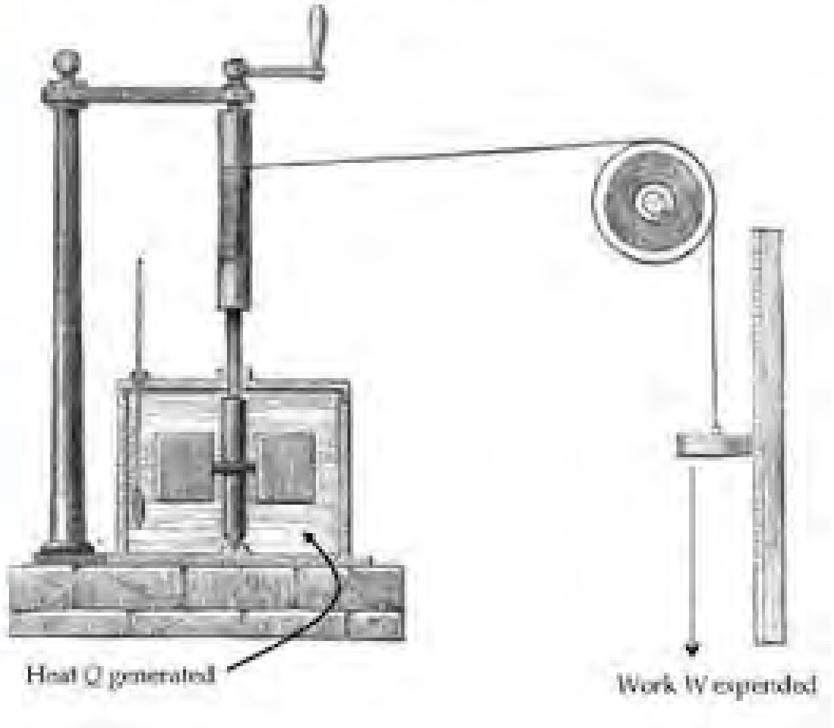
I will work with Engineering Advising to
pair ChemE-affiliated Peer Advisors
with ChemE faculty members.

Recap

The internal energy of an ideal gas
depends only on its temperature
(not pressure or volume).
Joule's Second law

Joule's Second law
was originally suggested
by Joule's experiments
with real gases.

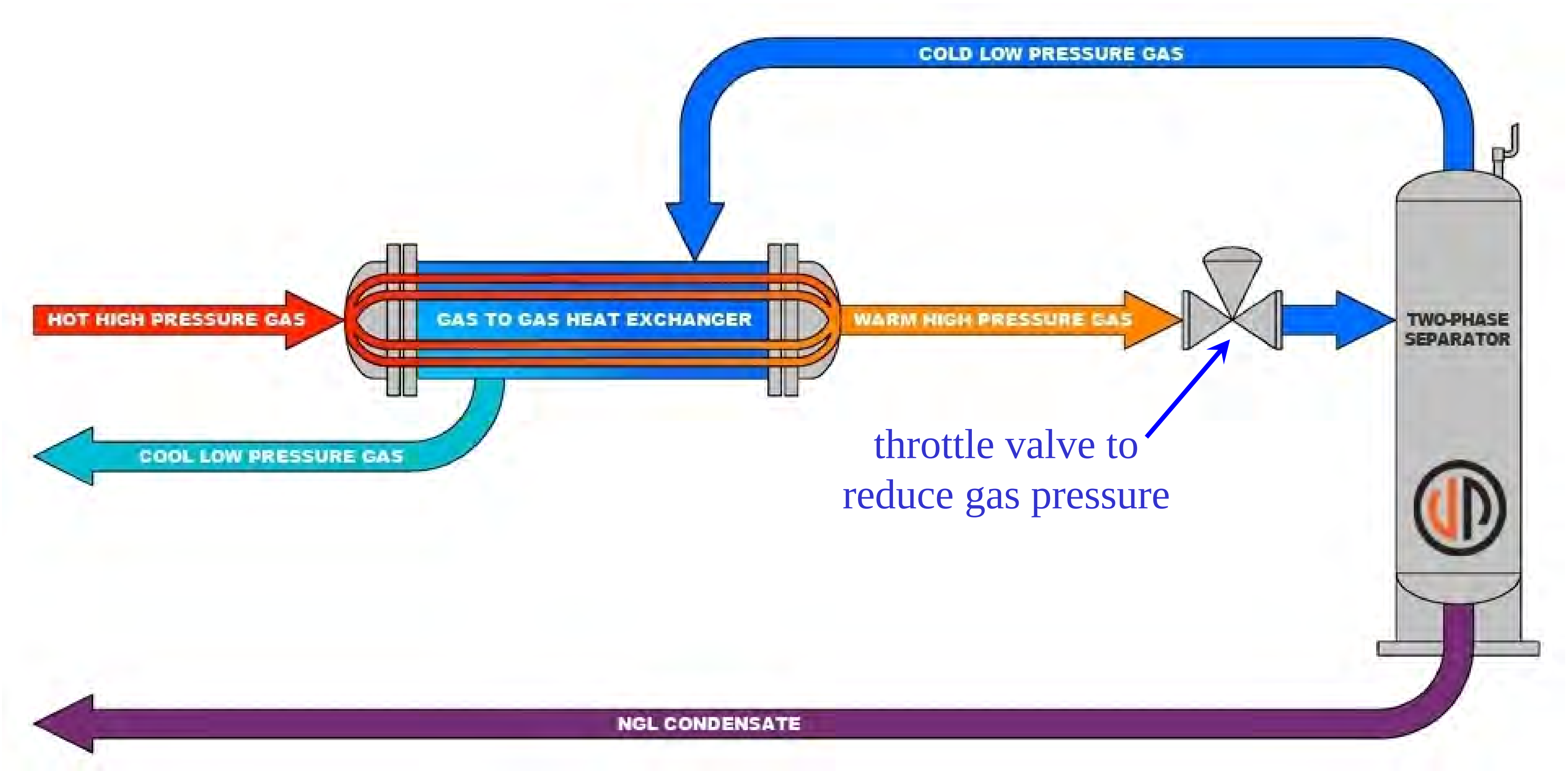




Gases passing through a restriction (a throttle)

Gas flow is throttled to control flow rate, to measure flow rate, and to cool the gas.

Process to remove condensible gases.

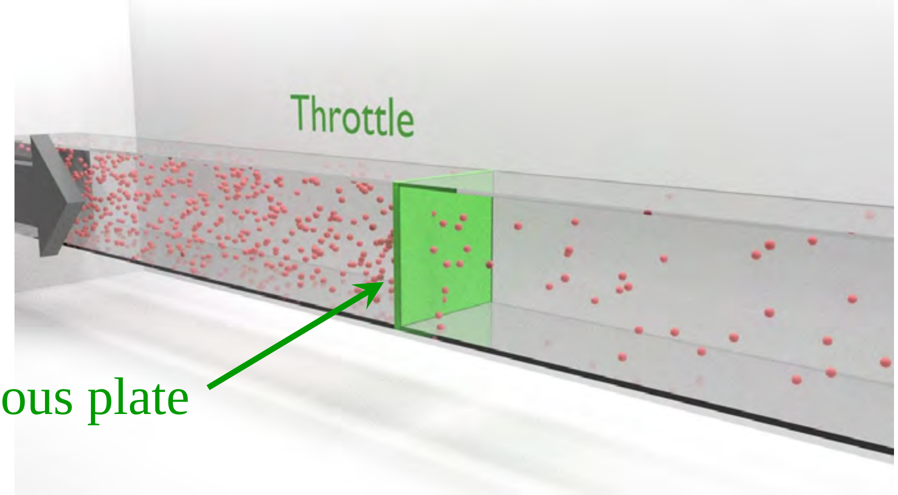


throttle valve to
reduce gas pressure

NGL = Natural Gas Liquid

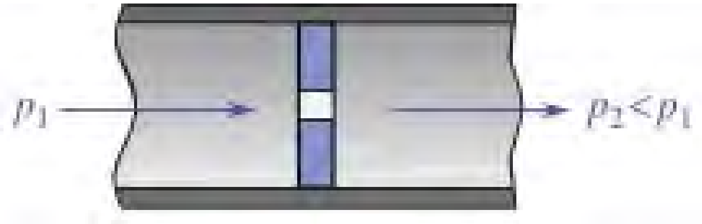
Image from Joule Processing, Houston TX

Devices to Throttle Gas Flows

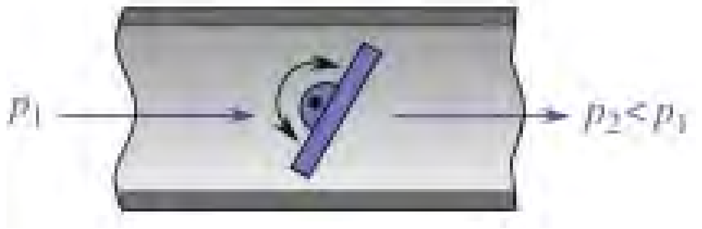


porous plate

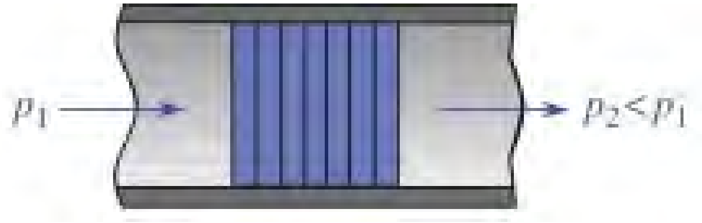
an orifice plate



a partially-open valve

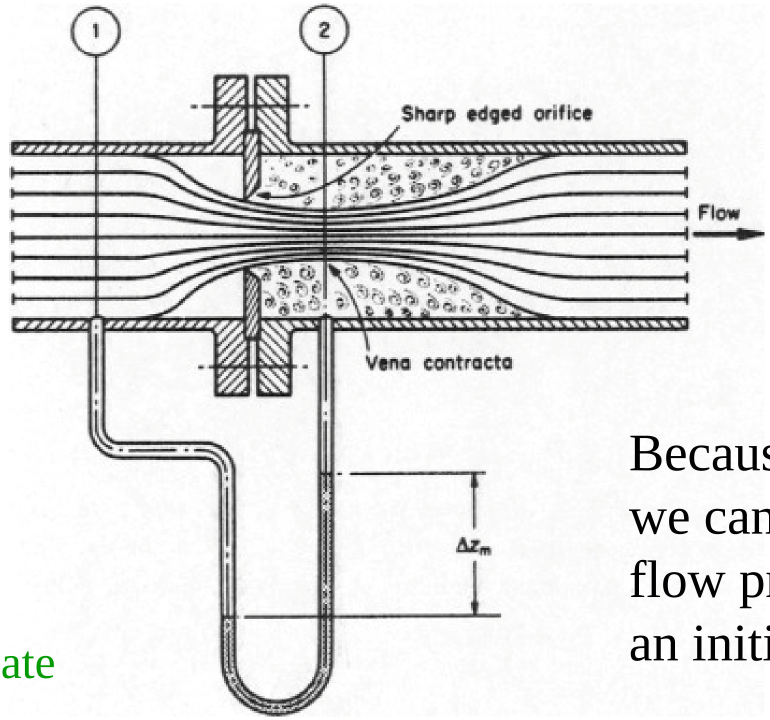


a porous plug



How much
does the gas cool?

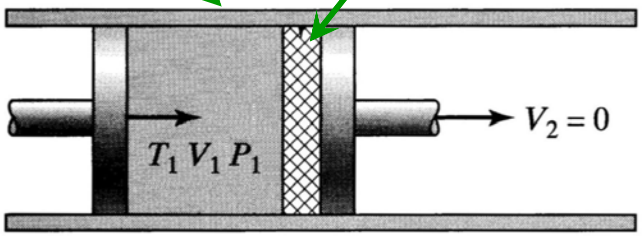
Joule-Thomson Expansion



Because energy is a state function, we can represent the steady-state flow process as the change from an initial state to a final state.

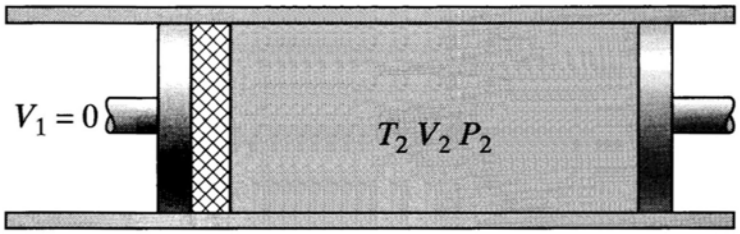
insulation

porous plate



adiabatic flow

through the porous plate



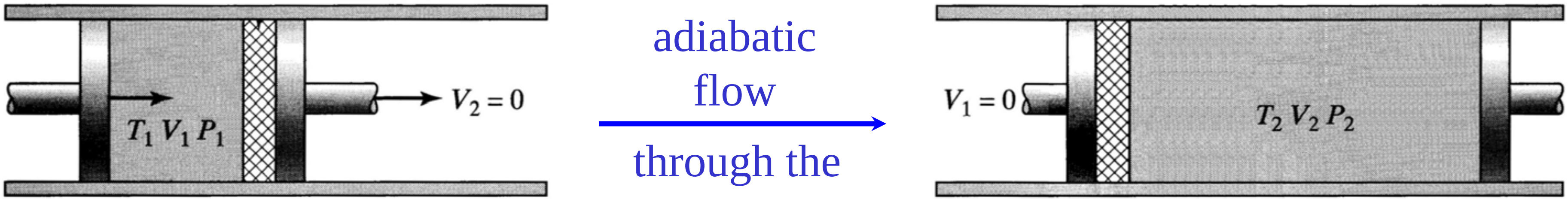
initial state: gas in an insulated cylinder is compressed reversibly at external pressure P_1. Gas passes through porous plate into volume V_2.

final state: gas expands against an external pressure P_2.

What is T_2?

Images adapted from Lionel M. Raff, *Principles of Physical Chemistry* (2001)

Thermodynamic Analysis of a Joule-Thomson Expansion



adiabatic flow

through the porous plate

initial state

final state: What is T_2?

Basis: 1 mol of gas

adiabatic

$$\Delta U = U_2 - U_1 = \cancelto{0}{q} + w_{\text{piston 1}} + w_{\text{piston 2}}$$

$$= -P_1(0 - V_1) - P_2(V_2 - 0)$$

$$= P_1V_1 - P_2V_2 \qquad (= 0 \ \text{ for an ideal gas} \Rightarrow \Delta T = 0)$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

A Joule-Thomson expansion is an isenthalpic process

Recall our goal: How does *T* change with *P*? We now know *H* is constant.

$$\left(\frac{\partial T}{\partial P}\right)_H = -\cancelto{= 1/C_\text{P}}{\left(\frac{\partial T}{\partial H}\right)_P}\left(\frac{\partial H}{\partial P}\right)_T$$

cyclic rule

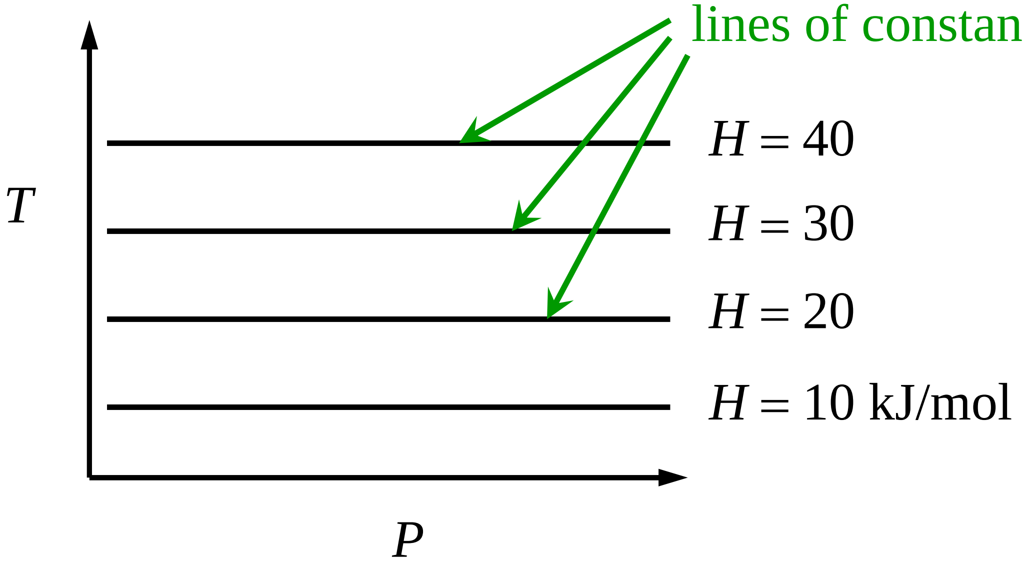
Define the Joule-Thomson coefficient:

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = \mu = -\frac{1}{C_\text{P}}\left(\frac{\partial H}{\partial P}\right)_T}$$

Temperature vs Pressure at Constant Enthalpy

The Joule-Thomson coefficient: $$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T}$$

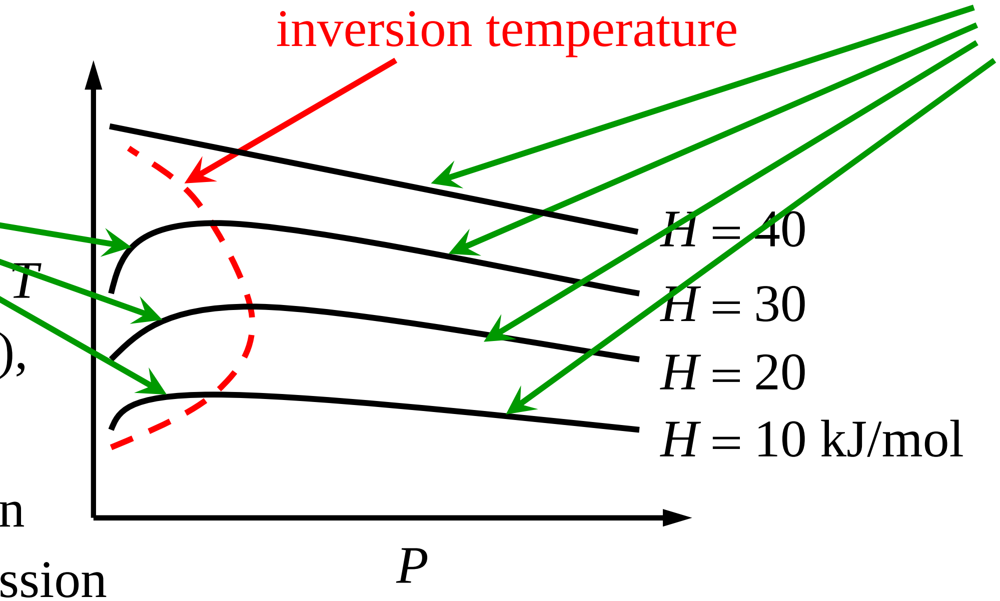
An Ideal Gas



lines of constant *H*; *isenthalps*

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = 0$$

A Real Gas



$$\mu = \left(\frac{\partial T}{\partial P}\right)_H > 0$$

for $\partial P < 0$ (expansion),
then $\partial T < 0$ (cooling).

gas cools on expansion

gas warms on compression

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H < 0$$

for $\partial P < 0$ (expansion),
then $\partial T > 0$ (warming).

gas warms on expansion

gas cools on compression

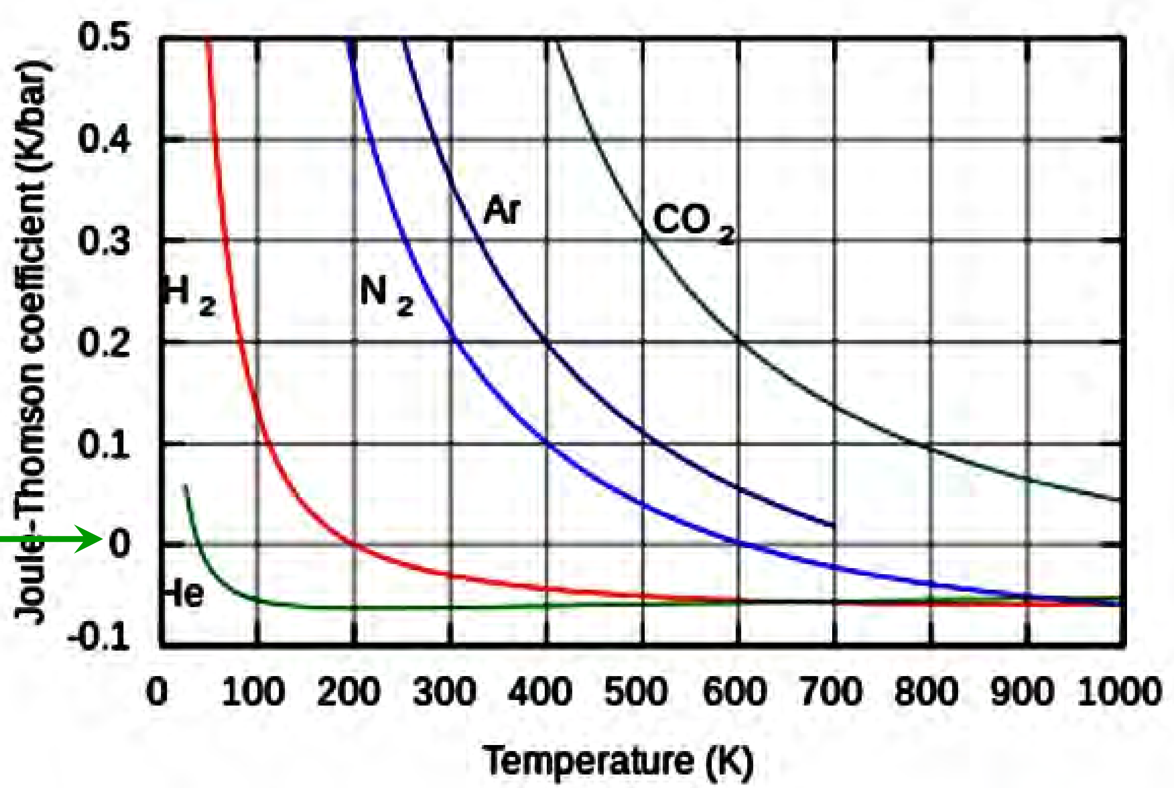
Joule-Thomson Coefficients

Temperature dependence of μ at 1 atm.

$\mu > 0$.
gas cools
on expansion.

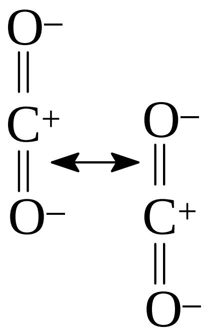
Ideal gas

$\mu < 0$.
gas warms
on expansion.



μ increases with
molecular weight

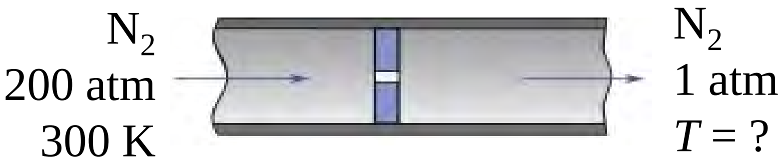
μ increases with
molecular polarity.



$O^{-}=C^{+}=O^{-} \leftrightarrow O^{-}=C^{+}=O^{-}$

CO_2 leaves a
fire extinguisher
as dry ice.

How to calculate ΔT for a Joule-Thomson Expansion



$$\left(\frac{\partial T}{\partial P}\right)_H = \mu \quad \Rightarrow dT = \mu dP \quad \text{at constant } H$$

Assume μ is independent of T $\Rightarrow$ separate 'n' integrate:

$$\int_{T_1}^{T_2} dT = \int_{P_1}^{P_2} \mu dP$$

Further assume μ is independent of P:

$$\int_{T_1}^{T_2} dT = \mu \int_{P_1}^{P_2} dP$$

$$T_2 - T_1 = \mu(P_2 - P_1)$$

Use μ for nitrogen at 1 atm and 300K:

$$\Delta T = 0.22 \frac{\text{K}}{\text{atm}}(1 - 200\,\text{atm})$$

$$\boxed{\Delta T = -44\,\text{K}}$$

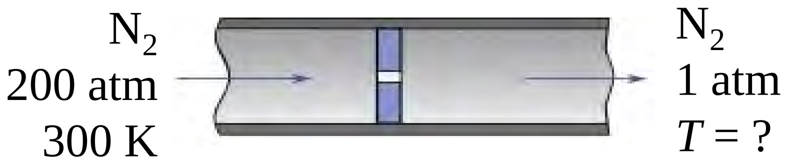
But μ depends on T and P.

μ = 0.22 at 1 atm and 300K

μ = 0.28 at 1 atm and 256K

μ = 0.078 at 200 atm and 300K

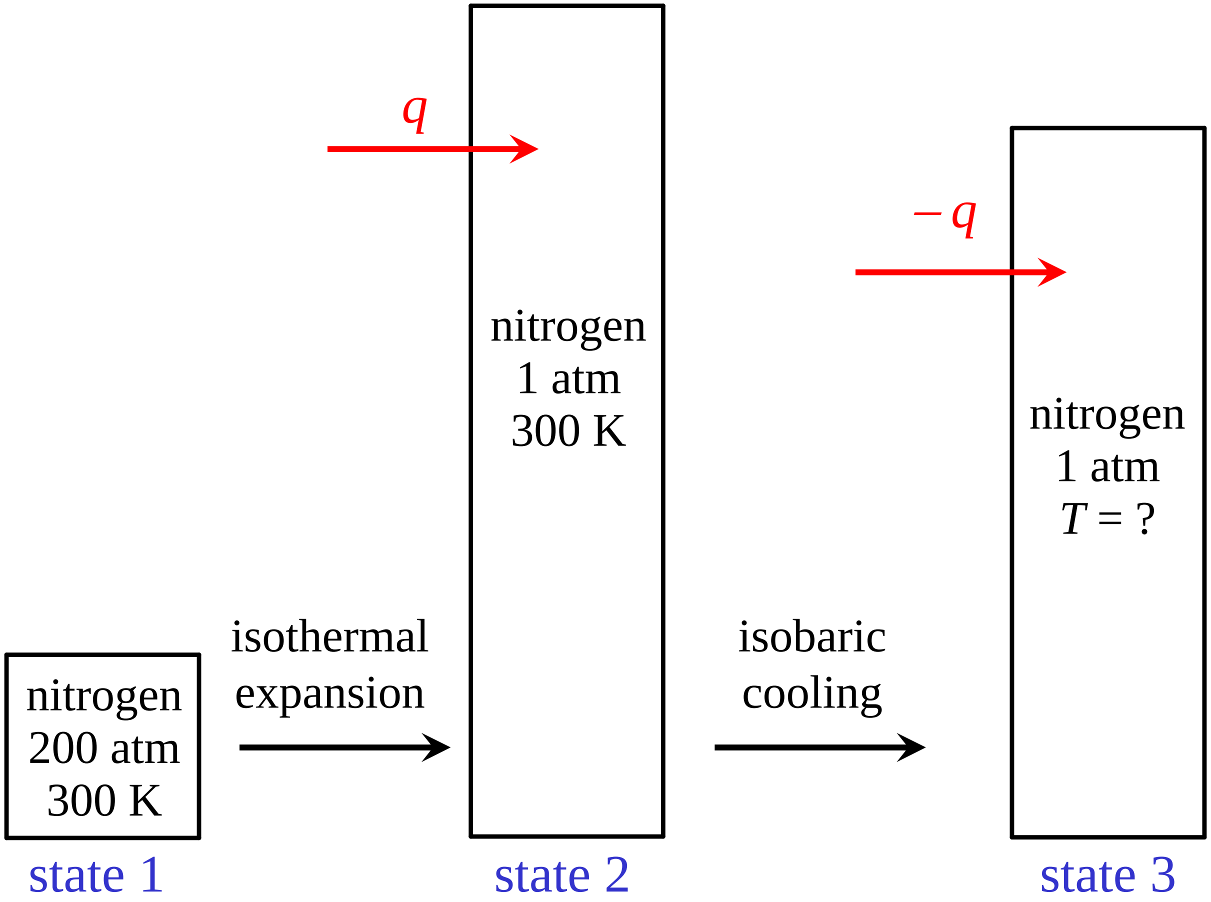
How to *more accurately* calculate ΔT for a Joule-Thomson Expansion



N_2
200 atm
300 K

N_2
1 atm
T = ?

Because enthalpy is a state function, we can model the actual process as a progression of convenient states: expand isothermally and then cool isobaricly.



nitrogen
200 atm
300 K
state 1

isothermal
expansion

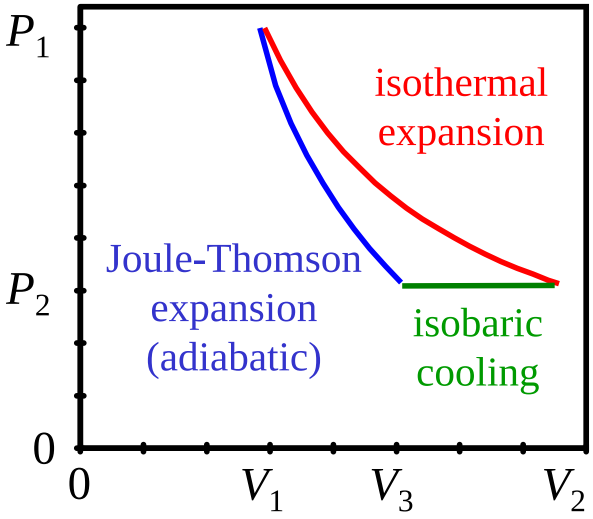
q

nitrogen
1 atm
300 K
state 2

isobaric
cooling

$-q$

nitrogen
1 atm
T = ?
state 3



How to *more accurately* calculate ΔT for a Joule-Thomson Expansion?

state 1: 200 atm, 300 K $\xrightarrow{\text{isothermal expansion}}$ state 2: 1 atm, 300 K $\xrightarrow{\text{isobaric cooling}}$ state 3: 1 atm, T = ?

Enthalpy is a state function, independent of path.

$$\Delta H_{1\to 3} = \Delta H_{1\to 2} + \Delta H_{2\to 3} = 0$$

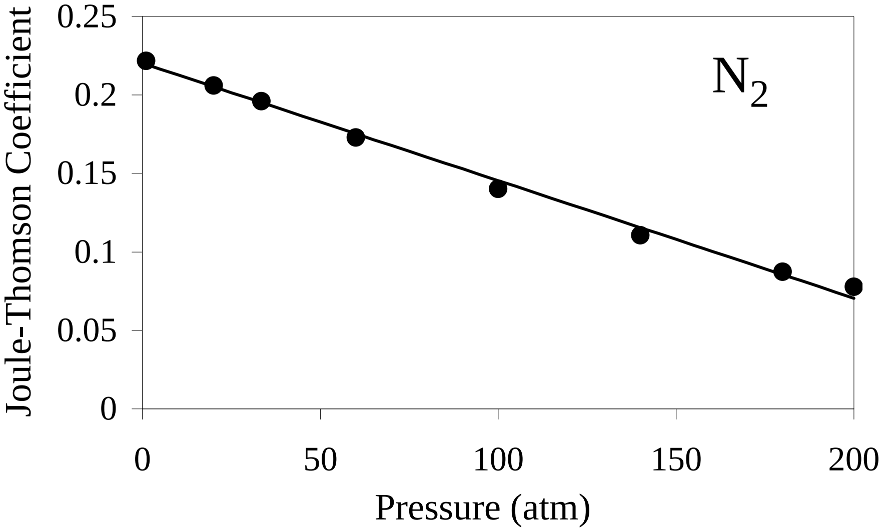
Because a Joule-Thomson expansion is isenthalpic

$$\Delta H_{1\to 2} = -\Delta H_{2\to 3}$$

1 → 2 is at constant T: $\left(\frac{\partial H}{\partial P}\right)_T = -n\mu\overline{C}_\mathrm{P} \quad \Rightarrow \quad dH = -n\mu\overline{C}_\mathrm{P}dP$ at constant T

$$\int_{H_1}^{H_2} dH = -n\int_{P_1}^{P_2} \mu\overline{C}_\mathrm{P}dP$$

Need μ and C_P as a function of P.



Best fit: $\mu = 0.22 - 7.5 \times 10^{-4}P$ K/atm at 300K

From Perry's Handbook, p. 3-237:

$$\overline{C}_\mathrm{P} = 29 + 0.040P \ \text{J/(K}\cdot\text{mol)} \ \text{at 300K}$$

see next slide…

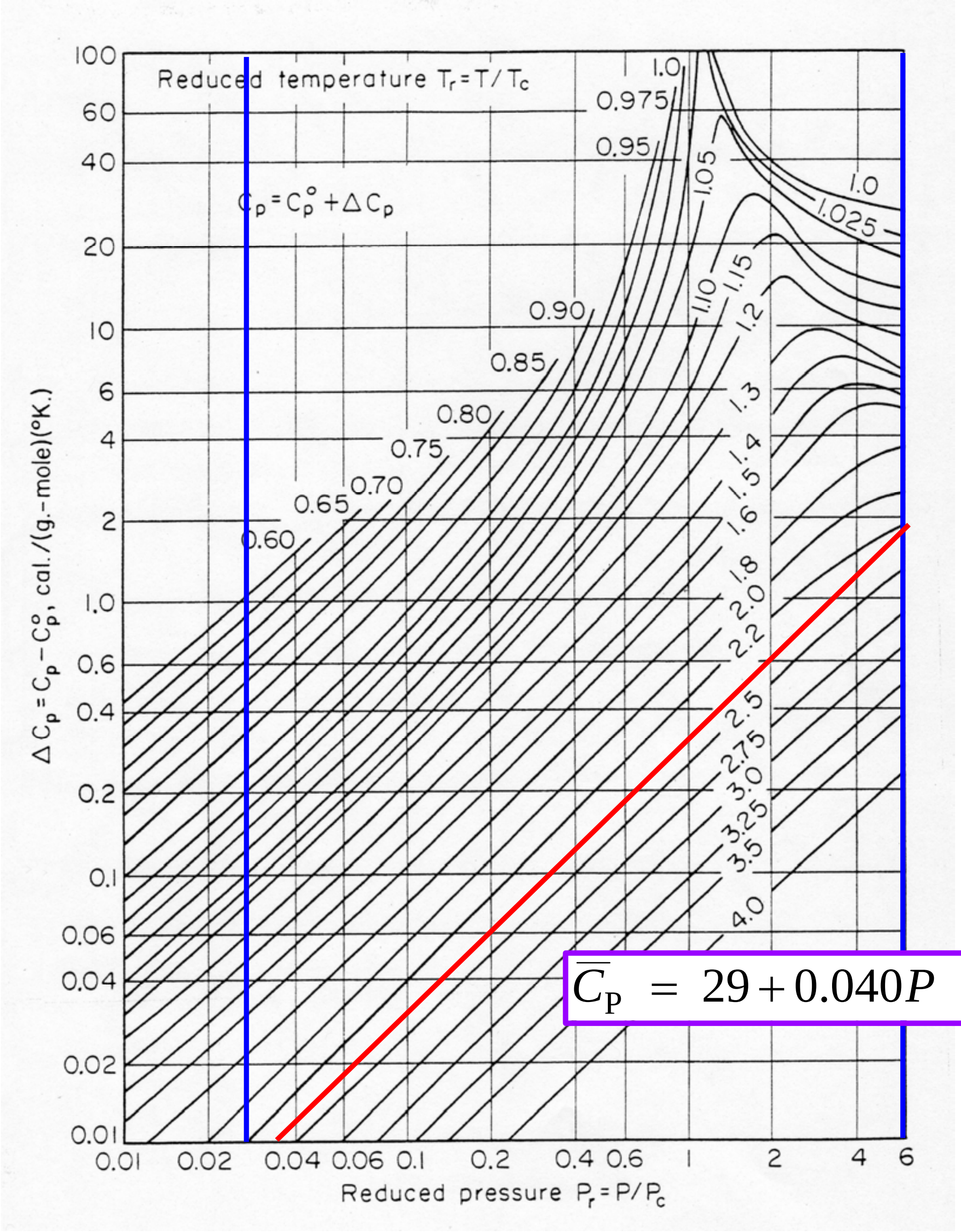
Universal Dimensionless Correlation for C_P

N_2: $T_c = 126$ K,
$P_c = 34$ bar

1 bar/34 bar = 0.03

200 bar/34 bar = 6

300 K/126 K = 2.4



$$\overline{C}_P = 29 + 0.040P \ \ \text{J/(K} \cdot \text{mol) at 300K}$$

From Perry's Handbook of Chemical Engineering, p. 3-237

How to *more accurately* calculate ΔT for a Joule-Thomson Expansion

state 1: 200 atm, 300 K $\xrightarrow[\text{expansion}]{\text{isothermal}}$ state 2: 1 atm, 300 K $\xrightarrow[\text{cooling}]{\text{isobaric}}$ state 3: 1 atm, T = ?

$1 \rightarrow 2$: $$\int_{H_1}^{H_2} dH = -n\int_{P_1}^{P_2} \mu \overline{C}_\mathrm{P}\, dP$$

$\mu = 0.22 - 7.5 \times 10^{-4}P$ K/atm at 300K

$\overline{C}_\mathrm{P} = 29 + 0.040P$ J/(K·mol) at 300K

$$\Delta H_{1\rightarrow 2} = -n\int_{P_1}^{P_2} (0.22 - 7.5\times 10^{-4}P)(29 + 0.040P)\, dP$$

$$= -n\int_{P_1}^{P_2} (6.38 - 0.013P - 3.0\times 10^{-5}P^2)\, dP$$

$$= -n\left(6.38P - \frac{0.013}{2}P^2 - \frac{3.0\times 10^{-5}}{3}P^3\right)\Bigg|_{200\text{ atm}}^{1\text{ atm}}$$

$$= -(1\text{ mol})(-1270. + 260. + 80.\text{ J/mol}) = 930.\text{ J}$$

$$\Delta H_{2\rightarrow 3} = -\Delta H_{1\rightarrow 2} = -930.\text{ J}$$

How to *more accurately* calculate ΔT for a Joule-Thomson Expansion

$$\text{state 1: 200 atm, 300 K} \xrightarrow{\text{isothermal expansion}} \text{state 2: 1 atm, 300 K} \xrightarrow{\text{isobaric cooling}} \text{state 3: 1 atm, } T = ?$$

$$2 \rightarrow 3: \quad \left(\frac{\partial H}{\partial T}\right)_P = n\overline{C}_\mathrm{P} \quad \Rightarrow \quad dH = n\overline{C}_\mathrm{P}dT \ \text{ at constant } P$$

$$\int_{H_2}^{H_3} dH = n\int_{T_2}^{T_3} \overline{C}_\mathrm{P}dT$$

Because the temperature change is small (~40ºC) assume C_P is independent of T.

$$H_3 - H_2 = n\overline{C}_\mathrm{P}(T_3 - T_2)$$

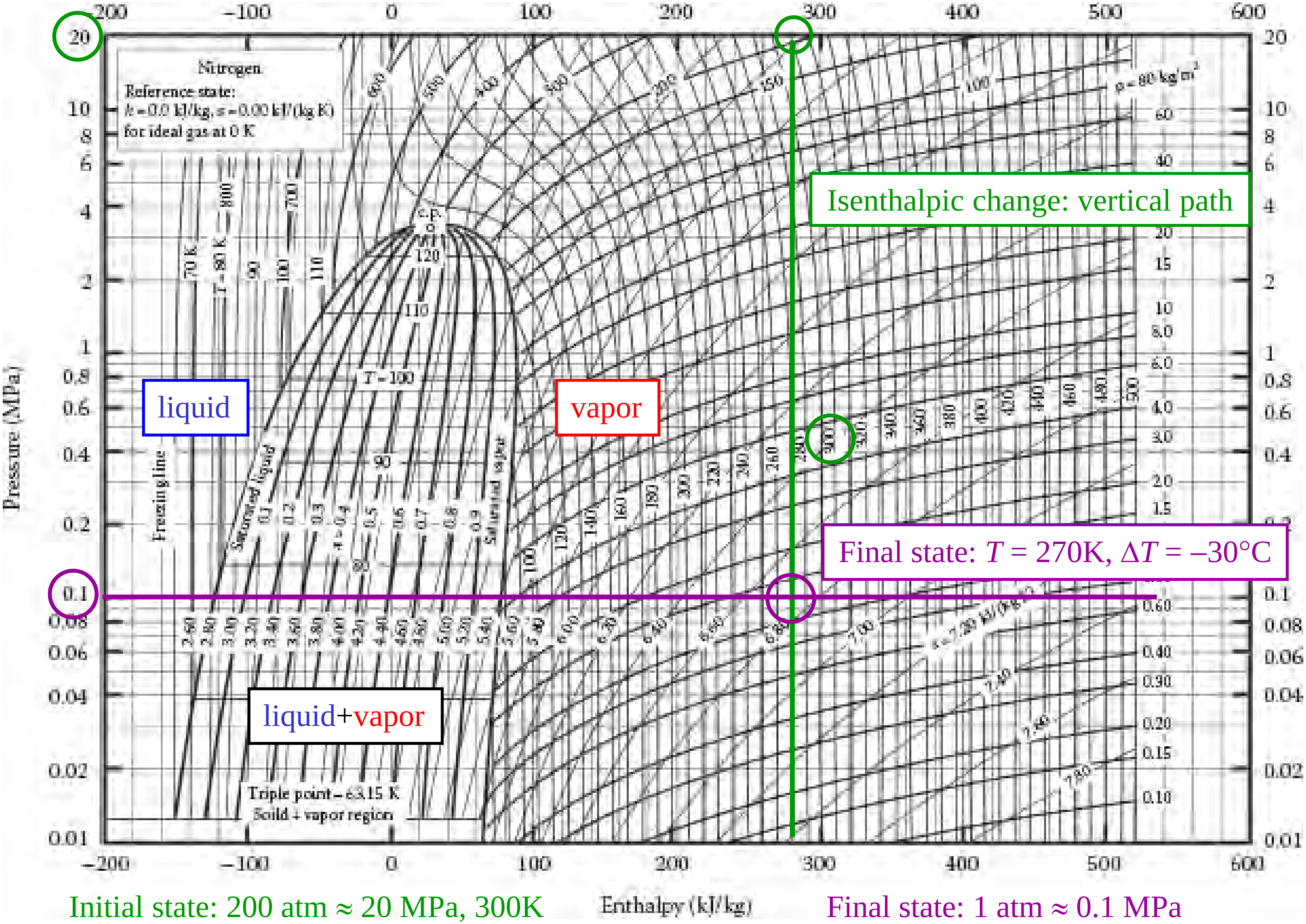
$$\frac{\Delta H_{2\rightarrow 3}}{n\overline{C}_\mathrm{P}} = \Delta T_{2\rightarrow 3} = \frac{930.\ \mathrm{J}}{(1\ \mathrm{mol})\left(\dfrac{29.\ \mathrm{J}}{\mathrm{K}\cdot\mathrm{mol}}\right)} = -32^\circ\mathrm{C}$$

If we assume C_P is *not* independent of T.

$$\overline{C}_\mathrm{P} = 25.79 + 8.09\times 10^{-3}T - 1.46\times 10^{-6}T^2 + \frac{4.5\times 10^4}{T^2} \quad \Rightarrow \quad \Delta T_{2\rightarrow 3} = -32.5^\circ\mathrm{C}$$

cf. $\Delta T = -44^\circ\mathrm{C}$ calculated assuming μ and C_P were independent of T and P.

Enthalpy-Pressure Diagrams (Mollier Diagrams)



Isenthalpic change: vertical path

liquid

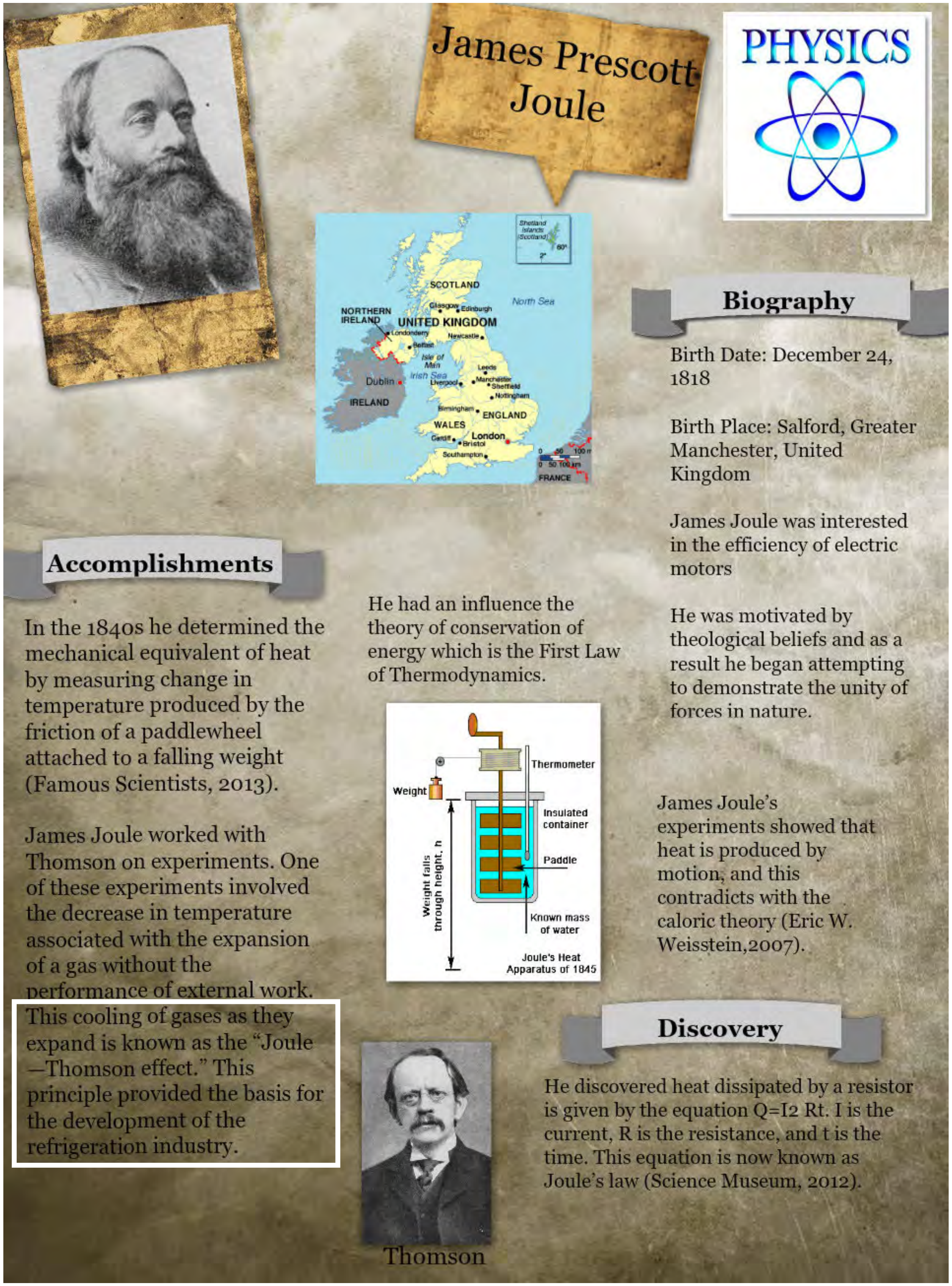
vapor

liquid+vapor

Final state: T = 270K, ΔT = –30°C

Initial state: 200 atm ≈ 20 MPa, 300K

Final state: 1 atm ≈ 0.1 MPa



James Prescott Joule

PHYSICS

Biography

Birth Date: December 24, 1818

Birth Place: Salford, Greater Manchester, United Kingdom

James Joule was interested in the efficiency of electric motors

He was motivated by theological beliefs and as a result he began attempting to demonstrate the unity of forces in nature.

Accomplishments

In the 1840s he determined the mechanical equivalent of heat by measuring change in temperature produced by the friction of a paddlewheel attached to a falling weight (Famous Scientists, 2013).

James Joule worked with Thomson on experiments. One of these experiments involved the decrease in temperature associated with the expansion of a gas without the performance of external work. This cooling of gases as they expand is known as the "Joule—Thomson effect." This principle provided the basis for the development of the refrigeration industry.

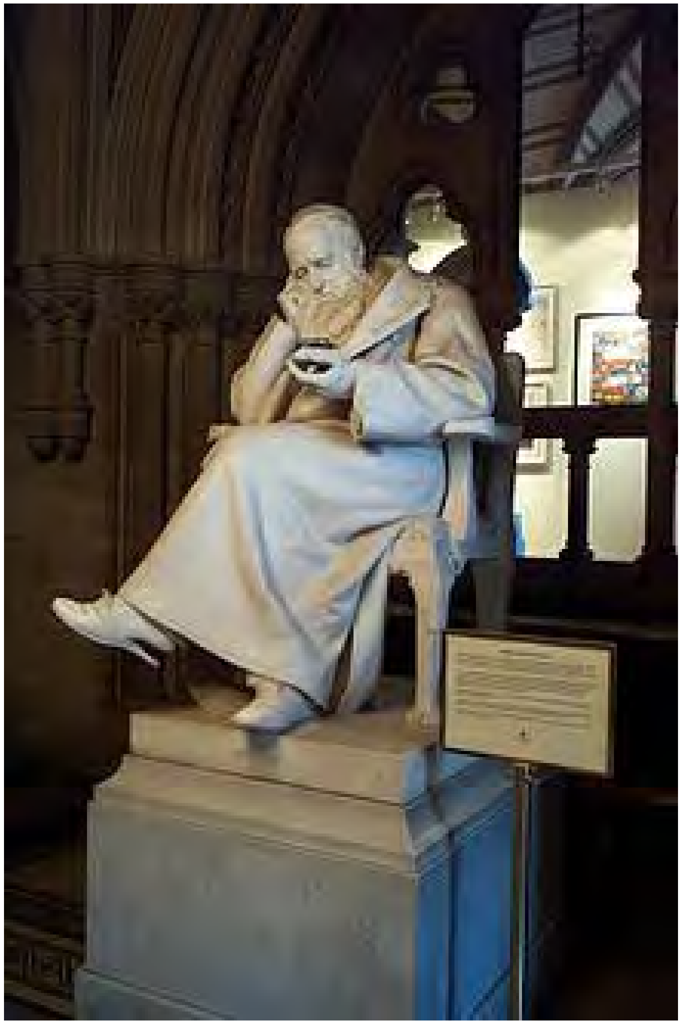
He had an influence the theory of conservation of energy which is the First Law of Thermodynamics.

James Joule's experiments showed that heat is produced by motion, and this contradicts with the caloric theory (Eric W. Weisstein,2007).

Discovery

He discovered heat dissipated by a resistor is given by the equation Q=I2 Rt. I is the current, R is the resistance, and t is the time. This equation is now known as Joule's law (Science Museum, 2012).

Thomson



Manchester Town Hall

"The Father of Thermodynamics"