Chapter 3. The Importance of State Functions. The Internal Energy and Enthalpy

Summary

- useful features of state functions are identified
- introduction to the mathematics of thermodynamic partial differential equations
- changes in the internal energy and enthalpy are related to easily measured changes in the state variables *T*, *V*, and *p*
- applications:
  - ∗ Joule-Thomson experiment
  - ∗ liquefaction of gases

Section 3.1 Mathematical Properties of State Functions: Partial Differential Equations

Partial Differential equations - the “language” of thermodynamics

(and many other branches of science and technology)

- What are **differential equations**?
- What are **“partial”** differential equations?
- Why are differential equations important?
- How can they be used?
- What rules apply?

First … **<u>“Ordinary” Differential Equations</u>**

<u>only one</u> independent variable

Example: independent variable x in the function $\boldsymbol{f(x) = 10x^3 - 3x}$

<u>derivative</u> of *f*(*x*)

[slope of $f(x)$ plotted against x]

$$\boxed{\frac{df(x)}{dx} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}}$$

<u>integral</u> of *f*(*x*)

“add up” the df differentials

[gives the change in $f(x)$]

$$\boxed{\Delta f = f(x_b) - f(x_a) = \int_{x_a}^{x_b} \frac{df(x)}{dx}\, dx = \int_{f(x_a)}^{f(x_b)} df}$$

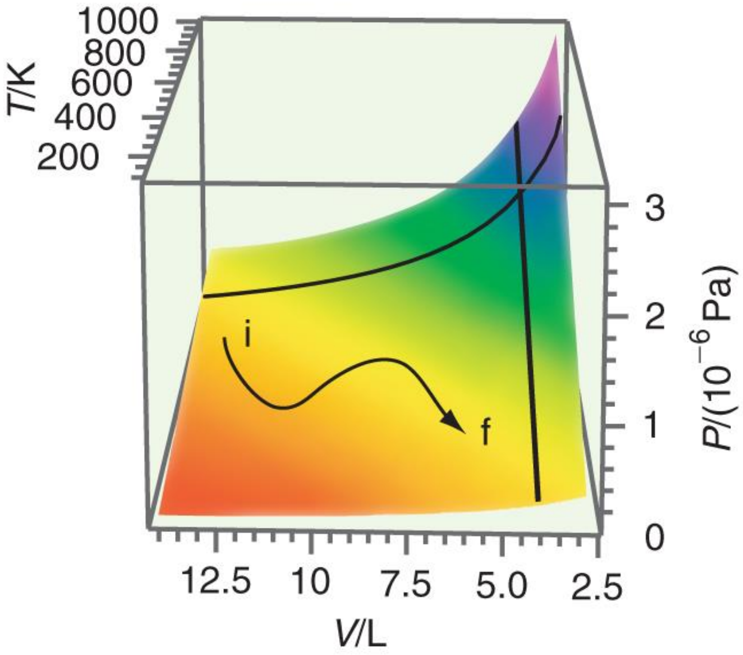
But thermodynamic functions generally depend on *two or more* independent variables

Example

The pressure of *n* moles of ideal gas is a function of *T* and *V*.

$$\boxed{p(T,V) = \frac{nRT}{V}}$$

p(T,V) surface



Ordinary derivatives

$$\frac{\mathrm{d}p}{\mathrm{d}T}\ ? \qquad \frac{\mathrm{d}p}{\mathrm{d}V}\ ?$$

are ambiguous and do not apply.

Why? At each point $p(T,V)$ an infinite number of different slopes $\mathrm{d}p/\mathrm{d}T$ and $\mathrm{d}p/\mathrm{d}V$ exist in an infinite number of different directions.

“Partial” Derivatives *to the Rescue*

For the derivatives of the function *p*(*T*,*V*), to avoid ambiguity, define the partial derivatives:

$$\left(\frac{\partial p}{\partial T}\right)_V = \lim_{\Delta T \to 0} \frac{p(T+\Delta T, V) - p(T,V)}{\Delta T}$$

slope of *p* against *T*
parallel to the *T* axis
(*V* fixed)

(Why “partial”? Only *T* and *p* are changing.)

$$\left(\frac{\partial p}{\partial V}\right)_T = \lim_{\Delta V \to 0} \frac{p(T, V+\Delta V) - p(T,V)}{\Delta V}$$

slope of *p* against *V*
parallel to the *V* axis
(*T* fixed)

(Only *V* and *p* are changing.)

Other Partial Differential Equations

1. Wave Equation

Vibration of an elastic string in one dimension:

$$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2}$$

u(*x*,*t*) is the displacement at time *t* and position *x* along the string.
c is the speed of the vibration moving along the string.

Three-dimensional vibration of an elastic medium (such as sound waves, ultrasonic or seismic waves):

$$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2} + c^2 \frac{\partial^2 u}{\partial y^2} + c^2 \frac{\partial^2 u}{\partial z^2} = c^2 \nabla^2 u$$

2. Heat Conduction Equation

Heat conduction in one dimension:

$$\frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2}$$

$T(x,t)$ is the temperature at time t and position x.
k is the thermal conductivity.

Three-dimensional heat conduction:

$$\frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial x^2} + k\frac{\partial^2 T}{\partial y^2} + k\frac{\partial^2 T}{\partial z^2} = k\nabla^2 T$$

3. Diffusion Equation

Diffusion in one dimension:

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2}$$

$C_{\mathrm{A}}(x,t)$ is the concentration of chemical A at time t and position x.
D is the diffusion coefficient.

Three-dimensional diffusion:

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} + D\frac{\partial^2 C_{\mathrm{A}}}{\partial y^2} + D\frac{\partial^2 C_{\mathrm{A}}}{\partial z^2} = D\nabla^2 C_{\mathrm{A}}$$

4. Equation of Continuity for Fluid Flow

Fluid flow in one dimension:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial (\rho \mathrm{v}_x)}{\partial x}$$

$\rho(x,t)$ is the density of the fluid at time t and position x.
v_x is the velocity of the fluid in the x direction.

Three-dimensional continuity equation:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial (\rho \mathrm{v}_x)}{\partial x} - \frac{\partial (\rho \mathrm{v}_y)}{\partial y} - \frac{\partial (\rho \mathrm{v}_z)}{\partial z}$$

5. Transmission Line Equation

Flow of electric current $I(x,t)$ along a wire:

$$\frac{\partial^2 I}{\partial x^2} = LC\frac{\partial^2 I}{\partial t^2} + (RC+GL)\frac{\partial I}{\partial t} + RGI$$

x is the position along the wire

R is the resistance

C is the capacitance

L is the induction

G is the loss

6. Lagrangian Equations of Motion

L = kinetic energy – potential energy for a mechanical system

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = \frac{\partial L}{\partial q_i}$$

q_i is the generalized position of mass i (*any* coordinate system)

$\dot{q}_i$ is the generalized velocity of mass i

7. Schrodinger Quantum Mechanical Equation

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi = E\psi$$

h = Planck constant

V = potential energy

E = total energy

m = particle mass

ψ = wave function

Solving the Schrodinger equation for an electron in the electric potential energy field of a proton gives the ψ_{1s}, ψ_{2s}, ψ_{2p}, ψ_{3s}, … orbitals used by chemists

Example: Partial Derivatives of *p*(*T*,*V*) for an Ideal Gas

partial *T* derivative:

_n_,_R_,_V_ constant

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial[nRT/V]}{\partial T}\right)_V = \frac{nR}{V}\cancelto{1}{\left(\frac{\partial T}{\partial T}\right)_V}$$

$$= \frac{nR}{V} = \frac{p}{T}$$

partial *V* derivative:

_n_,_R_,_T_ constant

same as d(1/*V*) / d*V* at fixed *T*

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

$$= -\frac{nRT}{V^2} = -\frac{p}{V}$$

"Exact" Differential of $p(T,V)$

Because p is a function of state variables T and V:

a) the infinitesimal change in p (the differential dp) produced by changes dT and dp is **exactly defined** (not path-dependent):

$$\boxed{\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V}$$

b) the change in p obtained by integrating dp is **exactly defined** by the initial state $p_i(T_i, V_i)$ and the final state $p_f(T_f, V_f)$ (also not path-dependent)

$$\boxed{\Delta p = \int_{T_i,V_i}^{T_f,V_f} \mathrm{d}p = p_f(T_f,V_f) - p_i(T_i,V_i)}$$

Useful Rules for Partial Derivatives

Inverse Rule

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_V}$$

Cyclic Rule

(*why cyclic?*)

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

Using the inverse rule, the cyclic rule is also written as:

Buy two partial derivatives, get one free!

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

Where Does the Cyclic Rule Come From?

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V$$

divide by dT at constant p
($\mathrm{d}p = 0$)

$$0 = \left(\frac{\partial p}{\partial T}\right)_V \frac{\mathrm{d}T}{\mathrm{d}T_p} + \left(\frac{\partial p}{\partial V}\right)_T \frac{\mathrm{d}V}{\mathrm{d}T_p}$$

$$0 = \left(\frac{\partial p}{\partial T}\right)_V (1) + \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

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

Cyclic Rule

Why the <u>minus sign</u>
in the Cyclic Rule?

At constant p, the change in p caused by dT cancels the change in p caused by dV so that dp = 0.

notice: $\left(\frac{\partial p}{\partial T}\right)_V \neq \left(\frac{\partial p}{\cancel{\partial} V}\right)_T \left(\frac{\cancel{\partial} V}{\partial T}\right)_p$

Why? dV at constant T does not equal dV at constant p.

Mixed Partial Derivatives: Order of Differentiation of a Function Doesn't Matter

∂T first, then ∂V

∂V first, then ∂T

Example:

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T\right]_V$$

Can be used as a test to show $\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V$ is an exact differential.

Exercise For an ideal gas ($p = nRT/V$), verify:

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right)_V\right]_T = -\frac{nR}{V^2} = \left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T\right]_V$$

Proof (*a bit tricky*)

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial V}\right)_T\right]_V = \left[\frac{\partial}{\partial T}\left(\lim_{\Delta V \to 0}\frac{p(T,V+\Delta V)-p(T,V)}{\Delta V}\right)\right]_V$$

$$= \lim_{\Delta T \to 0}\left(\lim_{\Delta V \to 0}\frac{\dfrac{p(T+\Delta T,V+\Delta V)-p(T+\Delta T,V)}{\Delta V} - \dfrac{p(T,V+\Delta V)-p(T,V)}{\Delta V}}{\Delta T}\right)$$

$$= \lim_{\Delta V \to 0}\left(\lim_{\Delta T \to 0}\frac{\dfrac{p(T+\Delta T,V+\Delta V)-p(T,V+\Delta V)}{\Delta T} - \dfrac{p(T+\Delta T,V)-p(T,V)}{\Delta T}}{\Delta V}\right)$$

$$= \left[\frac{\partial}{\partial V}\left(\lim_{\Delta T \to 0}\frac{p(T+\Delta T,V)-p(T,V)}{\Delta T}\right)\right]_T$$

$$= \left[\frac{\partial}{\partial V}\left(\frac{\partial p}{\partial T}\right)_V\right]_T$$

Important Application: *p*-*V*-*T* Calculations

Useful and convenient (intensive) experimental quantities:

Volumetric Thermal Expansion Coefficient β

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

gives the **fractional** change in volume per Kelvin

β is usually (*but not always*) positive.

Isothermal Compressibility κ (also called κ_T)

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

gives the negative **fractional** change in volume per Pa

$(\partial V/\partial p)_T$ is *always negative*, so κ is always positive.

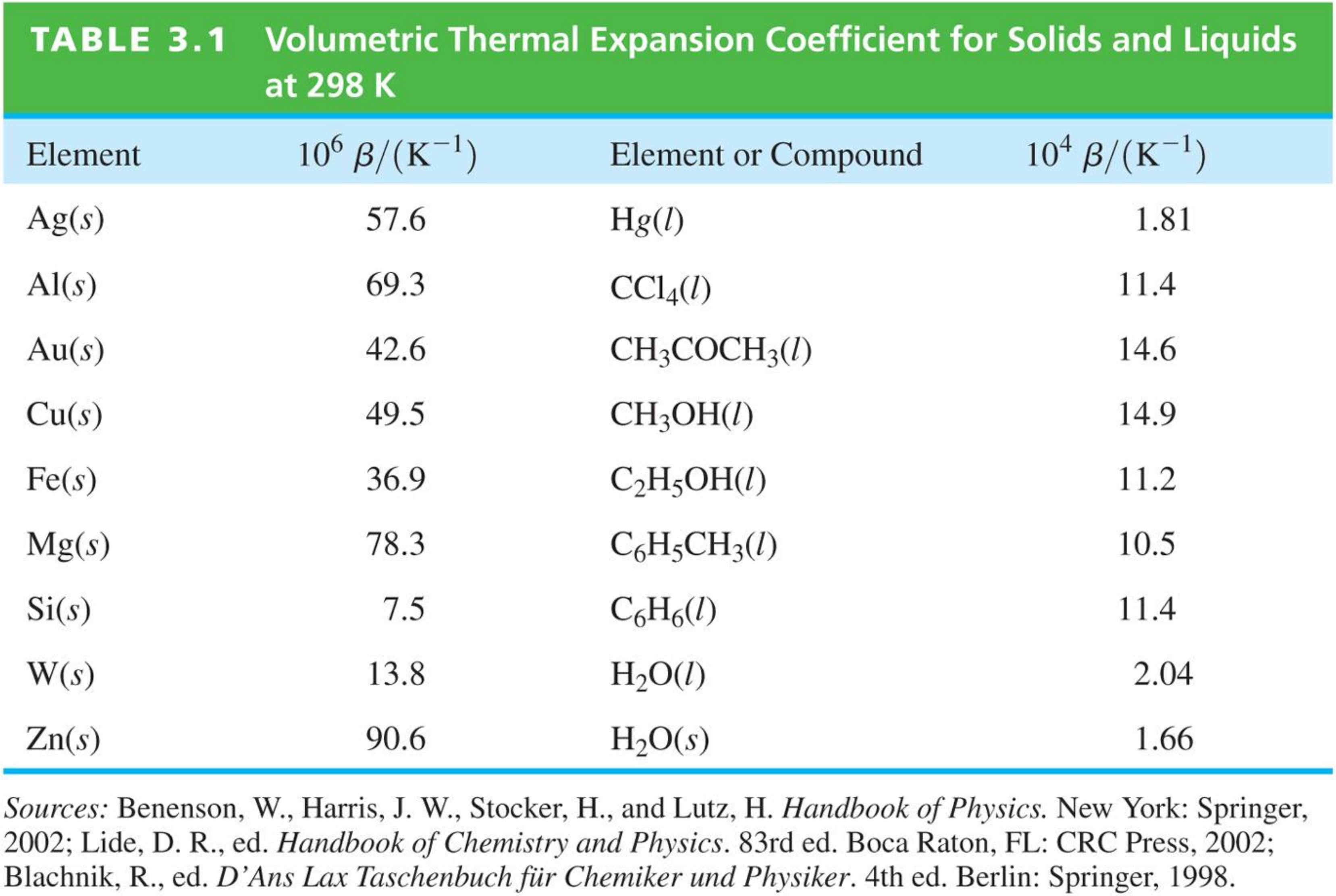


TABLE 3.1 Volumetric Thermal Expansion Coefficient for Solids and Liquids at 298 K

Element	$10^6\ \beta/(\mathrm{K}^{-1})$	Element or Compound	$10^4\ \beta/(\mathrm{K}^{-1})$
Ag(*s*)	57.6	Hg(*l*)	1.81
Al(*s*)	69.3	$CCl_4(l)$	11.4
Au(*s*)	42.6	$CH_3COCH_3(l)$	14.6
Cu(*s*)	49.5	$CH_3OH(l)$	14.9
Fe(*s*)	36.9	$C_2H_5OH(l)$	11.2
Mg(*s*)	78.3	$C_6H_5CH_3(l)$	10.5
Si(*s*)	7.5	$C_6H_6(l)$	11.4
W(*s*)	13.8	$H_2O(l)$	2.04
Zn(*s*)	90.6	$H_2O(s)$	1.66

Sources: Benenson, W., Harris, J. W., Stocker, H., and Lutz, H. *Handbook of Physics.* New York: Springer, 2002; Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press, 2002; Blachnik, R., ed. *D'Ans Lax Taschenbuch für Chemiker und Physiker*. 4th ed. Berlin: Springer, 1998.

Note: for H_2O(liquid) at 0 ^{o}C, $\boldsymbol{\beta} = \mathbf{-5.47 \times 10^{-5}\ K^{-1}}$ (shrinks when heated!)

Application of thermal expansion …

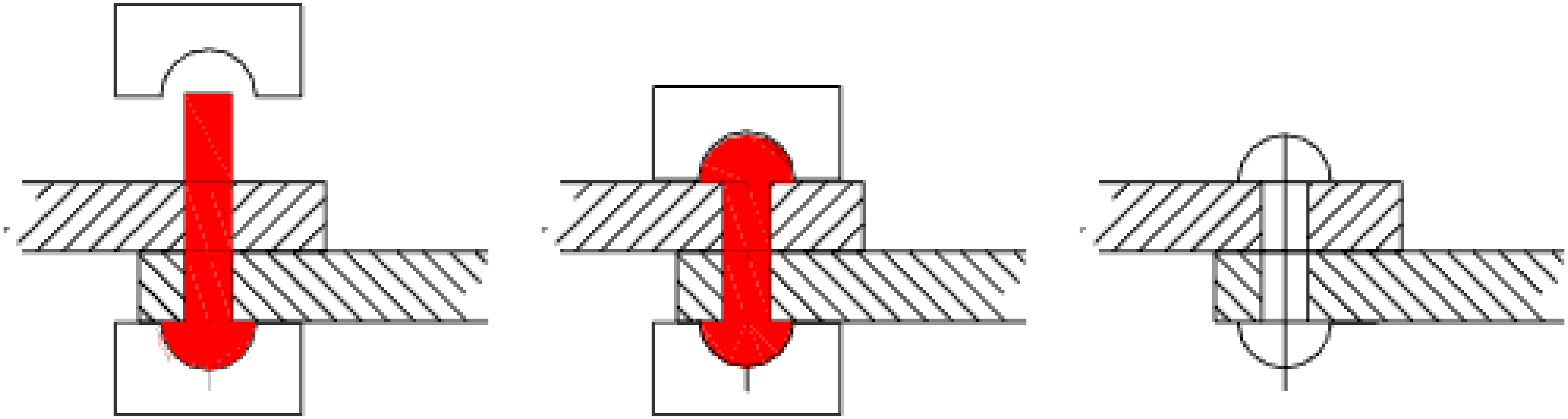
Liquid-in-Glass Thermometers

Liquid when heated expands more than the glass.

$$\beta_{\textbf{liquid}} > \beta_{\textbf{glass}}$$

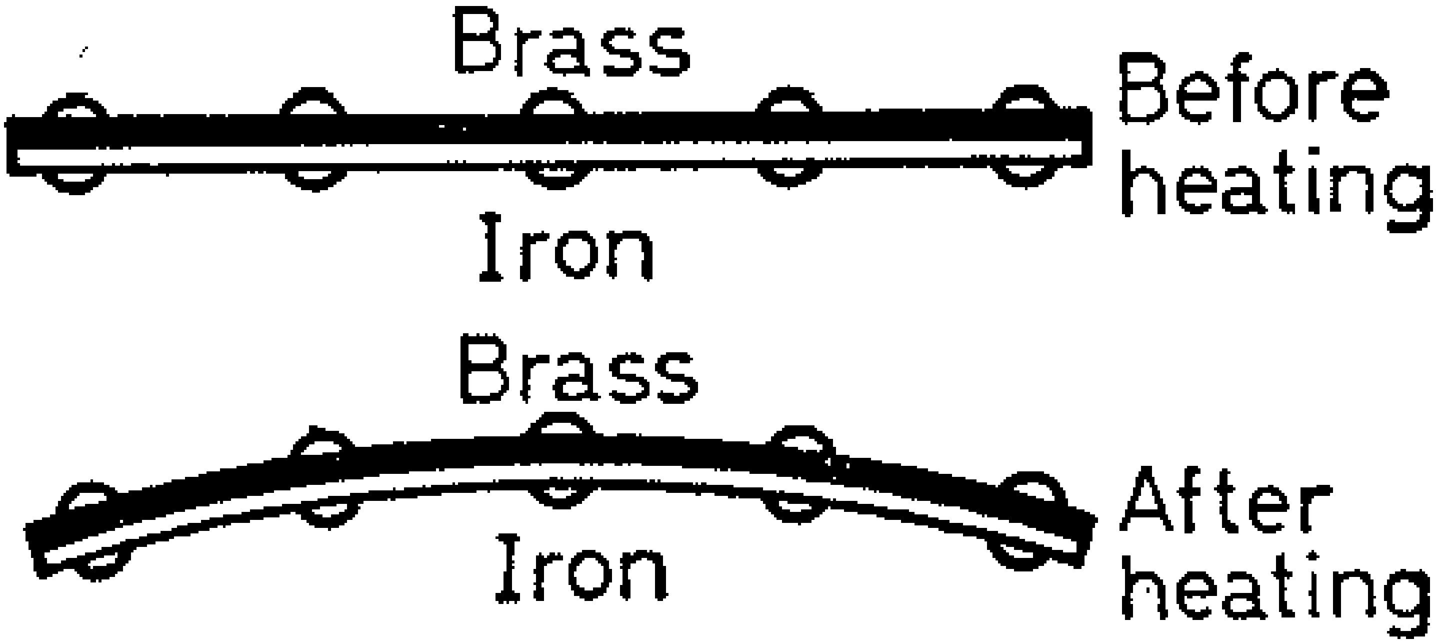
Related: ***Why can warm water sometimes be used to get a tight lid off a glass jar?***

Hot Rivet Fasteners



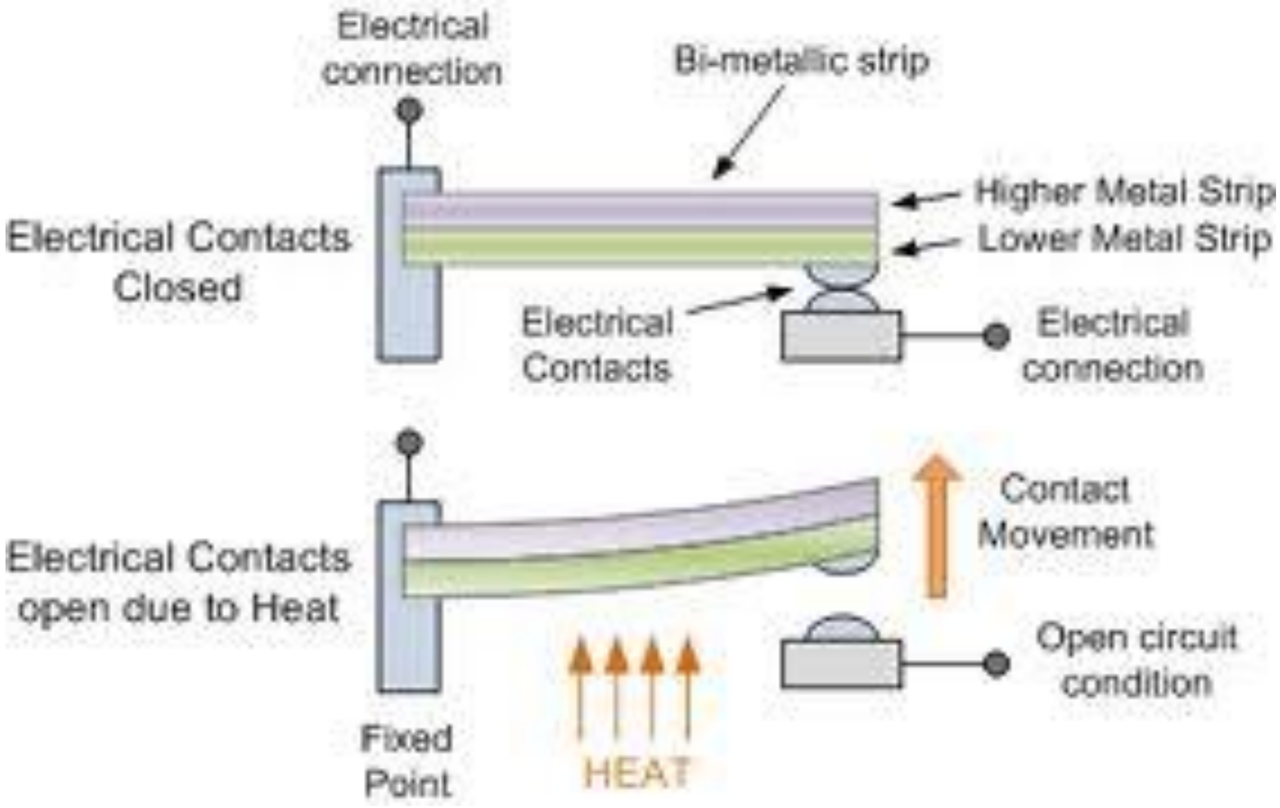
Hot rivet shrinks as it cools, tightly fastening two metal pieces.

Bimetallic Strip



$$\beta_{\text{Brass}} > \beta_{\text{Iron}}$$

Bimetallic Strip



thermostat switch to turn off the furnace

Volumetric Thermal Expansion Coefficient β

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

fractional change in volume per degree

Linear Thermal Expansion Coefficient β_{linear}

$$\beta_{\text{linear}} = \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_p = \frac{1}{3}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{\beta}{3}$$

Can you show this?

fractional change in length per degree

Example If the average temperature of the oceans increases by 1 °C, what is the increase in sea level?

Data: The average volumetric thermal expansion coefficient of seawater is β = 0.00011 K^{-1}. The average depth of the oceans is 3.7 km.

From $\beta_{\text{linear}} = \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_p$ get $\beta_{\text{linear}}\mathrm{d}T = \frac{\mathrm{d}\ell}{\ell} = \frac{\beta}{3}\mathrm{d}T$

$$\beta_{\text{linear}} \int_{T}^{T+\Delta T} \mathrm{d}T = \int_{\ell(T)}^{\ell(T+\Delta T)} \frac{\mathrm{d}\ell}{\ell} \qquad \beta_{\text{linear}}(\Delta T) = \ln\left(\frac{\ell(T+\Delta T)}{\ell(T)}\right)$$

$$\frac{\ell(T+\Delta T)}{\ell(T)} = \exp[\beta_{\text{linear}}(\Delta T)] = \exp\left[\frac{0.00011\,\mathrm{K}^{-1}}{3}\ 1\,\mathrm{K}\right] = 1.000037$$

$$\boxed{0.0037\ \%\ \text{of}\ 3.7\ \text{km} = 0.000037 \times 3.7\ \text{km} = 0.00014\ \text{km} = \mathbf{0.14\ m}}$$

What’s this? What does it have to do with thermal expansion?

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Concorde Supersonic (Mach 2.0) Passenger Aircraft

At cruising speed, twice the speed of sound, air friction heated the skin to about 150 ^{o}C, increasing the length of the aircraft by about one foot, an important design consideration for maintaining structural integrity.

TABLE 3.2 Isothermal Compressibility at 298 K

Substance	$10^6\ \kappa/\text{bar}^{-1}$	Substance	$10^6\ \kappa/\text{bar}^{-1}$
$Al(s)$	1.33	$Br_2(l)$	64
$SiO_2(s)$	2.57	$C_2H_5OH(l)$	110
$Ni(s)$	0.513	$C_6H_5OH(l)$	61
$TiO_2(s)$	0.56	$C_6H_6(l)$	94
$Na(s)$	13.4	$CCl_4(l)$	103
$Cu(s)$	0.702	$CH_3COCH_3(l)$	125
C(graphite)	0.156	$CH_3OH(l)$	120
$Mn(s)$	0.716	$CS_2(l)$	92.7
$Co(s)$	0.525	$H_2O(l)$	45.9
$Au(s)$	0.563	$Hg(l)$	3.91
$Pb(s)$	2.37	$SiCl_4(l)$	165
$Fe(s)$	0.56	$TiCl_4(l)$	89
$Ge(s)$	1.38		

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

How are β and κ measured?

One way: measure the density $\rho(T,p)$ of a gas, liquid, or solid
at different temperatures and pressures.

$\rho(T,p)$ = mass per unit volume at temperature T, pressure p

Then use:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p$$

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

- Can you derive the equations for β and κ in terms of the density?
- Are β and κ intensive or extensive quantities?

Exercise: **Evaluate the volumetric thermal expansion coefficient for an ideal gas ($V = nRT/p$) at 298 K**

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

$$= \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right)\right]_p$$

$$= \frac{1}{V}\left(\frac{nR}{p}\right)\left[\frac{\partial T}{\partial T}\right]_p$$

$$= \frac{nR}{pV} = \frac{nR}{nRT} = \frac{1}{T}$$

$$= \frac{1}{298\,\mathrm{K}} = 0.00335\ \mathrm{K}^{-1}$$

ideal gas

$$\boxed{\beta = \frac{1}{T}}$$

Exercise: **Evaluate the isothermal compressibility for an ideal gas (*V* = *nRT*/*p*) at *p* = 1.00 bar**

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

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

$$= -\frac{1}{V}(nRT)\left[\frac{\partial p^{-1}}{\partial p}\right]_T$$

$$= -\frac{nRT}{V}\left[\frac{-1}{p^2}\right] = \frac{nRT}{pV}\,\frac{1}{p} = \frac{1}{p}$$

$$= \frac{1}{1.00\ \text{bar}} = 1.00\ \text{bar}^{-1}$$

$$\boxed{\begin{array}{l}\text{ideal gas}\\ \kappa = \dfrac{1}{p}\end{array}}$$

Exercise: For a **nonideal gas** with second virial coefficient ***B*(*T*)** and the equation of state

$$Z = \frac{pV}{nRT} = 1 + \frac{nB(T)}{V}$$

show that the isothermal compressibility is

$$\boxed{\kappa = \frac{1}{p + \dfrac{n^2RTB(T)}{V^2}} = \frac{1}{p + \dfrac{RTB(T)}{V_\mathrm{m}^2}}}$$

Isothermal Compressibility of a Nonideal Gas with Second Virial Coefficient *B*(*T*)

$$\boxed{\kappa = \frac{1}{p + \dfrac{n^2 RTB(T)}{V^2}} = \frac{1}{p + \dfrac{RTB(T)}{V_\mathrm{m}^2}}}$$

Significance:

ideal gas with $B(T) = 0$ no molecular interactions

$$\boxed{\kappa = 1/p}$$

---

nonideal gas with $B(T) < 0$ attractive interactions dominate

$$\boxed{\kappa > 1/p}$$

gas is "more compressible"

---

nonideal gas with $B(T) > 0$ repulsive interactions dominate

gas is "less compressible"

$$\boxed{\kappa < 1/p}$$

Comparisons:

For an **ideal gas** at 298 K and 1.00 bar:

$\beta = 0.00335 \ \mathrm{K}^{-1}$ $\kappa = 1.00 \ \mathrm{bar}^{-1}$

For **liquid water** at 298 K and 1.00 bar:

$\beta = 0.000204 \ \mathrm{K}^{-1}$ $\kappa = 0.0000459 \ \mathrm{bar}^{-1}$

For **solid iron** at 298 K and 1.00 bar:

$\beta = 0.0000369 \ \mathrm{K}^{-1}$ $\kappa = 0.00000056 \ \mathrm{bar}^{-1}$

- **the volumes of solids and liquids are much less sensitive to temperature changes than gases**
- **solids and liquids are "almost" incompressible ($\kappa << 1 \ \mathrm{bar}^{-1}$)**

***Why*?**

Exercise: 2.00 L of ideal gas at 298 K (25 °C) and 1.00 bar is heated at constant pressure to 323 K (50 °C). Calculate the final volume.

Easy! The equation of state $pV = nRT$ is known. Use:

$$V_f / V_i = (nRT_f / p_f) / (nRT_i / p_i) = T_f / T_i = (323\text{ K} / 298\text{ K}) = 1.0839$$

$$V_f = 1.0839 \times 2.00\text{ L}$$

$$\boldsymbol{V_f = 2.17\text{ L}}$$

$$\%\text{ volume change} = \frac{V_f - V_i}{V_i}\,100\% = \frac{2.17\text{ L} - 2.00\text{ L}}{2.00\text{ L}}\,100\%$$

$$= 8.5\,\% \text{ volume increase}$$

Exercise: 2.00 L of **liquid** water at 298 K (25 °C) and 1.00 bar is heated at constant pressure to 323 K (50 °C). Calculate the final volume. **Data:** $\beta = 0.000204\ \text{K}^{-1}$ (assumed constant).

Note: The equation of state of liquid water is not provided.

Can't use $pV = nRT$ (liquid H_2O is not an ideal gas). Instead:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \boxed{\times\, \mathrm{d}T_p \quad \Rightarrow} \qquad \frac{\mathrm{d}V}{V} = \beta \mathrm{d}T$$

$$\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = \int_{T_i}^{T_f} \beta \mathrm{d}T$$

Integrate at constant pressure:

$$\ln\left(\frac{V_f}{V_i}\right) = \beta(T_f - T_i) = 0.000204\,\text{K}^{-1}(25\,\text{K}) = 0.0051$$

$$\frac{V_f}{V_i} = e^{0.0051} = 1.0051$$

$$V_f = 1.0051 \times V_i = 1.0051 \times 2.00\ \text{L}$$

$\boldsymbol{V_f = 2.01\ \text{L}}$ (only a 0.5 % increase)

Exercise: 2.00 L of ideal gas at 298 K (25 °C) and 1.00 bar is isothermally compressed to a final pressure of 5.00 bar. Calculate the final volume.

Easy! The equation of state $pV = nRT$ is known. Use:

$$V_f \,/\, V_i \;=\; (nRT_f \,/p_f) \,/\, (nRT_i \,/p_i) \;=\; p_i \,/\, p_f \;=\; (1.00\text{ bar} \,/\, 5.00\text{ bar}) = 0.200$$

$$V_f \;=\; 0.200V_i \;=\; 0.200 \times 2.00\text{ L}$$

$$\mathbf{V_f = 0.400\ L}$$

$$\%\,\text{volume change} \;=\; \frac{V_f - V_i}{V_i}\,100\% \;=\; \frac{0.400\text{ L} - 2.00\text{ L}}{2.00\text{ L}}\,100\%$$

$$= \;-80.0\;\%$$

Exercise: 2.00 L of **liquid** water at 298 K (25 °C) and 1.00 bar is isothermally compressed to a final pressure of 5.00 bar. Calculate the final volume. **Data:** $\kappa = 0.0000459\ \text{bar}^{-1}$ (assumed constant).

Note: The equation of state of liquid water is not provided.
Can't use $pV = nRT$ (liquid H_2O is not an ideal gas). Instead:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \boxed{\times\ \mathrm{d}p_T \quad \Rightarrow} \qquad \frac{\mathrm{d}V}{V} = -\kappa\,\mathrm{d}p$$

$$\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = -\int_{p_i}^{p_f} \kappa\,\mathrm{d}p$$

integrate at constant temperature:

$$\ln\left(\frac{V_f}{V_i}\right) = -\kappa(p_f - p_i) = -0.0000459\ \text{bar}^{-1}(4.00\ \text{bar}) = -0.000184$$

$$\frac{V_f}{V_i} = e^{-0.000184} = 0.99982$$

$V_f = 0.99982 \times V_i = 0.99982 \times 2.00$ L

V_f = 1.99963 L (–0.0184 % change)

⇒ ***volume almost independent of p***

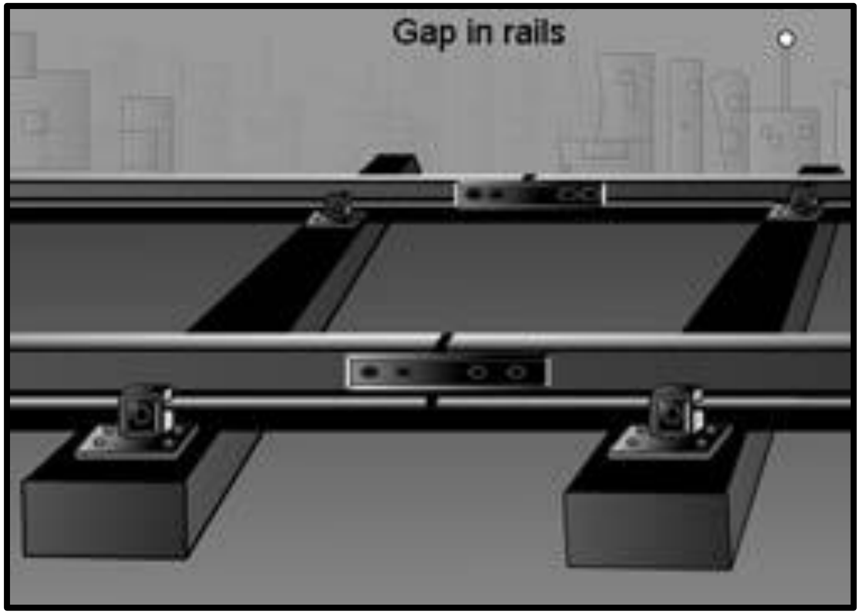
!!! Warning !!!

Heating a solid or a liquid at constant volume can produce dangerously large pressure increases.

- Railroads are constructed with small gaps between lengths of steel rails to allow for thermal expansion
- Bridges have small gaps between structural beams
- Liquid-in-glass thermometers break if heated beyond their temperature range
- ***Never*** ***fill a container to the brim with a liquid and seal it!***
- Useful application: **"shrink fits"** used by machinists

What does thermodynamics have to say about $\left(\frac{\partial p}{\partial T}\right)_V$ **?**

Thermal Expansion Gaps



No Thermal Expansion Gaps!

Change in Pressure with Temperature at Constant Volume

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

Cyclic Rule!

$$= \frac{\left(\frac{\partial V}{\partial T}\right)_p}{-\left(\frac{\partial V}{\partial p}\right)_T}$$

Inverse Rule!

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

Definition of $\beta,\ \kappa$

$$= \frac{\beta}{\kappa}$$

ratio of the volumetric thermal expansion coefficient to the isothermal compressibility

Changes in Pressure with Temperature at Constant Volume

For an **ideal gas** at 298 K and 1 bar:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{\frac{1}{T}}{\frac{1}{p}} = \frac{p}{T} = \frac{1.00\ \text{bar}}{298\ \text{K}} = 0.00335\ \text{bar K}^{-1}$$

(no problem)

For **solid iron** at 298 K and 1 bar:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{0.0000369\ \text{K}^{-1}}{0.00000056\ \text{bar}^{-1}} = 66\ \text{bar K}^{-1}$$

970 lb per square inch *per degree* !

Uh Oh!

Freezing liquid water in a confined space can split pipes, damage concrete, heave foundations, and crack porous rocks.

Why ?

Exercise: **Liquid water at 0 ^{o}C and 1.00 bar is frozen at constant volume. Calculate the final pressure.**

Data:

- Ice is less dense than liquid water. (*Ice floats!*) Freezing liquid water produces a 9 % increase in volume.
- isothermal compressibility of ice $\kappa = 51.0 \times 10^{-6}$ bar^{-1}

Solution: Freezing water at 1.00 bar increases the volume by 9 %. To maintain constant volume, the pressure on the ice must be increased to reduce the volume by 9 %.

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

multiply by d*p* at constant T

$$\kappa \, \mathrm{d}p = -\frac{dV}{V}$$

integrate from $p_i = 1.00$ bar to p_f

Exercise: **Liquid water at 0 ºC and 1.00 bar is frozen at constant volume. Calculate the <u>final pressure</u>.**

(*cont.*)

$$\int_{p_i}^{p_f} \kappa \, \mathrm{d}p = \kappa \int_{p_i}^{p_f} \mathrm{d}p = -\int_{V_i}^{V_f} \frac{dV}{V}$$

assume κ is constant
(no other information given)

$$\kappa(p_f - p_i) = -\ln\left(\frac{V_f}{V_i}\right)$$

$$p_f = p_i - \frac{1}{\kappa}\ln\left(\frac{V_f}{V_i}\right)$$

$$p_f = 1.00 \text{ bar} - \frac{1}{51.0 \times 10^{-6} \text{ bar}^{-1}} \ln\left(\frac{1}{1.09}\right)$$

$$p_f = 1.00 \text{ bar} + 1690 \text{ bar} \approx 1700 \text{ bar}$$

Conclusion: Freezing liquid water at constant volume generates a pressure of about **1700 bar**
(≈ 25,000 lb per square inch! Uh Oh!)

Sections 3.2 and 3.3 Dependence of the Internal Energy *U* on Temperature and Volume

- widely used for scientific and engineering calculations
- provides valuable information about molecular energy levels and molecular interactions

Because the internal energy of a system is a state function $U(T,V)$, the differential dU is exact. Mathematics provides:

$$\boxed{\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V}$$

A useful theoretical result. But for practical applications:

How are $(\partial U/\partial T)_V$ ***and*** $(\partial U/\partial V)_T$ ***calculated ?***

$$\boxed{(\partial U/\partial T)_V \quad ???}$$

from the First Law: $dU = dq + dw$

only p-V work possible: $dU = dq - p_{\text{external}}dV$

at constant volume: $dU_V = dq_V$

(dV = 0, no work)

heat capacity at constant volume

$$\boxed{C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V}$$

C_V is an experimental quantity, measured using calorimetry.

$\boxed{(\partial U/\partial V)_T \quad ???}$

from Chapters 1 and 2:

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

Plan A If the **equation of state of the system is known**, then $(\partial p/\partial T)_V$ and therefore $(\partial U/\partial V)_T$ are easily calculated.

Plan B If the **equation of state of the system is unknown**, then $(\partial p/\partial T)_V$ and $(\partial U/\partial V)_T$ can be calculated using measurable volumetric thermal expansion coefficients (β) and isothermal compressibilities (κ) (see Section 3.1) using

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\beta}{\kappa} - p$$

So What ???

Important result: Changes in the internal energy of any system can be calculated from measurable quantities.

“theoretical”

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

becomes “practical”

$$\boxed{dU = C_V dT + \left(T\frac{\beta}{\kappa} - p\right) dV}$$

in terms of the measurable quantities:

$$C_V = \frac{dq_V}{dT} \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

Exercise: For ideal gases, prove $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Hint: Recall that the volumetric expansion coefficient and isothermal compressibility of an ideal gas are $\boldsymbol{\alpha = 1/T}$ and $\boldsymbol{\kappa = 1/p}$

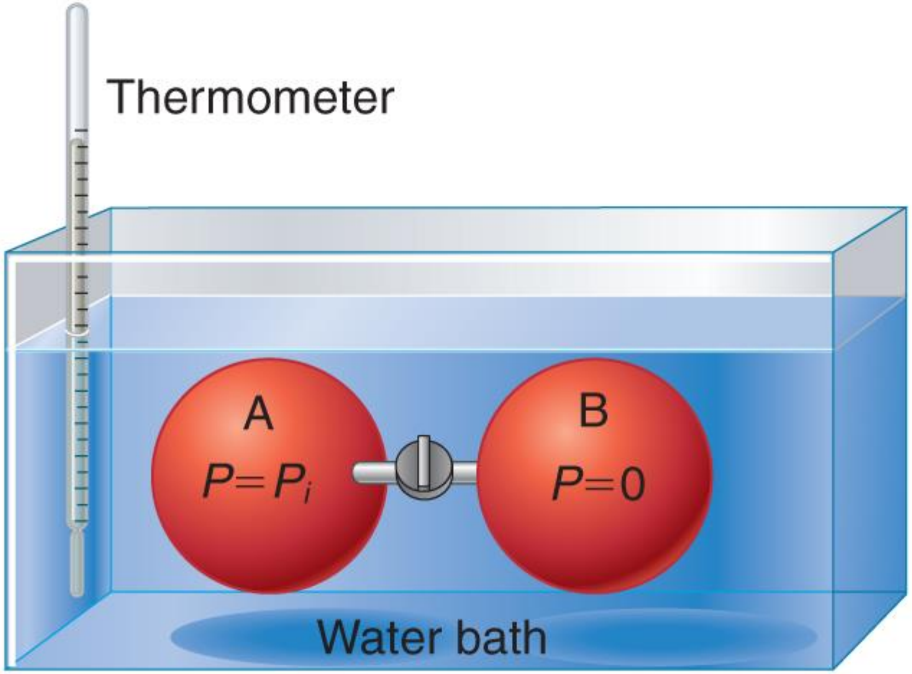
Exercise: Theory is fine, but can you suggest ***an experiment*** that could be used to show $(\partial U/\partial V)_T = 0$ for ideal gases?

One possibility:

Open a valve, allow gas at pressure p_i in flask A to expand into evacuated flask B.

If the gas is ideal, what is the change in temperature?

Why?



Sections 3.4 to 3.6 Dependence of the Enthalpy $H = U + pV$ on Temperature and Pressure

- recall from Chapter 2: $q_p = \Delta H$
- as a result, enthalpy changes are important for calorimetry, combustion reactions and other chemical reactions
- also important for flow processes (next Section)

T and *p* are therefore “natural” variables for the enthalpy.
***H* is a state function** $H(T,p)$, so the **differential d*H* is exact** and

$$\boxed{\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p}$$

Another useful theoretical result. But for practical applications

how are $(\partial H/\partial T)_p$ and $(\partial H/\partial p)_T$ calculated ?

$(\partial H/\partial T)_p$?

from the First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

only p-V work possible: $\mathrm{d}U = \mathrm{d}q - p_{\mathrm{external}}\mathrm{d}V$

at constant pressure: $\mathrm{d}U_p = \mathrm{d}q_p - p\mathrm{d}V$

$$\mathrm{d}q_p = \mathrm{d}U_p + p\mathrm{d}V = \mathrm{d}(U + pV)$$
$$= \mathrm{d}H$$

heat capacity at constant pressure

$$\boxed{C_p = \frac{\mathrm{d}q_p}{\mathrm{d}T} = \left(\frac{\partial H}{\partial T}\right)_p}$$

C_p is an experimental quantity measured using calorimeters operated at constant pressure

$\boxed{(\partial H/\partial p)_T \quad ?}$

$$
\begin{aligned}
\mathrm{d}H &= \mathrm{d}(U + pV) \\
&= \mathrm{d}U + \mathrm{d}(pV) \\
&= \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p \\
&= (\partial U/\partial T)_V\,\mathrm{d}T + (\partial U/\partial V)_T\,\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p \\
&= C_V\mathrm{d}T + [T\underbrace{(\partial p/\partial T)_V}_{\boxed{\beta/\kappa}} \cancel{-p}]\mathrm{d}V + \cancel{p}\mathrm{d}V + V\mathrm{d}p
\end{aligned}
$$

$$\mathrm{d}H_T = T(\beta/\kappa)\mathrm{d}V_T + V\mathrm{d}p_T$$

(dT = 0 at constant T, divide by dp_T)

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{T\beta}{\kappa}\left(\frac{\partial V}{\partial p}\right)_T + V = \frac{T\beta}{\kappa}(-\kappa V) + V$$

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \beta T)}$$

V, β, and T are all measurable quantities

So What ???

Important result: Changes in the enthalpy of any system can be calculated from measurable quantities.

“theoretical”

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

becomes “practical”

$$\boxed{\mathrm{d}H = C_p\mathrm{d}T + V(1-\beta T)\mathrm{d}p}$$

in terms of the measurable quantities:

$$C_p = \frac{\mathrm{d}q_p}{\mathrm{d}T} \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Exercise: **For ideal gases, show**

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

As a result, the enthalpy of an ideal gas depends only on temperature and

$\mathrm{d}H = C_p \mathrm{d}T$ (even if p is changing!)

Exercise: **For liquids and solids, show**

$$\left(\frac{\partial H}{\partial p}\right)_T \approx V$$

As a result

$\mathrm{d}H \approx C_p \mathrm{d}T + V\mathrm{d}p$ (liquids and solids)

Example Problem 3.9

Calculate the change in enthalpy when 124 g of liquid methanol at 1.00 bar and 298 K is heated and compressed to 2.50 bar and 425 K .

Data:	methanol molar mass	$M = 32.04 \text{ g mol}^{-1}$
	density of liquid methanol	$\rho = 0.791 \text{ g cm}^{-3}$
	heat capacity of liquid methanol	$C_{pm} = 81.1 \text{ J K}^{-1} \text{ mol}^{-1}$

Solution:

Enthalpy is a state function, so ΔH can be calculated for any path between the initial and final states. We will heat first, then compress:

$$\mathrm{CH_3OH(298\ K,\ 1\ bar)} \xrightarrow[\text{Step 1}]{\text{heat}} \mathrm{CH_3OH(425\ K,\ 1\ bar)} \xrightarrow[\text{Step 2}]{\text{compress}} \mathrm{CH_3OH(425\ K,\ 2.50\ bar)}$$

Example Problem 3.9 *(cont.)*

Step 1 **Heat** 124 g of liquid methanol from 289 K to 425 K at 1 bar.

$$\boxed{\Delta H_p = \int_{T_i}^{T_f} C_p \mathrm{d}T = nC_{pm}\int_{T_i}^{T_f} \mathrm{d}T = nC_{pm}(T_f - T_i)}$$

$$\Delta H_p = \frac{124\ \mathrm{g}}{32.04\ \mathrm{g\ mol^{-1}}}\,(81.1\ \mathrm{J\ K^{-1}\ mol^{-1}})\,(425\ \mathrm{K} - 298\ \mathrm{K}) = 39{,}900\ \mathrm{J}$$

Step 2 **Compress** 124 g of liquid methanol from 1.00 bar to 2.50 bar at a constant temperature of 425 K.

$$\boxed{\Delta H_T = \int_{p_i}^{p_f} \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \approx \int_{T_i}^{T_f} V \mathrm{d}p \approx V\int_{T_i}^{T_f} \mathrm{d}p = V(p_f - p_i)}$$

$$\Delta H_T = (124\ \mathrm{g} / 0.791\ \mathrm{g\ cm^{-3}})(10^{-6}\ \mathrm{m^3\ cm^{-3}})(2.50 - 1.00\ \mathrm{bar})(10^5\ \mathrm{Pa\ bar^{-1}}) = 39.9\ \mathrm{J}$$

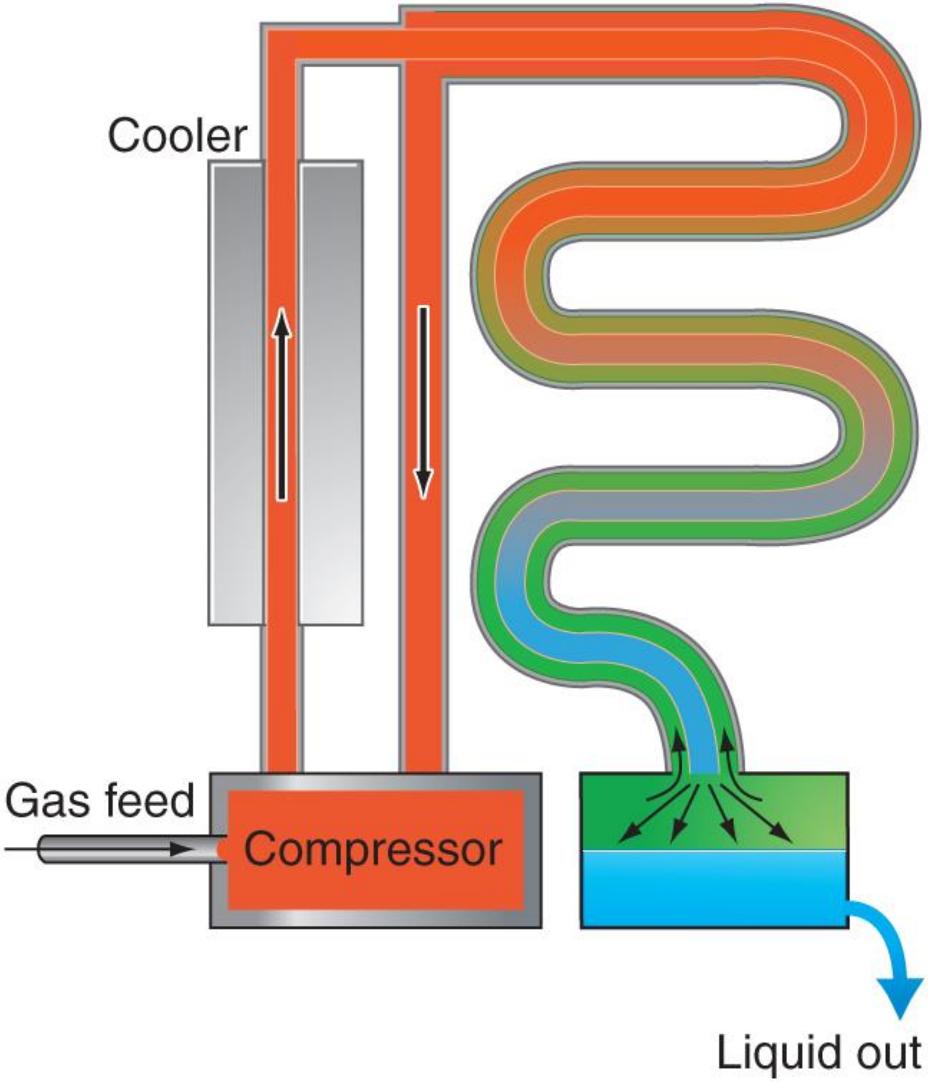
Overall $\Delta H = \Delta H_p$ **(step 1)** $+\ \Delta H_T$ **(step 2)**
$= 39{,}900\ \mathrm{J} + 40\ \mathrm{J}$
$\approx 39{,}900\ \mathrm{J}$ from **step 1**

For solids and liquids, changes in pressure usually cause small enthalpy changes

Section 3.7 The Joule-Thomson (JT) Experiment

- irreversible expansion of gas through a porous barrier or throttle valve under adiabatic conditions (no heat flow)
- ideal gases: no temperature change
- real gases: can **cool down** or **warm up** during JT expansion
- important applications
    - refrigeration
    - air conditioning
    - heat pumps
    - gas liquefaction

Gas Liquefaction



For **<u>industrial</u> applications**:

(*not university lab experiments*!)

- **continuous flow** (more economical than batch processing)
- **re-cycle** gas that does not liquefy (no wastage)
- **heat-exchange** – use cool gas that does not liquefy to pre-cool gas from compressor
- **large-scale production** (thousands of tons per day)
- use the expanding gas to **run a generator** (adiabatic cooling)

Applications of Liquefied Gases

- **liquid air** is distilled to produce liquid N_2 and liquid O_2
- N_2 is used to make **ammonia** for the production of nitric acid, fertilizers, explosives, and many other industrial chemicals
- cold liquefied natural gas (**LNG**) can be shipped economically over large distances in **cheap low-pressure tanks** (at $\approx$ 1 atm)
- liquid N_2 and liquid He are important **cryogens** (liquid He is used to operate superconducting nmr magnets)
- **liquid propane** allows barbecuing without charcoal
- many other important uses

Refrigeration and Air Conditioning

- expanding nonideal gases cool and absorb heat
- keeps perishable food products fresh, nutritious and safe to eat
- air conditioners provide cooling and humidity reduction, making large regions “habitable” for “modern” people

Ever tried working (or living) at 30 ^{o}C and 95 % humidity?

LNG Ship Carrying Liquefied Natural Gas (at about –260 ^{o}C)

Application of Liquefied Gases:
Space Exploration

store liquid fuel and oxidizer in **light** thin-wall **low pressure** tanks

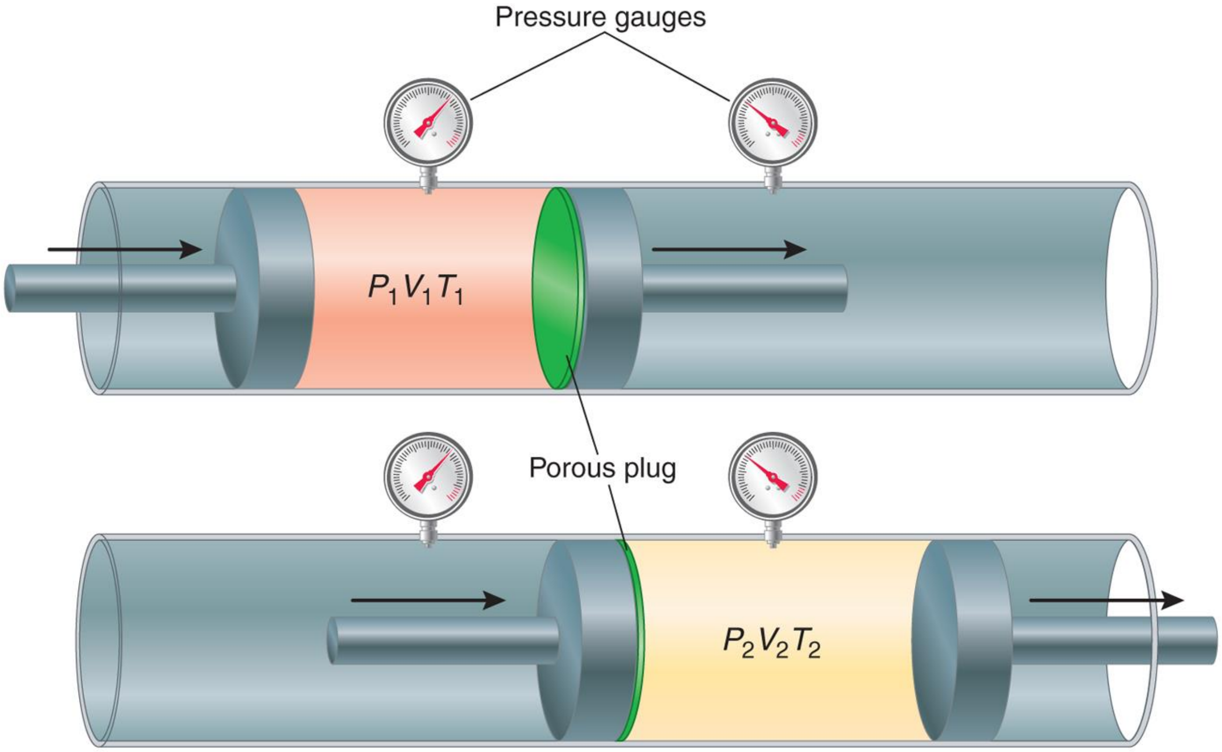
Saturn V Heavy-Lift Vehicle

("Apollo Moon Rocket")

- most powerful rocket ever built
- operational 1967 to 1973
- 7.6 million pounds thrust
- launched 130-ton payloads into earth orbit
- never failed, even when hit by lighting (Apollo 12 mission)
- kerosene / **liquid oxygen** first stage
- **liquid hydrogen** / **liquid oxygen** second and third stages
- mileage: about five inches per gallon

Joule Thomson (JT) Flow Experiment – *How does it work?*

- gas initially at p_1, V_1, T_1
- expands **adiabatically** through a porous plug or throttle valve
- gas downstream leaves at p_2, V_2, T_2



work p_1V_1 done
on the gas to force
it through the plug

work p_2V_2 done
on the surroundings
by the expanding gas

Thermodynamic Analysis of Joule-Thomson (JT) Expansions

$$p_1, V_1, T_1 \quad \rightarrow \quad p_2, V_2, T_2$$

First Law: $\Delta U = \cancelto{0}{q} + w$

$$U_2 - U_1 = p_1V_1 - p_2V_2$$

$$U_2 + p_2V_2 = U_1 + p_1V_1$$

$$H_2 = H_1$$

$$\Delta H = 0$$

Conclusion: Joule-Thomson expansions are “**isenthalpic**”
(occur at constant enthalpy)

Joule-Thomson Coefficient of Performance

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H$$

μ_{JT} gives the change in temperature per unit change in pressure of the expanding gas. But what is μ_{JT} ?

Using the **cyclic and inverse rules** of partial derivatives:

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T = -\overset{\boldsymbol{V(1-\beta T)}}{\left(\frac{\partial H}{\partial p}\right)_T} \Big/ \overset{\boldsymbol{Cp}}{\left(\frac{\partial H}{\partial T}\right)_p}$$

$$\boxed{\mu_{\mathrm{JT}} = -\frac{V(1-\beta T)}{C_p}}$$

Gives temperature change of the expanding gas in terms of **measurable quantities**.

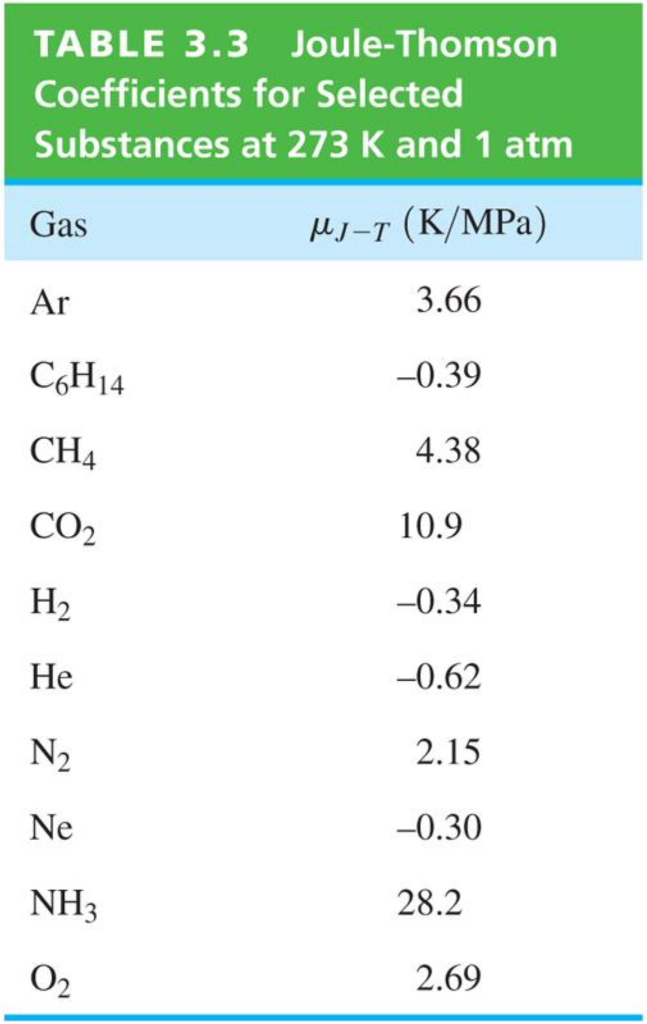


TABLE 3.3 Joule-Thomson Coefficients for Selected Substances at 273 K and 1 atm

Gas	μ_{J-T} (K/MPa)
Ar	3.66
C_6H_{14}	–0.39
CH_4	4.38
CO_2	10.9
H_2	–0.34
He	–0.62
N_2	2.15
Ne	–0.30
NH_3	28.2
O_2	2.69

$$\boxed{\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H}$$

$\mu_{\mathrm{JT}} > 0$: **expanding gas cools down**

$$\Delta T < 0 \quad \text{if} \quad \Delta p < 0$$

$\mu_{\mathrm{JT}} < 0$: **expanding gas warms up**

$$\Delta T > 0 \quad \text{if} \quad \Delta p < 0$$

Which of the listed substances would make the best refrigerant? *Why*?

Exercise: **Evaluate the Joule-Thomson coefficient μ_{JT} for an ideal gases.**

$$\mu_{\mathrm{JT}} = -\frac{V(1-\beta T)}{C_p}$$

For an ideal gas ($pV = nRT$), recall $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}$

which gives $\mu_{\mathrm{JT}} = -\frac{V(1-\frac{1}{T}T)}{C_p} = 0$ **(ideal gas)**

Conclusion: Warming or cooling during Joule-Thomson expansions occurs **<u>only for nonideal gases</u>** (molecular interactions).

Why Does Warming or Cooling Occur During JT Expansions?

For a nonideal gas obeying the van der Waals equation with attractive *a* and repulsive *b* coefficients

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

the Joule-Thomson coefficient is

$$\mu_{JT} = \frac{1}{C_{pm}}\left(\frac{2a}{RT} - b\right)$$

Joule-Thomson Coefficient of a Nonideal van der Waals Gas

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_{pm}}\left(\frac{2a}{RT} - b\right)}$$

Low Temperatures: $(2a/RT) - b > 0$ $\mu_{\mathrm{JT}} > 0$

Cooling on Expansion. Attractive forces dominate.
"Sticky" molecules fly apart more slowly, with less kinetic energy.

High Temperatures: $(2a/RT) - b < 0$ $\mu_{\mathrm{JT}} < 0$

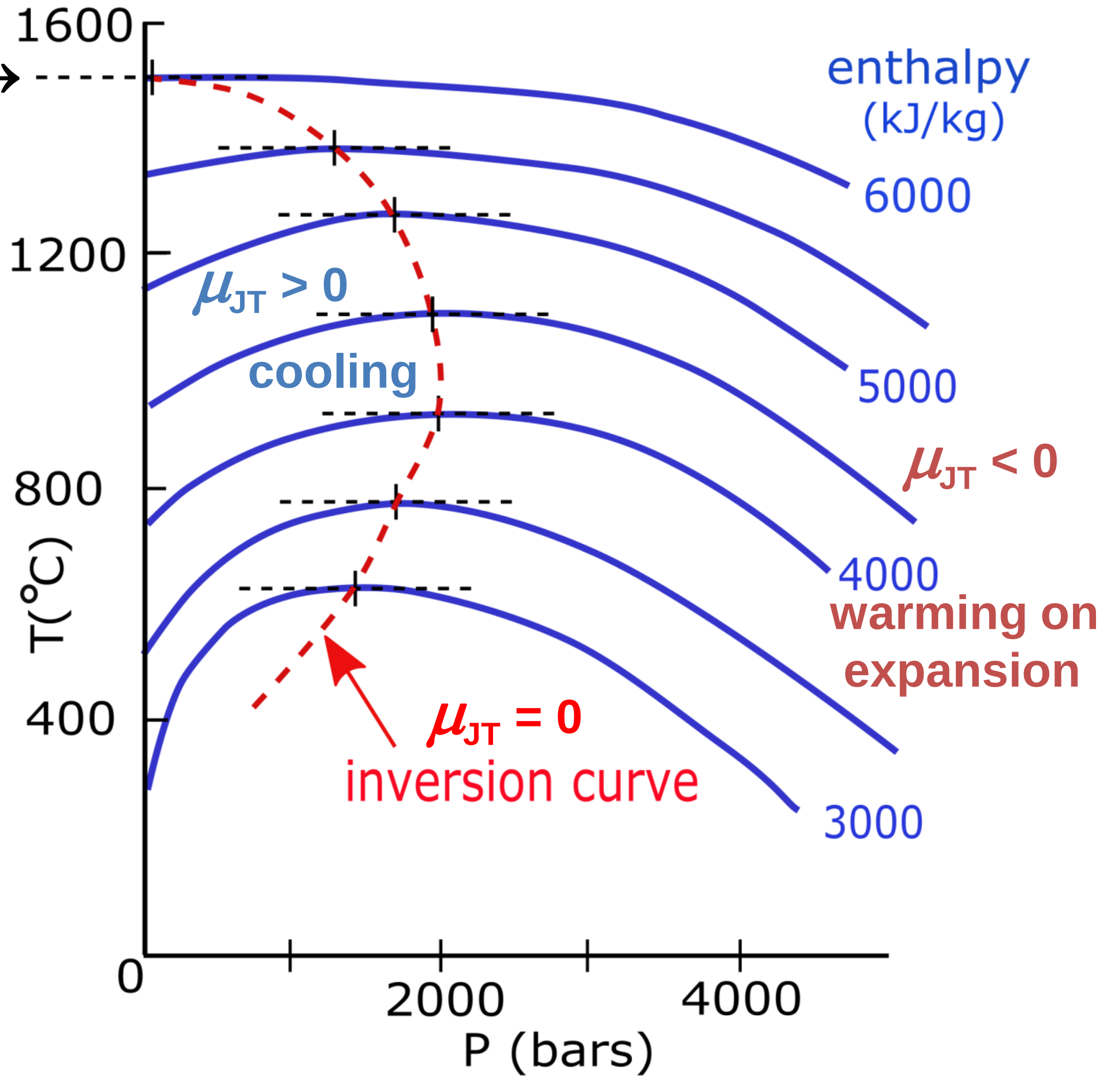
Warming on Expansion. Repulsive forces dominate.
Repelling molecules fly apart more quickly, with more kinetic energy.

Max. Inversion temperature: $(2a/RT) - b = 0$ $\mu_{\mathrm{JT}} = 0$

No temperature change. Attractive and repulsive forces balanced at the Boyle (not Boil!) temperature $T_{\mathrm{Boyle}} = 2a/Rb$.

Isenthalps: States of Constant Enthalpy

Boyle temperature →
(max. inversion temp.)



Graphical interpretation of the Joule-Thomson coefficient:

isenthalp slope:

$$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{\mathrm{JT}}$$

(JT coefficient)

Joule-Thomson Inversion Temperatures for N_2 and H_2

Use liquid N_2 to cool liquid H_2 below its inversion temperature.

Then use liquid H_2 to cool and liquefy He.

Liquid helium is the ultimate cryogen.

Used for super-conducting magnets and low-temperature research **($T < 4$ K)**.