
The First Law: Machinery

Chapter 3 of Atkins, 6th, 7th Ed: The First Law: the machinery
8/9th Edition: Sections 2.10-2.12 & Further Information in Ch. 2

State Functions

Exact and inexact differentials

Changes in internal energy

The Joule experiment

Changes in internal energy at constant p

Temperature Dependence of Enthalpy

Changes in enthalpy at constant volume

Isothermal compressibility

Joule-Thomson effect

C_V vs. C_p

State vs. Path Functions

state functions: Properties are independent of how the substance is prepared, and are functions of variables such as pressure and temperature (define the state of system)

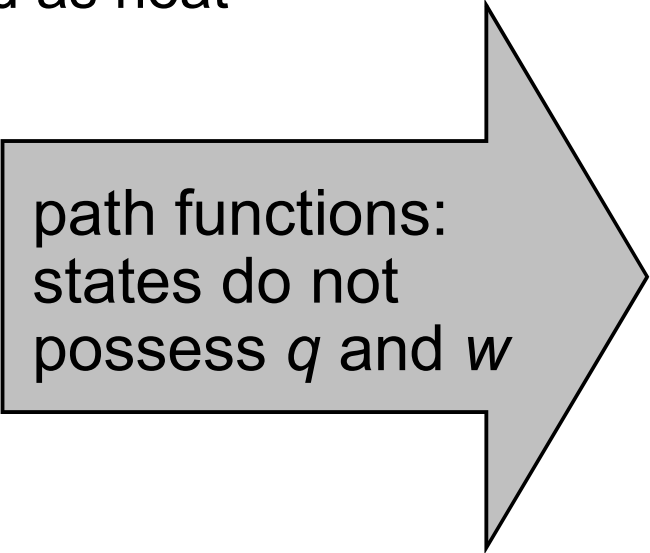
examples: U : internal energy
 H : enthalpy

path functions: Properties that relate to the preparation of the state of the substance

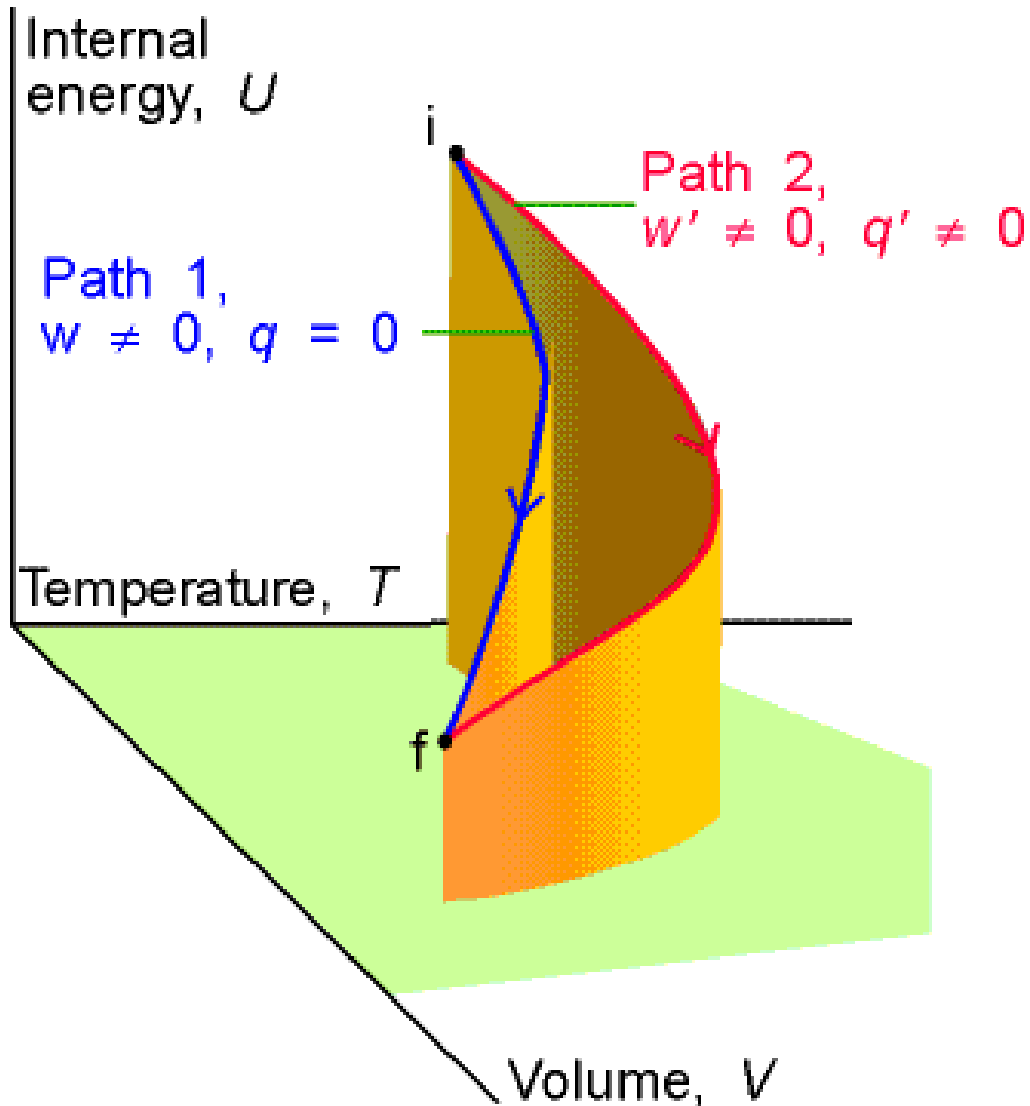
examples: w : work done preparing a state
 q : energy transferred as heat

state functions:
system possesses
 U and H

path functions:
states do not
possess q and w



State Functions



Initially:

state has internal energy U_i

Path 1:

adiabatic expansion to final state with internal energy U_f

- work done on system is w

Path 2:

non-adiabatic expansion to final state with U_f

- q' and w' are both done on the system

U : property of state

(same value of ΔU in both cases)

w, q : property of path

Exact & Inexact Differentials

Exact Differential:

System is taken along a path, with $\Delta U = U_f - U_i$, and the overall change is the sum of the infinitesimal changes along the path (i.e., an integral):

$$\Delta U = \int_i^f dU$$

ΔU is independent of path - path independence is expressed by saying that dU is an **exact differential** - an infinitesimal quantity, which when integrated gives a path independent result

Inexact Differential:

System is heated, total energy transferred as heat is the sum of individual contributions along each point of the path:

$$q = \int_{i, \text{ path}}^f dq$$

Do not write Δq : q is not a state function, energy is not $q_f - q_i$
■ q depends upon the path of integration (e.g., adiabatic vs. non-adiabatic) - path independence is expressed by saying that dq is an **inexact differential** - infinitesimal quantity that depends upon the path (dw is also an **inexact differential**)

Work, heat, internal energy and pathways

Consider a perfect gas in a cylinder with a piston:

Initial state T, V_i

Final state T, V_f

Change of state:

Path 1: free expansion against no external pressure

Path 2: reversible isothermal expansion

Path 3: irreversible isothermal expansion against $p_{\text{ext}} \neq 0$

Calculate q , w and ΔU for each pathway

All pathways: internal energy arises from kinetic energy of molecules, so since processes are isothermal, $\Delta U = 0$, so $q = -w$

Path 1: free expansion, $w = 0$, so $q = 0$

Path 2: $w = -nRT \ln (V_f/V_i)$, so $q = nRT \ln (V_f/V_i)$

Path 3: $w = -p_{\text{ext}}\Delta V$, so $q = p_{\text{ext}}\Delta V$ (since $\Delta U = 0$)

Changes in Internal Energy, 1

For a closed system of constant composition, U is function of V and T (possible to express p in terms of V and T , so p is not independent here)

Say V makes a small change to $V + dV$ at constant T :

$$U' = U + \left(\frac{\partial U}{\partial V} \right)_T dV$$

or T changes to $T + dT$ at constant V :

$$U' = U + \left(\frac{\partial U}{\partial T} \right)_V dT$$

The coefficients $(\partial U/\partial V)_T$ and $(\partial U/\partial T)_V$ are **partial derivatives** of U w.r.t. V and T , respectively (slopes of U vs V at constant T and U vs T at constant V) - if both V and T change infinitesimally (recall $dVdT \approx 0$):

$$U' = U + \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Changes in Internal Energy, 2 †

These infinitesimal changes in conditions imply U' differs from U by an infinitesimal amount dU ; thus,

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

Infinitesimal changes in V and T result in an infinitesimal change in U , with constants of proportionality being the **partial derivatives**

- remember: these give a *slope of property of interest against one variable*, with all other variables held constant
- it is important to keep in mind that partial derivatives all have physical meaning, as well as being a useful mathematical tool

Recall that $(\partial U/\partial T)_V = C_V$ (i.e., the change in internal energy at constant volume with change temperature is the heat capacity at constant volume)

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

Changes in Internal Energy, 3

$(\partial U/\partial V)_T$, the change in internal energy as the volume a substance occupies changes, is denoted as π_T , and is called the **internal pressure**

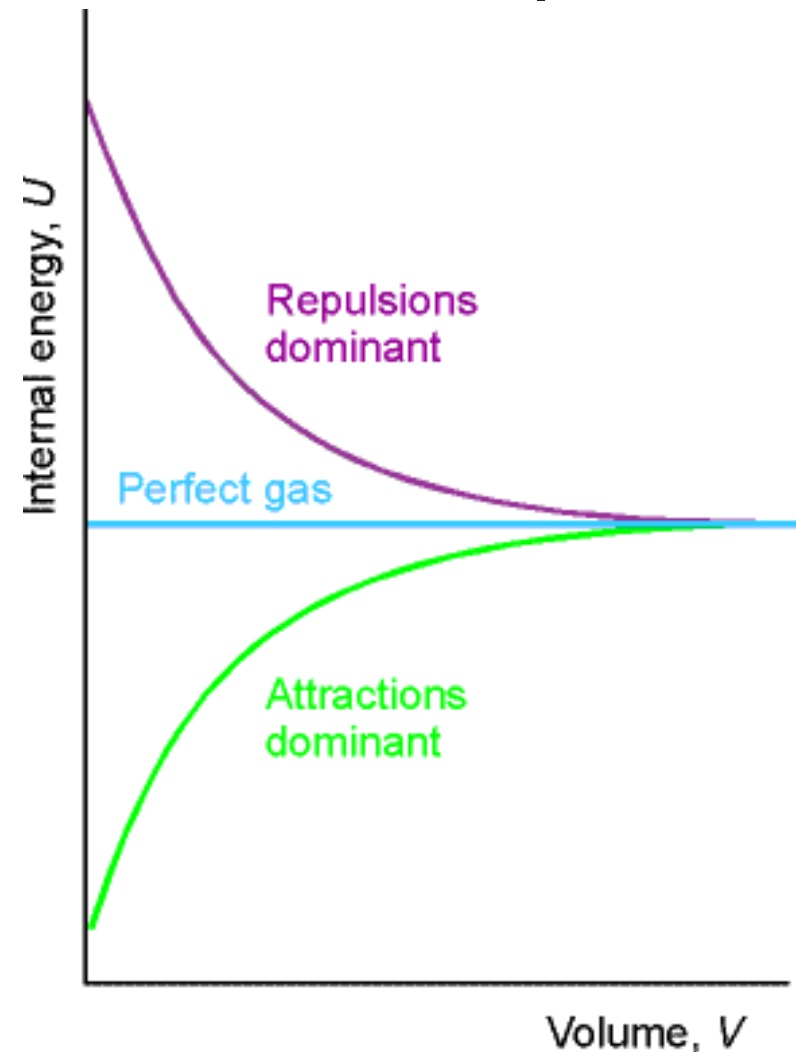
$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

π_T is a measure of *cohesive forces* in the sample:

$$dU = \pi_T dV + C_V dT$$

$dU > 0$, internal energy increases, $dV > 0$, volume expands isothermally, and with **attractive** forces dominating, $\pi_T > 0$

For a perfect gas, $\pi_T = 0$, and internal energy is independent of the volume of gas in the sample

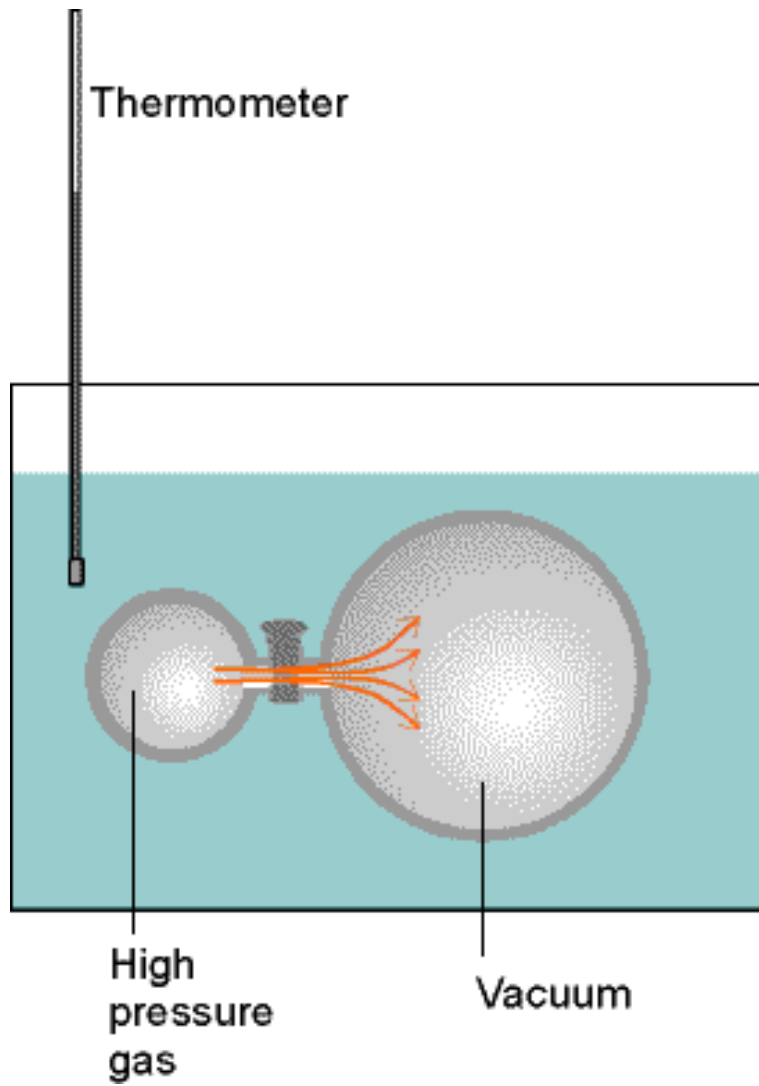


Joule Experiment

James Joule thought he could measure internal pressure with the following apparatus - high pressure gas expands into a vacuum - however, no change in temperature is measured: WHY?

- expansion into vacuum: $w = 0$
- no heat transfer: $\Delta T = 0$, so $q = 0$
- consequently: $\Delta U = w + q = 0$
- therefore: $\pi_T = 0$

Actually, the heat capacity of his crude apparatus was so large, that the temperature change caused by this expansion of gas was simply too small to measure - so small deviations of real gases were not detected...



Changes in Internal Energy at Constant p †

How does internal energy vary with temperature at constant pressure?

$$dU = \pi_T dV + C_V dT$$

Take the derivative of both sides w.r.t T , and impose constant pressure:

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

The **differential on the RHS** describes change in volume at constant pressure with changing temperature, and is denoted as the **expansion coefficient**, α , of a pure substance

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

Large α : big responses to changes in temperature - WHY?

$$\alpha = \frac{1}{V} \left(\frac{\partial(nRT/p)}{\partial T}\right)_p = \frac{nR}{pV} = \frac{1}{T}$$

Changes in Internal Energy at Constant p

Substitute in α into the expression for $(\partial U/\partial T)_p$:

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$$

The dependence of internal energy upon temperature at constant pressure can be measured in terms of α or π_T (two different experiments)

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \leftarrow \quad \pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$


and for a perfect gas, since $\pi_T = 0$:

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V$$

So we know $(\partial U/\partial T)_v = C_V$ and $(\partial U/\partial T)_p = C_V$ above - in our experiments, we can easily use the simpler first expression by **controlling volume**: i.e., at constant volume, $w = 0$, and $\Delta U = q_v$

Changes in Enthalpy at Constant Volume

constant pressure heat capacity, C_p , is the variation of enthalpy with temperature at constant pressure

enthalpy, $H = U + pV$, is an important thermodynamic state function, notably when the pressure is controlled; thus, dH is an exact differential

Since $\Delta H = q_p$, we will write H as a function of p and T , and develop the equations describing variation of H with T at constant V - this will help us understand heat capacities C_p and C_v

Starting the same way as we did for U :

For a closed system of constant composition, H is a function of p and T :

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT$$

What does this equation mean?

An infinitesimal change in enthalpy results from infinitesimal changes in pressure (at constant temperature) and temperature (at constant pressure) - the coefficients are the usual *partial derivatives*

Changes in Enthalpy at Constant Volume

From the previous slide, if $(\partial H/\partial T)_p = C_p$, the heat capacity at constant p

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + C_p dT$$

which can be rearranged and rewritten as (see next page)

$$\left(\frac{\partial H}{\partial T} \right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T} \right) C_p$$

where κ_T is the **isothermal compressibility**

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

and μ is the **Joule-Thomson coefficient**

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

Justifying ΔH at constant volume

Starting with

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + C_p dT$$

divide by dT and impose constant volume to get

$$\left(\frac{\partial H}{\partial T} \right)_V = \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V + C_p$$

the third coefficient looks familiar - it looks like it is related to $(\partial V/\partial T)_p$ (which is α the expansion coefficient).

The useful rules of partial derivatives help us here (in Atkins 6th Edition, **Further Information 1**) - we can use the **chain rule**

since:
$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

thus:
$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{1}{(\partial T/\partial V)_p (\partial V/\partial p)_T}$$

Justifying ΔH at constant volume, 2

The term $(\partial T/\partial V)_p$ shows up in the denominator instead of $(\partial V/\partial T)_p$ - but we can use another useful property of partial derivatives - **inversion**:

$$\text{since: } \left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{(\partial y/\partial x)_z}$$

$$\text{thus: } \left(\frac{\partial p}{\partial T} \right)_V = - \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

where α is the expansion coefficient of a substance, and κ_T is the isothermal compressibility (both defined earlier in this lecture)

Now, change $(\partial H/\partial p)_T$ into something useful

$$\left(\frac{\partial H}{\partial p} \right)_T = - \frac{1}{(\partial p/\partial T)_H (\partial T/\partial H)_p} = - \left(\frac{\partial T}{\partial p} \right)_H \left(\frac{\partial H}{\partial T} \right)_p$$

RHS: expressions for C_p and the Joule-Thomson coefficient, μ ; so,

$$\left(\frac{\partial H}{\partial p} \right)_T = -\mu C_p$$

Isothermal compressibility, κ_T

Recall,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

The negative sign makes κ_T positive - an increase in p (+ve dp) brings about a decrease in V (-ve dV) at constant temperature

Isothermal compressibility is obtained from a plot of p vs. V at constant temperature

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial(nRT/p)}{\partial p} \right)_T = -\frac{nRT}{V} \left(-\frac{1}{p^2} \right) = \frac{1}{p}$$

The higher the pressure of the gas, the lower the compressibility

Example:

Consider the isothermal compressibility of water, which at 20°C and 1 atm is $4.94 \times 10^{-6} \text{ atm}^{-1}$.

What volume change occurs when a sample of volume 50 cm^3 is subjected to a additional 1000 atm of pressure at constant temperature?

Example of isothermal compressibility

Isothermal compressibility: an infinitesimal change in volume results from an infinitesimal change in pressure at constant temperature

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp = -\kappa_T V dp$$

For measurable change, ΔV , we must integrate

$$\int_{V_i}^{V_f} dV = - \int_{p_i}^{p_f} \kappa_T V dp$$

The LHS above is ΔV . If κ_T and V are approximately constant over the pressure range of interest

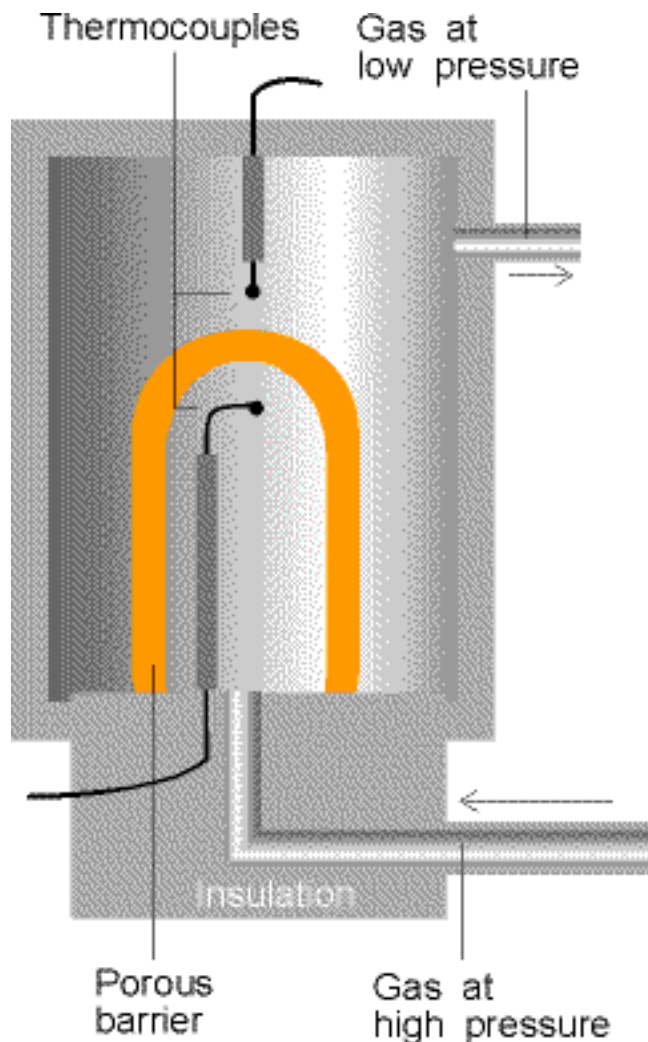
$$\Delta V = -\kappa_T V \int_{p_i}^{p_f} dp = -\kappa_T V \Delta p$$

$$\Delta V = -(4.94 \times 10^{-6} \text{ atm}^{-1}) \times (50 \text{ cm}^3) \times (1000 \text{ atm}) = -0.25 \text{ cm}^3$$

Notice that compression is only 0.5%, so assumption that κ_T and V are approximately constant is valid

The Joule-Thomson Effect

The **Joule-Thomson effect** and the associated coefficient, μ , help us to understand the **liquefaction** of gases



- Gas expands through a porous barrier from constant high pressure to constant low pressure
- The container has insulated walls, so the process is adiabatic
- The difference in temperature results from expansion is monitored

What is observed?

- Low temperature on the low pressure side
- High temperature on the high pressure side
- $\Delta p \propto \Delta T$

Joule-Thomson effect:
cooling by adiabatic expansion

Thermodynamic Basis of Joule-Thomson Effect

Joule-Thomson throttle describes the thermodynamic basis of J-T expansion:

Starting conditions:

- Adiabatic, $q = 0$
- Gas on high-pressure side, p_i at T_i , occupying volume V_i
- Gas on low-pressure side, p_f at T_f , occupying volume V_f
- Upstream and downstream pressures act as “pistons” which compress the gas

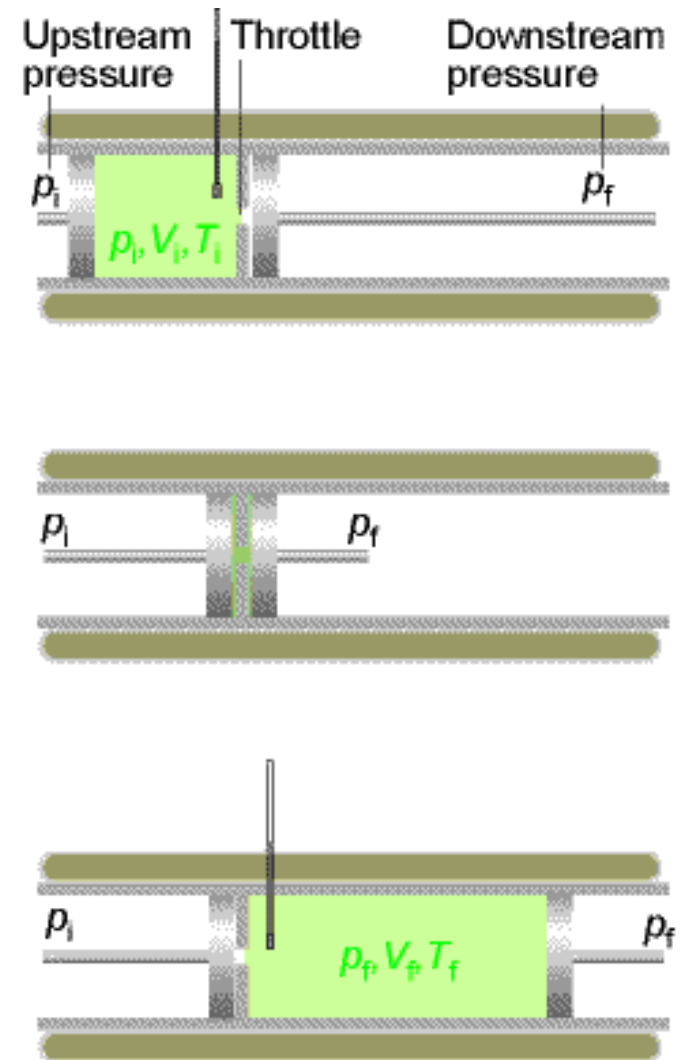
Isothermal compression and expansion:

- Gas on left is **compressed isothermally** by the upstream piston (pressure is p_i and volume V_i becomes 0), so the work is $w = -p_i(0 - V_i) = p_i V_i$
- Gas **expands isothermally** on right of throttle (maybe different T) against p_f , with work $w = -p_f(V_f - 0) = -p_f V_f$

Final result:

ΔU of gas moving from one side to the other:

$$\Delta U = w = p_i V_i - p_f V_f$$



Joule-Thomson Effect & Enthalpy

The change in internal energy for J-T expansion:

$$\Delta U = U_f - U_i = w = p_i V_i - p_f V_f$$

Rearrange:

$$U_f + p_f V_f = U_i + p_i V_i \quad \text{or} \quad H_f = H_i$$

Process is said to be **isoenthalpic** (i.e., **process at constant enthalpy**)

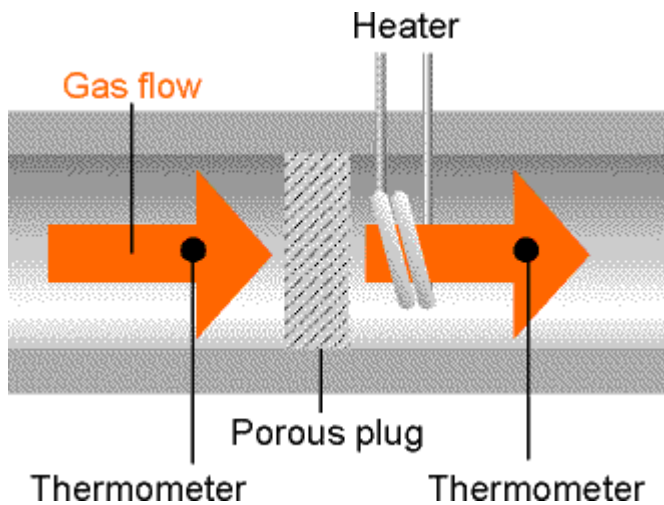
- Property measured: $\Delta T/\Delta p$
- Adding the constraint of constant enthalpy, for a small change in p , we measure $(\partial T/\partial p)_H$, which is the **Joule-Thomson coefficient**, μ

Physical interpretation of μ : the ratio of change in temperature to the change in pressure under adiabatic conditions

Modern method of measuring μ : **isothermal Joule-Thomson coefficient**

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T = -C_p \mu$$

Isothermal J-T Coefficient, μ_T



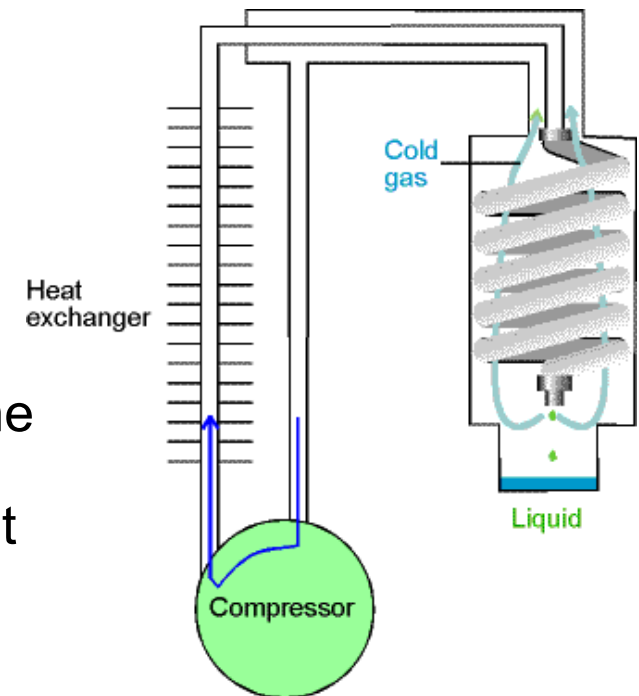
Measuring μ_T :

- Gas is pumped at steady pressure through a heat exchanger (sets temperature) through a porous plug in an adiabatic container
- Steep pressure drop is measured, Δp , with cooling offset by a heater
- Heater energy is monitored ($\Delta H = q_p$)
- μ_T obtained from $\Delta H/\Delta p$ as $\Delta p \rightarrow 0$
- μ can then be calculated

Linde Refrigerator:

uses J-T expansion to liquefy gases

- Gas expands through the throttle
- Cools and circulated past incoming gas
- Gas cools, subsequent expansion cools it further
- Circulating gases cool enough to condense into the liquid phase
- If gas beneath upper **inversion temperature**, T_i , it cools on expansion through throttle



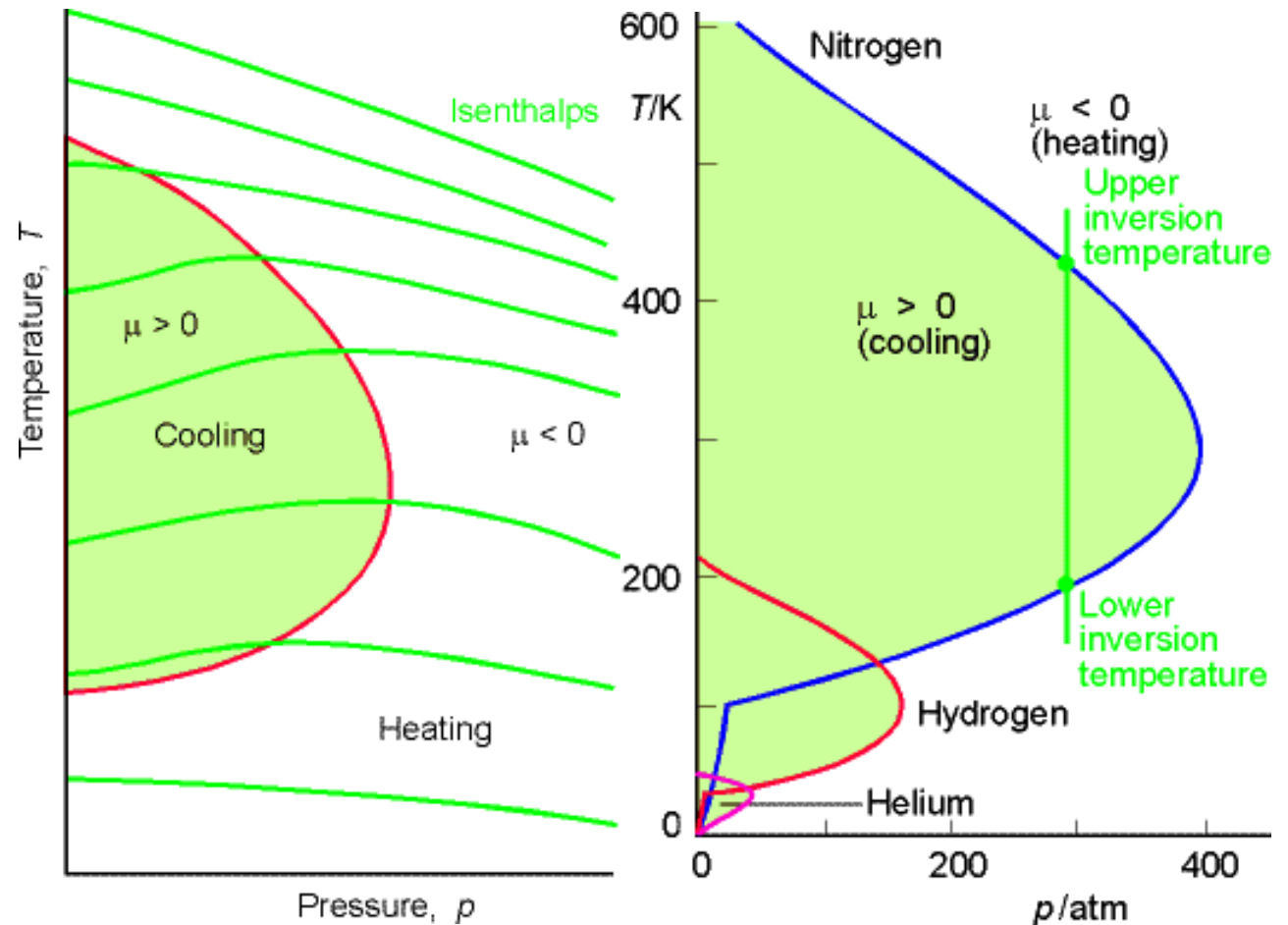
More on J-T Coefficients

Real gases have non-zero J-T coefficients: depends on gas, pressure, attractive and repulsive intermolecular interactions & temperature:

$\mu > 0$: dT is -ve when dP is -ve, gas cools on expansion

$\mu < 0$: dT and dP have opposite signs, gas heats up on expansion

$\mu = 0$: perfect gas, T unchanged by J-T expansion



Gases have upper and lower **inversion temperatures**, where the heating and cooling properties of the gas change along an **isenthalp**

Relation Between C_V and C_p †

For a perfect gas, $\pi_T = 0$, so $C_V = (\partial U/\partial T)_p$; thus we can write:

$$C_p - C_V = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_p$$

Since $H = U + pV = U + nRT$

Then,

$$C_p - C_V = \left(\frac{\partial U}{\partial T} \right)_p + nR - \left(\frac{\partial U}{\partial T} \right)_p = nR$$

For a real gas, we can write the following thermodynamic expression which applies to any substance, reducing to the equation above when the $\alpha = 1/T$ and $\kappa_T = 1/p$

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$$

Justifying Relation Between C_V and C_p

Express C_p and C_V in terms of partial derivatives, and sub in $H = U + pV$

$$\begin{aligned}C_p - C_V &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial U}{\partial T} \right)_p + \left(\frac{\partial(pV)}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V\end{aligned}$$

Difference of 1st and 3rd terms on the RHS is $\alpha\pi_T V$, where αV describes change in V with changing T and π describes change in U from this change in volume. The contribution of work pushing atmosphere back is

$$\left(\frac{\partial(pV)}{\partial T} \right)_p = p \left(\frac{\partial V}{\partial T} \right)_p = \alpha p V$$

Combining expressions:

$$C_p - C_V = \alpha(p + \pi_T)V$$

From Section 5.1 Atkins,

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

Subbing in:

$$C_p - C_V = \alpha T V \left(\frac{\partial p}{\partial T} \right)_V$$

We have shown that $(\partial p / \partial T)_V = \alpha / \kappa_T$, so subbing this in gives the relationship between C_p and C_V