Chapter 1. Basic Concepts of Thermodynamics

Section 1.1 What is "thermodynamics"?

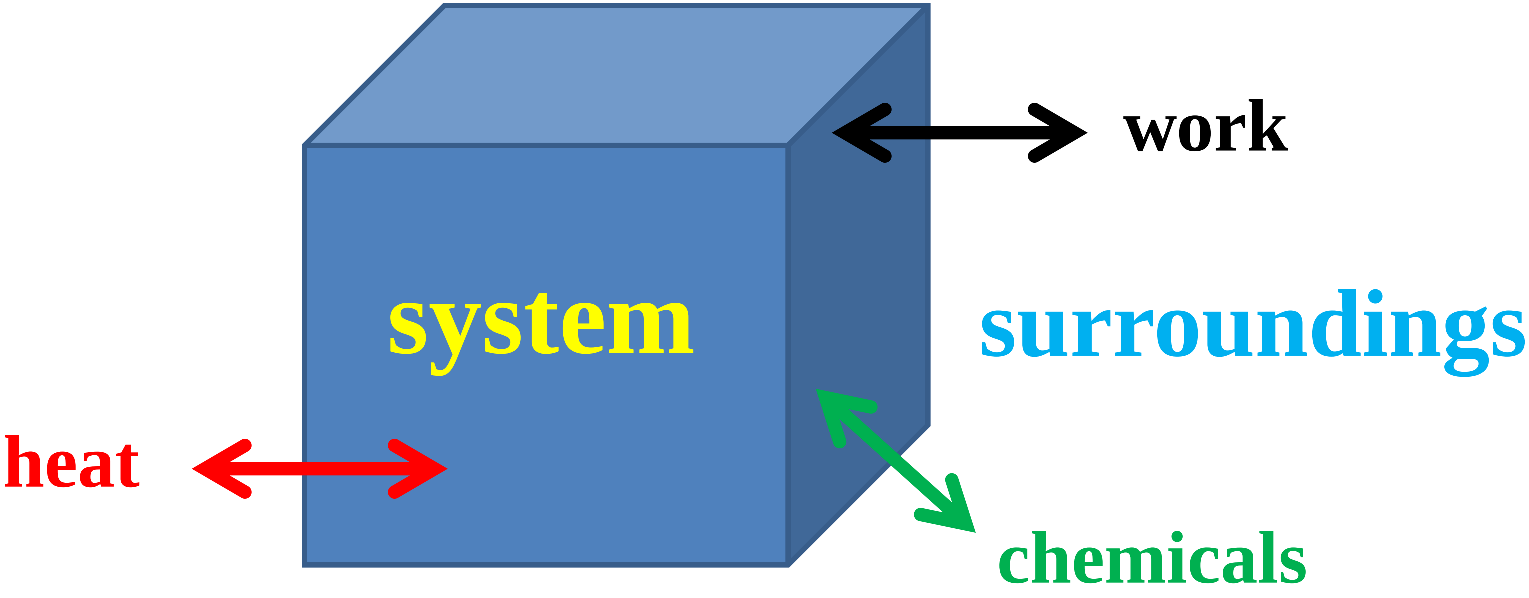
- a fundamental branch of physical science
- describes the behavior of matter on a **macroscopic scale** in terms of pressure, temperature, volume, and other **measurable variables**
- used to analyze transformations between heat, work, and different kinds of energy
- **applies to *any* system** (gas, liquid, solid, pure substances, mixtures, …)
- **does not require microscopic information** (*e.g.*, molecular or atomic structure, quantum mechanical wave functions, *etc*.)
- exact, no approximations, and no hand waving

Sections 1.2 and 1.3 Macroscopic Variables and Thermodynamic Definitions

mass	m	kg
temperature	T	K ($T/\mathrm{K} = t/^{\mathrm{o}}\mathrm{C} + 273.15$)
pressure	p	Pa (1 atm = 101325 Pa)
volume	V	m^3
density	ρ	$\mathrm{kg\ m}^{-3}$

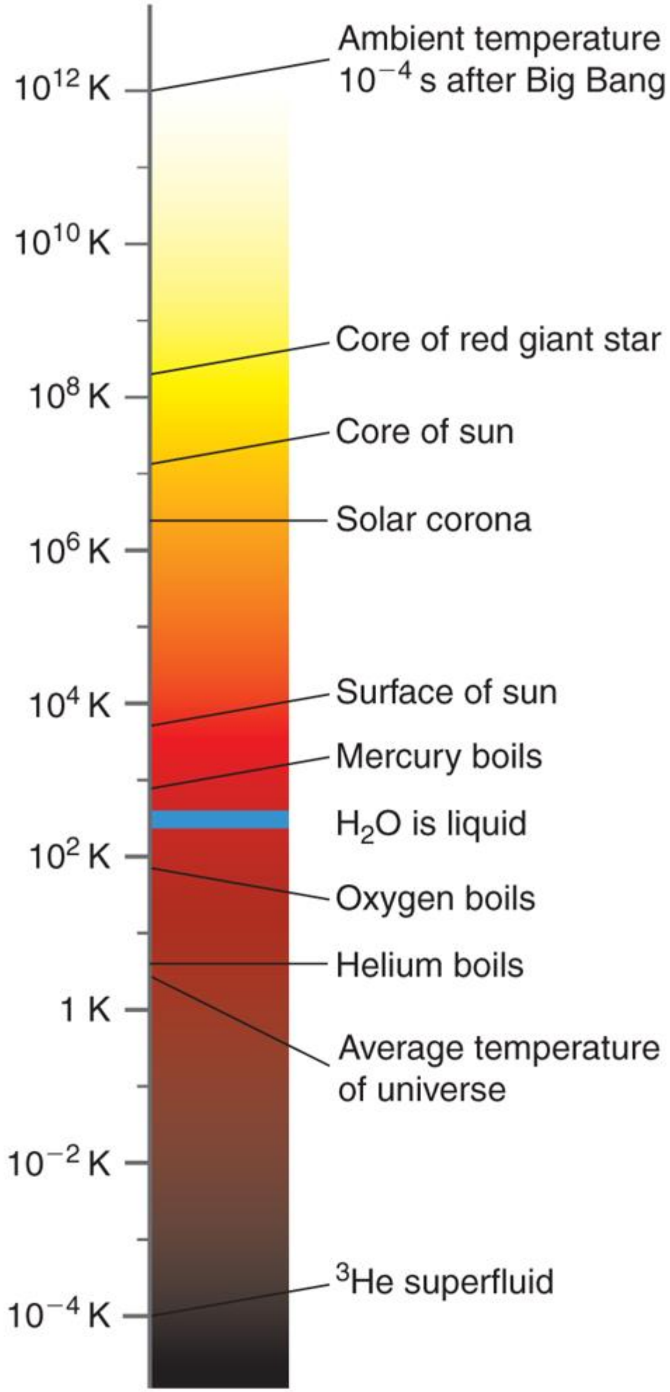
Thermodynamic Systems

System	material on which attention is focused for calculations and carrying out processes
Surroundings	the rest of the universe



Thermodynamic Systems

Closed System	no exchange of matter with the surroundings
Open System	exchanges matter with the surroundings
Isolated System	no exchange of matter or energy with the surroundings
Homogenous System	uniform chemical composition and uniform intensive properties (*e.g.*, aqueous NaCl solution at 300 K, 1 bar)
Heterogenous System	variable chemical composition and variable intensive properties (*e.g.*, solid NaCl + aqueous NaCl solution at 300 K, 1 bar)
Adiabatic System	no exchange of heat with the surroundings
Diathermal System	can exchange heat with the surroundings



Thermodynamic ("Absolute") Temperature

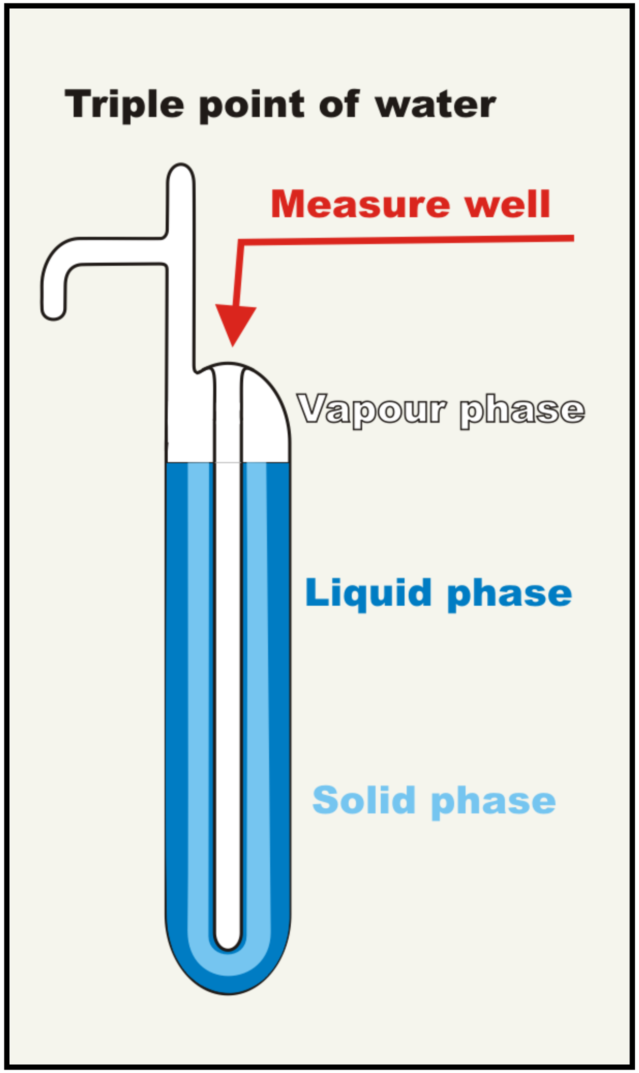
$$\boxed{T/\mathrm{K} \equiv t/{}^{\mathrm{o}}\mathrm{C} + 273.15}$$

Ideal Gas Thermometer

$$pV = nRT$$

$$T = \lim_{p \to 0} (pV)/(nR)$$

Thermodynamic Temperature



At the **triple point** of pure water:

$$\begin{tikzcd} & H_2O\text{ (vapour)} \arrow[dl, leftrightarrow] \arrow[dr, leftrightarrow] & \\ H_2O\text{ (solid)} \arrow[rr, leftrightarrow] & & H_2O\text{ (liquid)} \end{tikzcd}$$

Solid water (ice), liquid water, and water vapor are in equilibrium.

$$\boxed{\boldsymbol{T_{\mathrm{tp}}} \equiv \mathbf{273.16\ K}\quad (= 0.01\ {}^{\mathrm{o}}\mathrm{C})}$$

(exact)

Extensive System Properties

Proportional to the size and to the amount of material in a system.

Examples:

mass	m
number of moles	n
volume	V
energy	U
enthalpy	H
entropy	S
heat capacity	C

derivatives such as $(\partial V/\partial T)_p$, $(\partial V/\partial p)_T$

Intensive System Properties

Depend on the nature of a system (its composition and state), but not on the size of a system (can be therefore be more convenient than some extensive properties). **Examples:**

temperature	T	
pressure	p	
density	$\rho = m/V$	(mass per unit volume)
molar volume	$V_\mathrm{m} = V/n$	(for pure substances)
molar energy	$U_\mathrm{m} = U/n$	“
molar enthalpy	$H_\mathrm{m} = H/n$	“
molar entropy	$S_\mathrm{m} = S/n$	“
molar heat capacity	$C_\mathrm{m} = C/n$	“
mole fraction	$x_i = n_i/(n_1 + n_2 + n_3 + \ldots)$	(for mixtures)
thermal expansivity	$\alpha = V^{-1}(\partial V/\partial T)_p$	(isobaric)
compressibility	$\kappa = -V^{-1}(\partial V/\partial p)_T$	(isothermal)

Section 1.4 Equations of State

Equations relating the thermodynamic variables describing macroscopic systems. (Example: $pV = nRT$ for an ideal gas)

Why important?

- essential for understanding the bulk properties of matter
- equations of state are the macroscopic analogs of quantum mechanical wave functions for single atoms and molecules
- used to calculate thermodynamic properties and to design and operate industrial processes, engines, turbines, refrigerators, …
- molecular models are used to develop equations of state
- inverting this procedure, equations of state are used to provide valuable information about molecular behavior and interactions

Thermodynamic Equation of State

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

- ***Where from?*** Will be derived later using the First and Second Laws of thermodynamics.
- Describes how the energy (*U*) of a system changes as the system expands or contracts at constant temperature.
- $(\partial U/\partial V)_T$ is positive for molecules that attract each other, negative for molecules repelling each other.
- ***Useful in practice.*** The right side of the equation contains easily-measured temperatures, pressures, and volumes. Applies to any system.
- ***Exercise:*** Show $(\partial U/\partial V)_T = 0$ for an ideal gas (non-interacting molecules, no attractive or repulsive forces).

Section 1.5 Ideal Gases

- no interactions between the molecules
- molecules are assumed to be point masses (zero molecular volume)

$$pV = nRT \qquad pV_{\mathrm{m}} = RT \qquad pV = Nk_{\mathrm{B}}T$$

p = pressure

V = volume

$V_{\mathrm{m}} = V/n$ = molar volume

n = number of **moles** of gas

$N = N_{\mathrm{A}}n$ = number of gas **molecules**

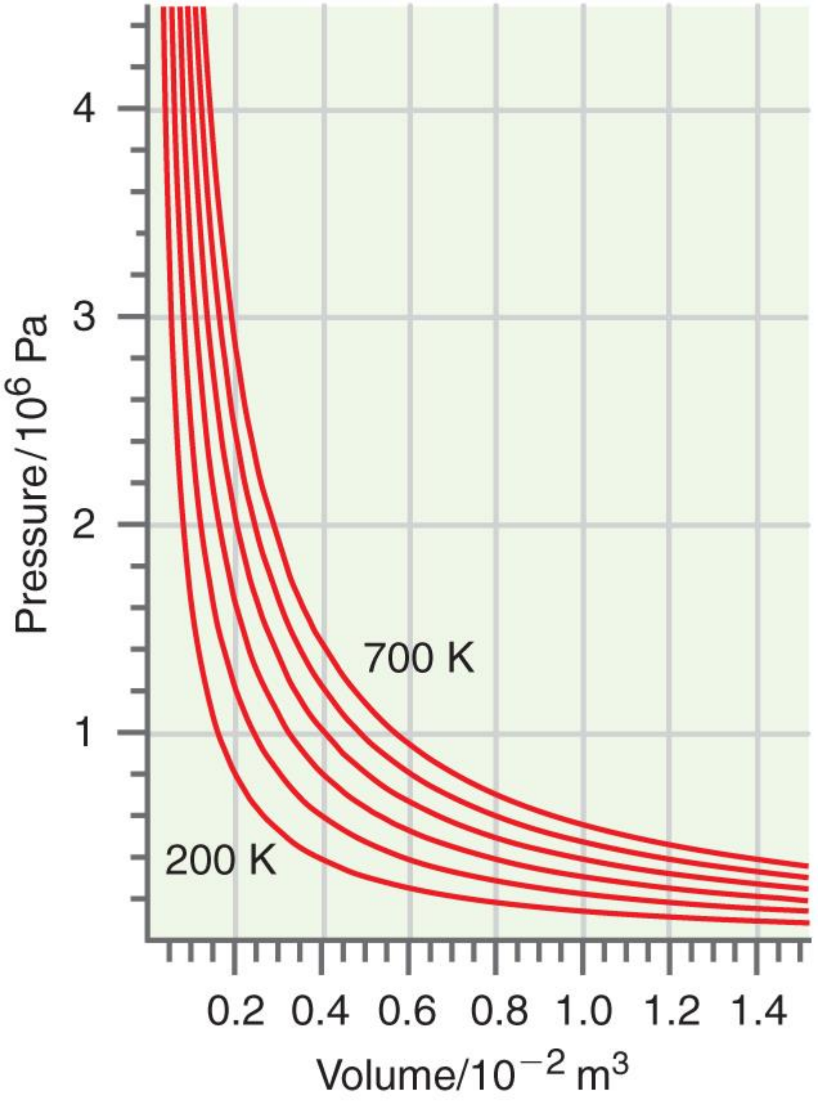
N_{A} = Avogadro number (6.02214×10^{23} mol^{-1})

T = thermodynamic temperature

R = gas constant (8.31451 J K^{-1} mol)

$k_{\mathrm{B}} = R/N_{\mathrm{A}}$ = Boltzmann constant (1.38066×10^{-23} J K^{-1})

Ideal Gas Isotherms



at a fixed temperature:

pV = constant

(hyperbola in p, V)

- Why is He more likely than NH_3 to behave ideally?
- Why are all gases ideal in the limit $p \to 0$?
- The fluid at the center of the sun is under enormous pressure ($p \approx 2.5 \times 10^9$ atm, $T \approx 15 \times 10^6$ K) but behaves almost like an ideal gas. *Why*?

Ideal Gas Mixtures

total moles of gas $n = n_1 + n_2 + n_3 + \cdots$

total gas pressure $p = p_1 + p_2 + p_3 + \cdots$

$$= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \cdots$$

notice:

$$\frac{p_i}{p} = \frac{\dfrac{n_i RT}{V}}{\sum_j \dfrac{n_j RT}{V}} = \frac{n_i}{\sum_j n_j} = \frac{n_i}{n} = x_i \quad \text{(mole fraction of gas } i\text{)}$$

$$\boxed{\text{partial pressure of gas } i \qquad p_i = x_i p}$$

Section 1.5 Real Gases (Brief Introduction – more in Chapter 7)

The equation $pV = nRT$ is a useful approximation for the for the equation of state of gases. *But* …

- real gases liquefy (attractive intermolecular forces)
- real gas molecules occupy volume (not point masses) and resist compression at high densities (repulsive intermolecular forces)

Challenges**:** **• understand the causes of nonideal gas behavior**

• develop accurate equations of state for real gases

Compression Factor *Z*

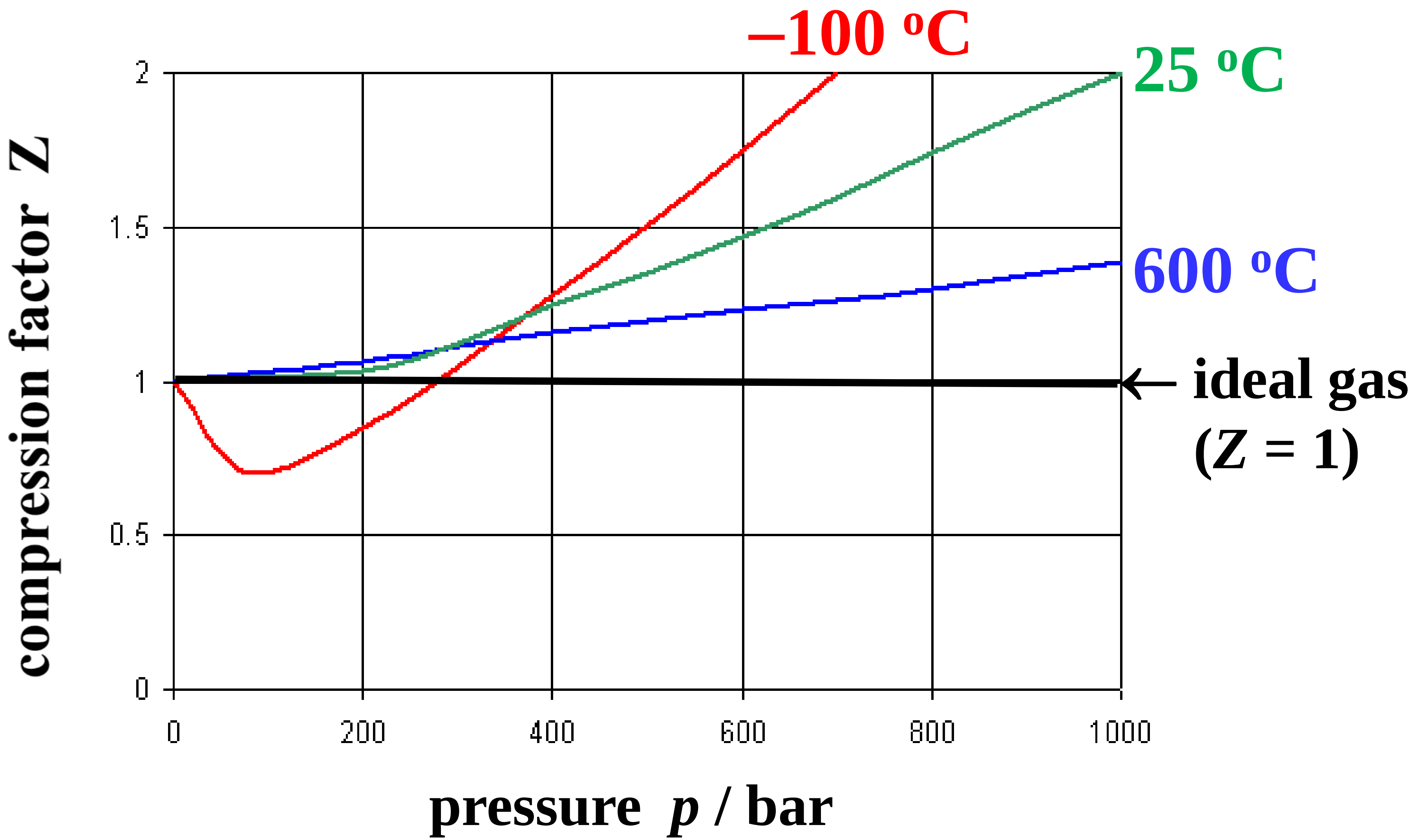
$$\boxed{Z = \frac{pV}{nRT} = \frac{pV_\mathrm{m}}{RT}}$$

- ***Z*** is dimensionless (no units)
- convenient interpretation:

$$Z = \frac{p}{\frac{nRT}{V}} = \frac{p}{p_\mathrm{ideal}}$$

- $Z = 1$ for **ideal gases** (at all temperatures and pressures)
- $Z < 1$ pressure lower than expected relative to an ideal gas (attractive forces dominate, $p < p_\mathrm{ideal}$)
- $Z > 1$ pressure higher than expected relative to an ideal gas (repulsive forces dominate, $p > p_\mathrm{ideal}$)

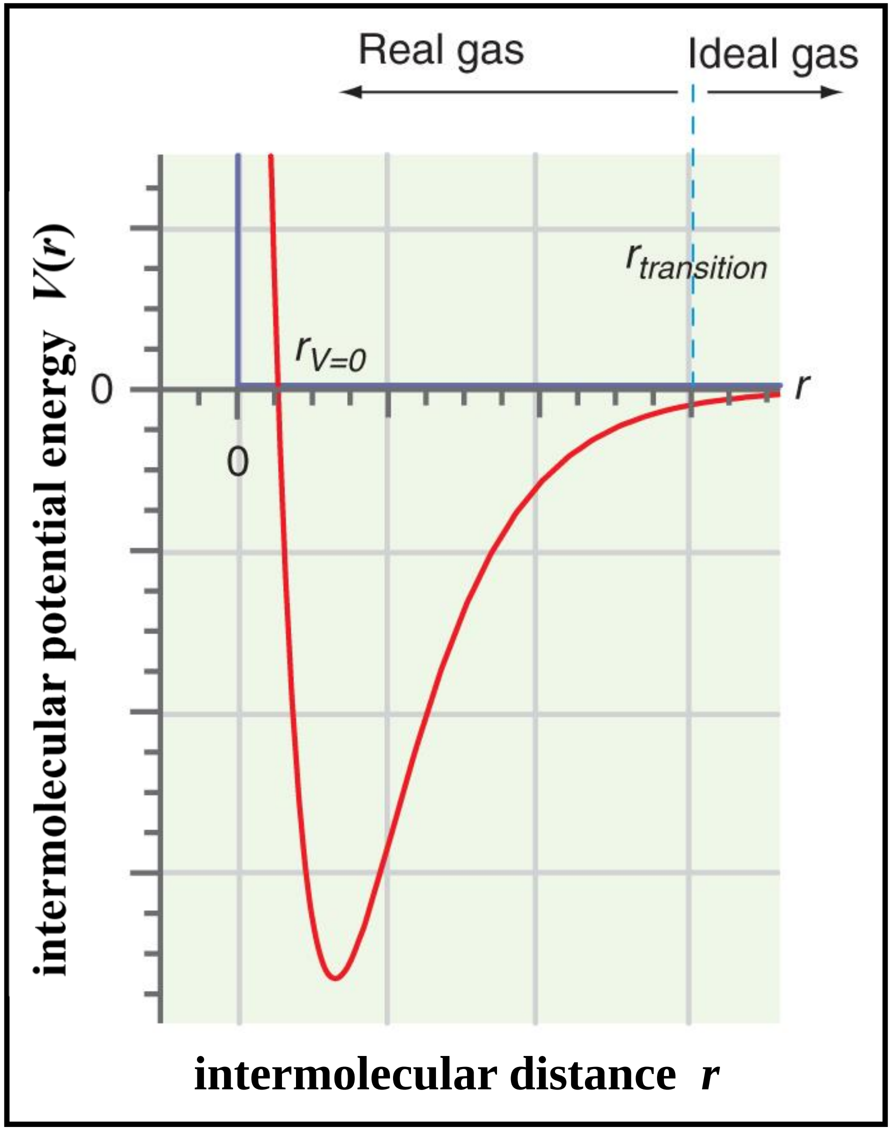
Compression Factor $Z = pV/nRT$ of Methane



Typical behavior of real (nonideal) gases:

$Z < 1$ at low temperatures and moderate pressures
$Z > 1$ at high pressures
$Z = 1$ as $p \rightarrow 0 \quad (V_m \rightarrow \infty)$

Why?



At very low pressures, molecules are far apart. No interactions. $Z = 1$

As the pressure and density increase, molecules a few diameters apart experience attractive forces. $Z < 1$

At very high densities, molecules Experience short-range repulsive Forces. $Z > 1$

van der Waals equation of State for Real Gases

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

$$= \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

Johannes van der Waals

1910 Nobel Physics Prize

- parameter ***a*** reduces the gas pressure (representing attractive intermolecular forces)
- parameter ***b*** increases the gas pressure (representing repulsive intermolecular forces)
- for ideal gases: $a = 0$, $b = 0$

Selected van der Waals *a* and *b* Parameters

Gas	***a*** / bar L^2 mol^{-2}	***b*** / L mol^{-1}
He	**0.0358**	**0.0240**
Ne	**0.220**	**0.0176**
Ar	**1.34**	**0.0317**
Kr	**2.36**	**0.0399**
CH_4	**2.28**	0.0427
NH_3	**4.24**	0.0373
C_3H_8	9.38	0.0903

- Why do parameters ***a*** and ***b*** for the noble gases increase with the number of electrons per atom?
- CH_4 and NH_3 both have 10 electrons. Why is ***a*** for NH_3 significantly larger than ***a*** for CH_4?
- Parameter ***b*** is similar the molar volume of the liquefied gases.

Exercises

- Use the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

  to show $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$ for a van der Waals gas.

- Why does the energy of a van der Waals gas increase as the gas expands isothermally?

- At high temperatures, why does the van der Waals equation simplify to $p = RT/(V_m - b)$?

- Show that the van der Waals equation reduces to $p = RT/V_m$ (the ideal gas equation) in the limit $p \to 0$.

Exercise

Calculate the pressure of ethane at 350 K (77 ºC) and a density of 218.1 g L^{-1} using:

a) the ideal gas equation

b) the van der Waals equation.

Data for ethane:

30.07 g mol^{-1} molecular weight
a = 5.58 L^2 bar mol^{-2}

b = 0.0651 L mol^{-1}

TABLE 1.1 Units of Pressure and Conversion Factors

Unit of Pressure	Symbol	Numerical Value
Pascal	Pa	$1\,\mathrm{N\,m^{-2}} = 1\,\mathrm{kg\;m^{-1}\,s^{-2}}$
Atmosphere	atm	1 atm = 101,325 Pa (exactly)
Bar	bar	1 bar = 10^5 Pa
Torr or millimeters of Hg	Torr	1 Torr = 101,325/760 = 133.32 Pa
Pounds per square inch	psi	1 psi = 6,894.8 Pa

TABLE 1.2 The Ideal Gas Constant, *R*, in Various Units

$R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$

$R = 8.314\,\mathrm{Pa\,m^3\,K^{-1}\,mol^{-1}}$

$R = 8.314 \times 10^{-2}\,\mathrm{L\,bar\,K^{-1}\,mol^{-1}}$

$R = 8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}$

$R = 62.36\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}$

Exercise (*cont.*)

a) Calculate the pressure of ethane at 350 K (77 °C) and a density of 218.1 g L^{-1} using the **ideal gas law**.

ethane molar volume:

$$V_\mathrm{m} = \frac{\text{molar mass}}{\text{density}} = \frac{30.07\ \cancel{\mathrm{g}}\ \mathrm{mol}^{-1}}{218.1\ \cancel{\mathrm{g}}\ \mathrm{L}^{-1}} = 0.1379\ \mathrm{L\ mol}^{-1}$$

ethane pressure (using the ideal gas law):

$$\boxed{p = \frac{RT}{V_\mathrm{m}} = \frac{(0.08314\ \cancel{\mathrm{L}}\ \mathrm{bar}\ \cancel{\mathrm{K}}^{-1}\ \mathrm{mol}^{-1})\ 350\ \cancel{\mathrm{K}}}{0.1379\ \cancel{\mathrm{L}}\ \mathrm{mol}^{-1}} = 211\ \mathrm{bar}}$$

Calculated pressure is too high! (Measured pressure is 100 bar.)

Exercise (*cont.*)

b) Calculate the pressure of ethane at 350 K (77 $^{\mathrm{o}}$C) and a density of 218.1 g L^{-1} using the **van der Waals equation**.

ethane pressure:

$$p = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2}$$

$$= \frac{(0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}})\ 350\ \mathrm{K}}{0.1379\ \mathrm{L\ mol^{-1}} - 0.0651\ \mathrm{L\ mol^{-1}}} - \frac{5.58\ \mathrm{L^2\ bar\ mol^{-2}}}{(0.1379\ \mathrm{L\ mol^{-1}})^2}$$

$$= 399.7\ \mathrm{bar} - 293.4\ \mathrm{bar}$$

$$= 106\ \mathrm{bar}$$

Close! (Measured pressure is 100 bar, ideal-gas pressure is 211 bar.)

Many other equations of state have been developed.

Important example:

Virial Equation of State for Real Gases

(a power series in $1/V_m$)

$$\boxed{Z = \frac{pV}{nRT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots}$$

1 = first virial coefficient

$B(T)$ = second virial coefficient

$C(T)$ = third virial coefficient

$D(T)$ = fourth virial coefficient

$B(T)$, $C(T)$, $D(T)$, *etc*. are temperature dependent (not constant)

Exercise

Show that the second virial coefficient $B(T)$, a measure of the pairwise interaction of molecules, is related to the van der Waals a and b coefficients:

$$\boxed{B(T) = b - \frac{a}{RT}}$$

Why do this? It shows two models of nonideal gases are related, and gives useful and interesting information.

Low Temperature Limit **($1/T \rightarrow \infty$)**

$$B(T) = -\frac{a}{RT}$$

attractive forces dominate

High Temperature Limit **($1/T \rightarrow 0$)**

$$B(T) = b$$

repulsive forces dominate

At the Boyle Temperature **($T_B = a/Rb$)**

$$B(T_B) = 0 = b - \frac{a}{RT_B}$$

Attractive and repulsive forces are balanced. Looks ideal. ***Fooled ya!***

Exercise

Show that the second virial coefficient $B(T)$, a measure of the pairwise interaction of molecules, is related to the van der Waals a and b coefficients:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

multiply the van der Waals equation by V_m/RT to get Z

$$\frac{pV_m}{RT} = Z = \frac{V_m}{V_m - b} - \frac{a}{RT}\frac{1}{V_m}$$

$$\frac{pV_m}{RT} = \frac{1}{1 - (b/V_m)} - \frac{a}{RT}\frac{1}{V_m}$$

$$\frac{pV_m}{RT} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \cdots - \frac{a}{RT}\frac{1}{V_m}$$

Exercise

Calculate the Boyle temperature for methane, where $B(T) = 0$ and the gas “appears” to be ideal.

Data: $a = 2.28 \text{ L}^2 \text{ bar mol}^{-2}$, $b = 0.0427 \text{ L mol}^{-1}$

$$T_B = a/Rb$$

$$= (2.28 \text{ L}^2 \text{ bar mol}^{-2})/((0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(0.0427 \text{ L mol}^{-1})$$

$$= 642 \text{ K} \quad (370\ ^{o}\text{C})$$

Chapter 2. The First Law of Thermodynamics.
Heat, Work, Internal Energy, and Enthalpy

Summary

- the **internal energy *U*** of systems and its significance are discussed
- the First Law of Thermodynamics **($\Delta U = q + w$)** is used to relate changes in internal energy to the heat absorbed by a system **(q)** and the work done on a system **(w)**
- **enthalpy $H = U + pV$**, heat capacities, and calorimetry are introduced
- **state functions** (*e.g.*, U and H) and **path functions** (*e.g.*, q, w) are distinguished
- ΔU, ΔH, q, and w calculations are illustrated for ideal gases
- differences between **reversible and irreversible processes** are noted

Section 2.1 Internal Energy and the First Law

The internal energy of a system can take many different forms:

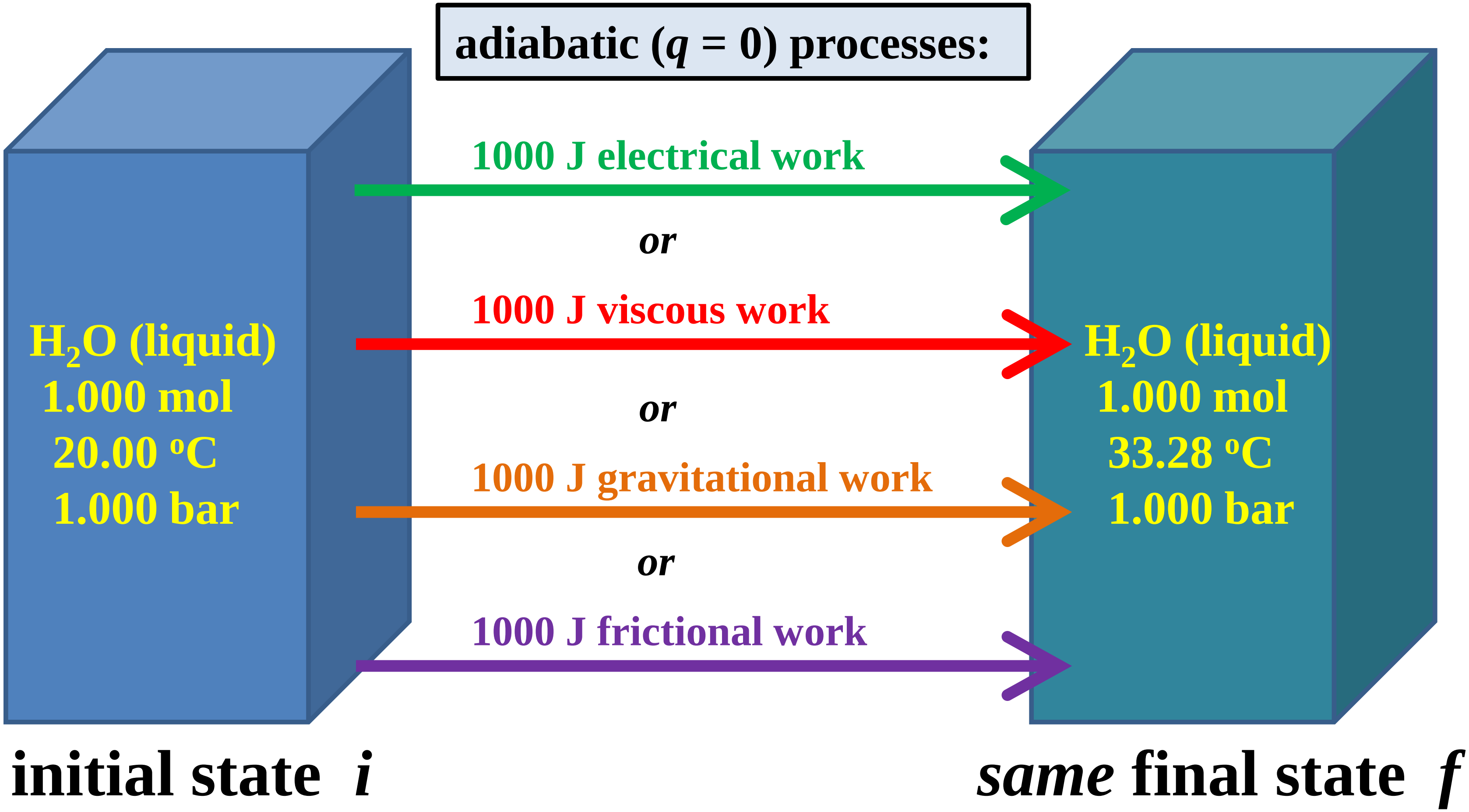
- molecular translational, rotational, vibrational energy
- energy stored in chemical bonds
- potential energy due to interactions between atoms or molecules
- potential energy due to applied electrical, magnetic, or gravitational fields

The **internal** energy **does not include** kinetic energy of a system moving with respect to an **external** coordinate system, such as the kinetic energy of a pizza moving in a delivery vehicle.

Joule's Brilliant Experiment, Leading to the First Law

Before the development of microscopic theory, heat was treated (*incorrectly!*) as a "caloric fluid", flowing from warmer to cooler objects, leading to much confusion.

For a system in a thermally insulated container (*no confusing heat flow!*) changing from an initial state to a final state, Joule showed that the work done is the same for all processes, ***independent of the path connecting the two states***.



adiabatic (q = 0) processes:

H_2O (liquid)
1.000 mol
20.00 ^{o}C
1.000 bar

1000 J electrical work

or

1000 J viscous work

or

1000 J gravitational work

or

1000 J frictional work

H_2O (liquid)
1.000 mol
33.28 ^{o}C
1.000 bar

initial state *i*

same* final state *f

The First Law of Thermodynamics

If a system changes from an initial state to a final state, the work done is the same for all adiabatic processes (q = 0) connecting the two states.

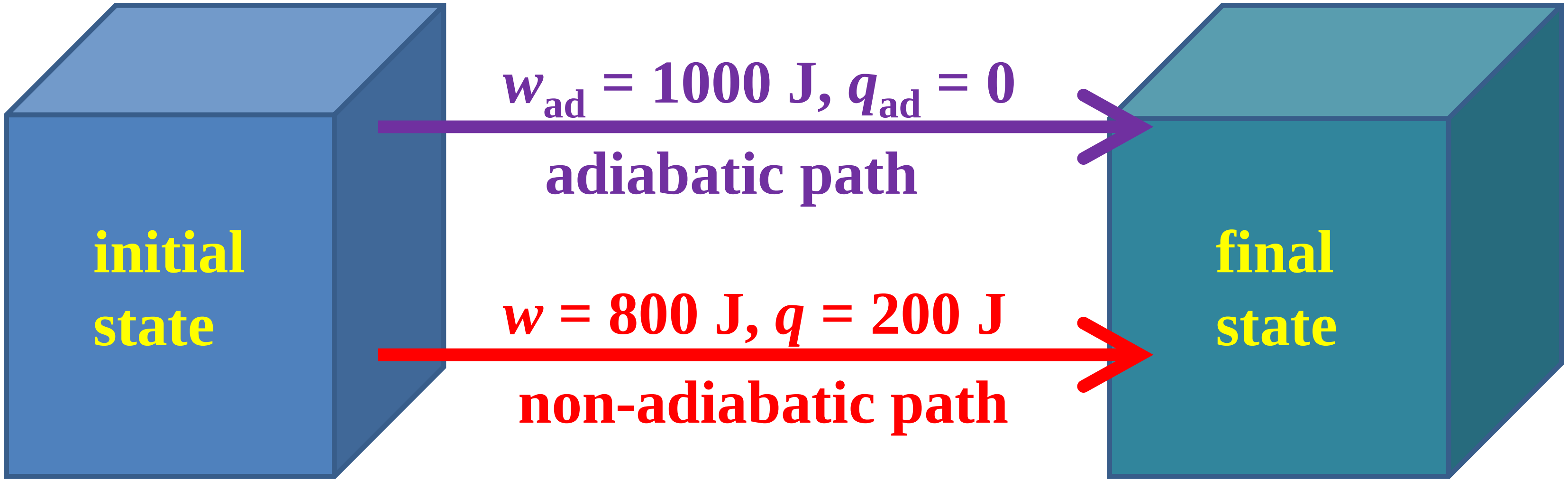
So what? Well, there are important consequences:

I) Because $\Delta U = U_{\text{final}} - U_{\text{initial}} = w_{\text{adiabatic}}$ is independent of the path taken from the initial to the final state of a system,
an internal energy function *U* exists that is a function only of the state variables of systems [*e.g.*, $\Delta U = U(T_f,V_f) - U(T_i,V_i)$].

II) Because *U* is a function, it can be differentiated and integrated.

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \qquad \Delta U = \int_i^f \mathrm{d}U$$

III) Mechanical definition of heat



initial state

$w_{ad} = 1000$ J, $q_{ad} = 0$

adiabatic path

$w = 800$ J, $q = 200$ J

non-adiabatic path

final state

$$\Delta U = w_{ad} = q + w \quad \text{(path-independent)}$$

$$\boxed{q = w_{ad} - w}$$

Allows heat flows to be calculated in terms of well-known mechanical work quantities (a force acting through a distance).

IV) Heat and work are path-dependent, not state functions.

$\xcancel{q(T,V)}$ $\xcancel{(\partial q/\partial T)_V}$ $\xcancel{(\partial q/\partial V)_T}$ $\xcancel{\Delta q = q_f - q_i}$

$\xcancel{w(T,V)}$ $\xcancel{(\partial w/\partial T)_V}$ $\xcancel{(\partial w/\partial V)_T}$ $\xcancel{\Delta w = w_f - w_i}$

V) For any **cyclic process** (initial state …→… same initial state):

$$\oint_i^i \mathrm{d}U = 0$$

VI) From $\boldsymbol{\Delta U = q + w}$ it follows that the energy of an isolated system (q = 0, w = 0) is constant.

$$\mathbf{(\Delta \mathit{U} = 0)_{isolated\ system}}$$

The energy of the universe (“everything”!) is constant.

⇒ Conservation of Energy

Section 2.2 Work

Thermodynamic work w is defined as energy entering a system from the surroundings due to a force **F** acting through a distance **x**.

$$\boxed{w = \int_{\mathbf{x}_i}^{\mathbf{x}_f} \mathbf{F} \cdot d\mathbf{x}}$$

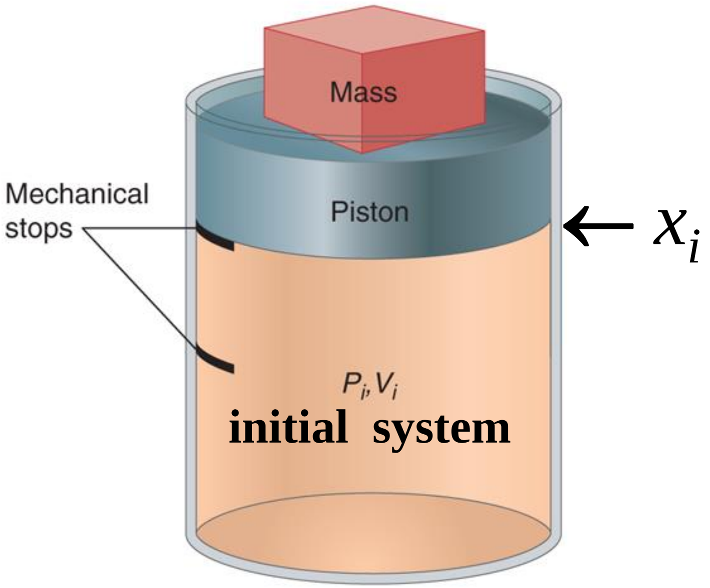
$$\boxed{\Delta U = q + w}$$

if w is positive: the surroundings does work on the system and the internal energy of the system increases

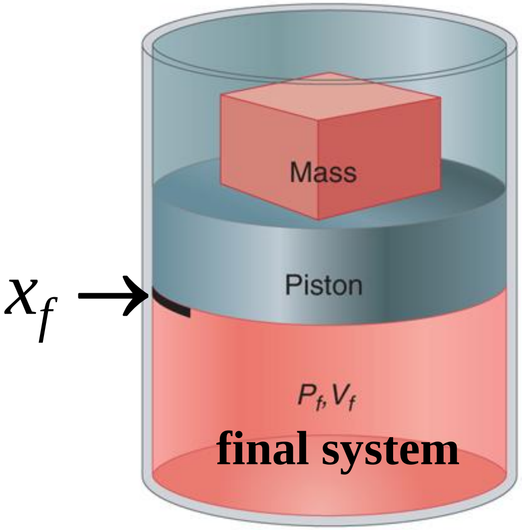
if w is negative: the system does work on the surroundings and the internal energy of the system decreases

!! *Warning* !! In some treatments of thermodynamics, especially mechanical engineering courses, the opposite convention is used: $\Delta U = q - w$. In this case, w is positive if the system (*e.g.*, an engine) does work on the surroundings.

Volume Expansion Work
(also called *pV* work)



Initial state



Final state

Piston of area *A* applies force *F* on the system in the cylinder. The applied force per unit area equals the external pressure acting on the system.

$$w = \int_{x_i}^{x_f} \mathbf{F} \cdot \mathrm{d}\mathbf{x} = -\int_{x_i}^{x_f} p_{\text{external}} A \mathrm{d}x$$

Why the minus sign? Because vectors **F** and d**x** point in opposite directions. Note also that *A*d*x* = d*V*, the change in volume of the system, which gives

$$w = -\int_{V_i}^{V_f} p_{\text{external}} \mathrm{d}V$$

Different Kinds of Thermodynamic Work

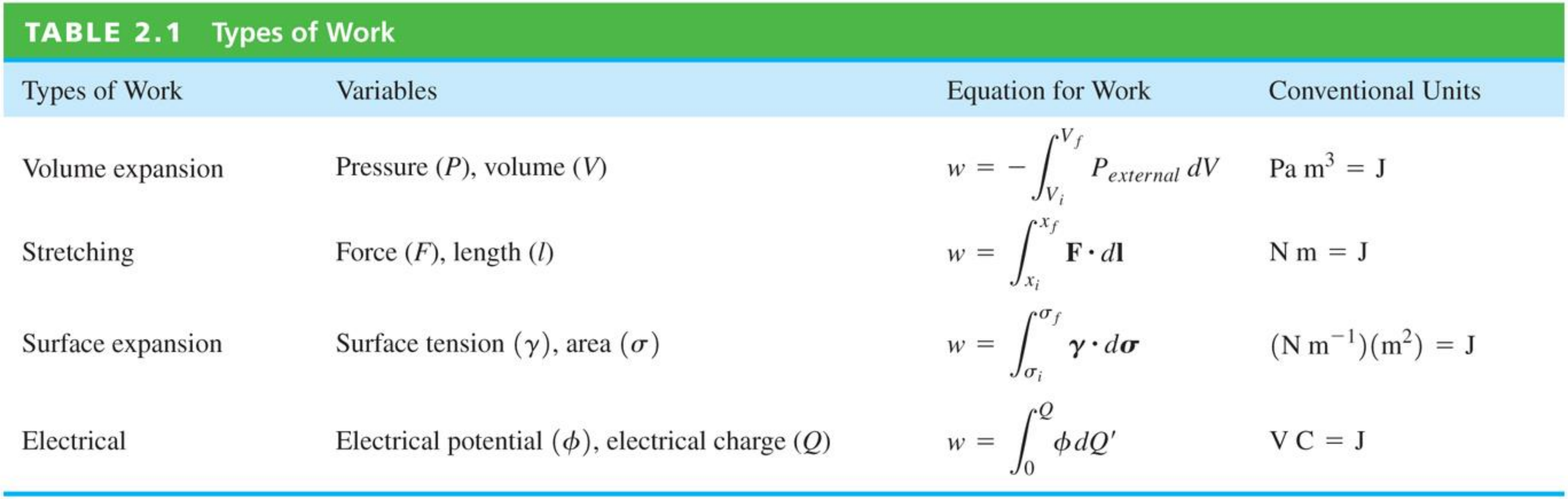


TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int_{V_i}^{V_f} P_{external}\, dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{l}$	$\text{N m} = \text{J}$
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \boldsymbol{\gamma} \cdot d\boldsymbol{\sigma}$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi\, dQ'$	$\text{V C} = \text{J}$

SI (*Systeme International d'Unites*) Base Units

length	meter (m)	from Greek ***metros*** (measure)
mass	kilogram (kg)	1000 grams, from Greek ***gramma*** (small amount)
time	second (s)	***second*** division of an hour, after minutes

SI Units Named after Scientists

force (mass times acceleration): Newton (N) = $\mathrm{kg\ m\ s^{-2}}$

energy (force times distance): Joule (J) = $\mathrm{kg\ m^{2}\ s^{-2}}$

pressure (force per unit area): Pascal (Pa) = $\mathrm{kg\ m^{-2}\ s^{-2}}$

temperature Kelvin (K)

Other Units

liter (L) = 0.001 m^3	from French ***litron*** (a unit of volume)
bar (bar) = 100,000 Pa	from Greek ***baros*** (weight)
atmosphere (atm) = 101,325 Pa	from Greek ***atmos*** (vapor) and ***sphaira*** (sphere)
torr (torr) = 1/760 atm = 101325/760 Pa	named after **Torricelli** (who developed barometers to measure pressure), the pressure exerted by a 1 mm tall column of liquid mercury
mole (mol) = number of atoms in 12 grams of ^{12}C	from German ***molekul*** (molecule)

Exercise

2.00 moles of an ideal gas expands isothermally at 300 K from an initial pressure of 5.00 bar to a final pressure of 2.00 bar.

a) The expansion is carried out rapidly and **irreversibly** with the external pressure suddenly reduced to 2.00 bar: $\boldsymbol{p_{\text{external}} < p}$

b) The expansion is carried out slowly and **reversibly** with the external pressure infinitesimally less than the gas pressure: $\boldsymbol{p_{\text{external}} = p}$

$$V_i = \frac{nRT}{p_i} = \frac{(2.00\text{ mol})(0.08314\text{ L bar K}^{-1}\text{ mol}^{-1})(300\text{ K})}{5.00\text{ bar}} = 9.977\text{ L}$$

$$V_f = \frac{p_i}{p_f}V_i = \left(\frac{5.00\text{ bar}}{2.00\text{ bar}}\right)9.977\text{ L} = 24.94\text{ L}$$

Exercise (*cont.*)

a) 2.00 moles of an ideal gas at 300 K and 5.00 bar expands isothermally and **irreversibly** against a constant 2.00 bar external pressure to a final pressure of 2.00 bar. Calculate the work.

$$w = -\int_{V_i}^{V_f} p_{\text{external}}\,\mathrm{d}V = -p_{\text{external}}\int_{V_i}^{V_f}\mathrm{d}V$$

Why? p_{external} is <u>constant</u>.

$$= -p_{\text{external}}\int_{V_i}^{V_f}\mathrm{d}V = -p_{\text{external}}(V_f - V_i) = -p_{\text{external}}\,\Delta V$$

$$= -(2.00\ \text{bar})\,(24.94\ \text{L} - 9.977\ \text{L})\,(10^{5}\ \text{Pa bar}^{-1})\,(10^{-3}\ \text{m}^{3}\ \text{L}^{-1})$$

$$\boxed{w = -2993\ \text{J}}$$

Work is negative for the expanding gas.
Does this make sense?

Exercise (*cont.*)

b) 2.00 moles of an ideal gas at 300 K and 5.00 bar expands isothermally and **reversibly** to 2.00 bar against a slowly reducing external pressure equal to the gas pressure ($p_{\mathrm{external}} = p$).

$$w = -\int_{V_i}^{V_f} p_{\mathrm{external}}\,\mathrm{d}V = -\int_{V_i}^{V_f} p\,\mathrm{d}V = -\int_{V_i}^{V_f} \frac{nRT}{V}\,\mathrm{d}V$$

$$= -nRT\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = -nRT\int_{V_i}^{V_f} \mathrm{d}\ln V = -nRT\ln(V_f/V_i)$$

$$= -(2.00\,\mathrm{mol})\,(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\,(300\,\mathrm{K})\,\ln\left(24.94/9.977\right)$$

$$\boxed{w = -4570\ \mathrm{J}}$$

Important! <u>More</u> work is done on the surroundings if the expansion is reversible.

Indicator Diagrams: plot p_{external} against V

Area under the curve is $-w$. *Graphical* representation of work done.

a) Irreversible Expansion

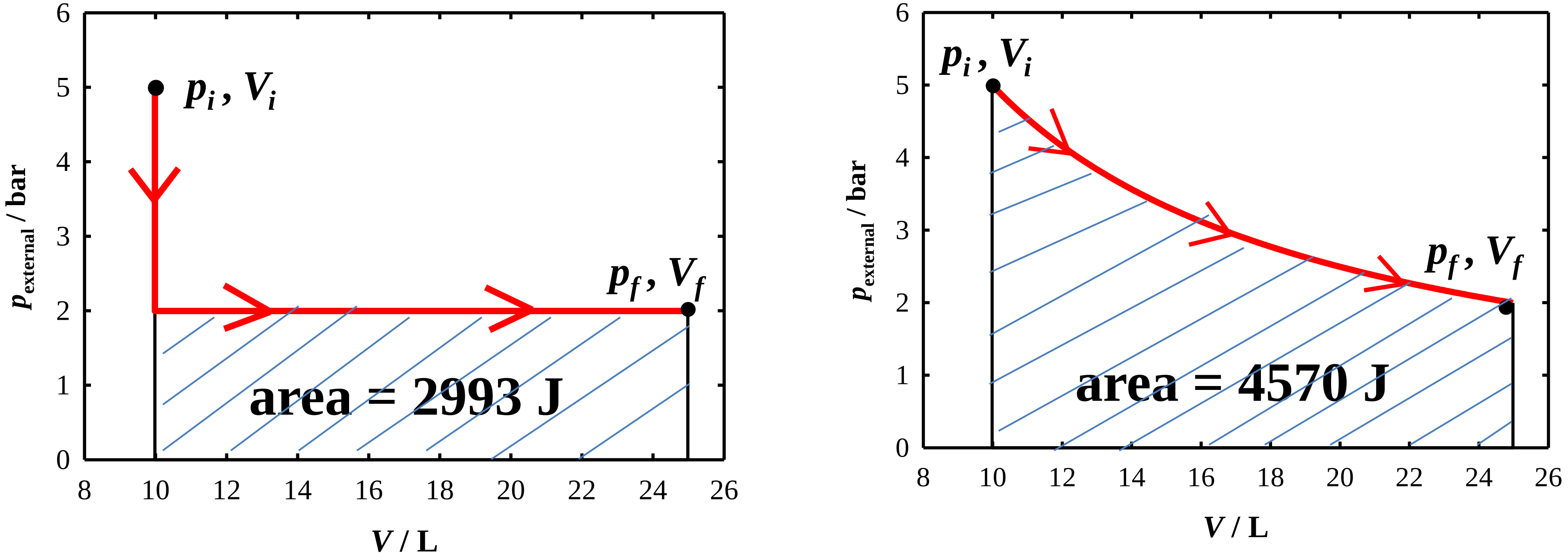
$p_{\text{external}} = 2\text{ bar} < p$

$w = -2993\text{ J}$

b) Reversible Expansion

$p_{\text{external}} = p$

$w = -4570\text{ J}$



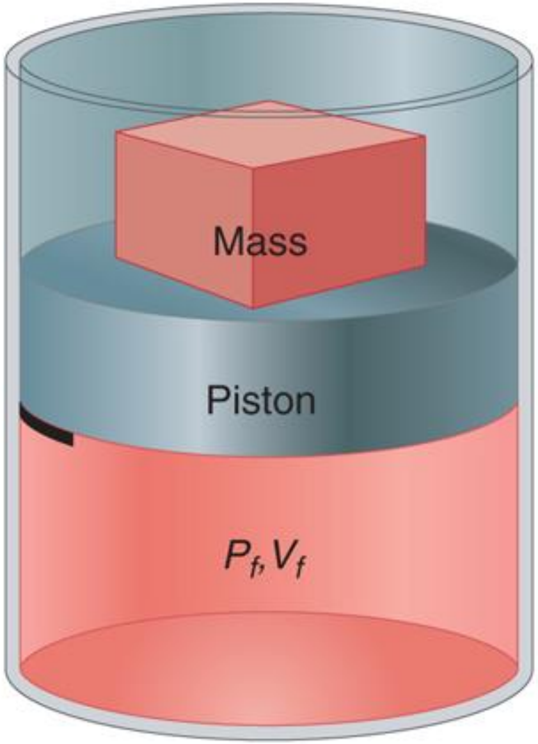
How do these calculations show that the work is a path function, not a state function?

$$w = -\int_{V_i}^{V_f} p_{\text{external}}\,\mathrm{d}V$$

Reversible and Irreversible Expansions

Reversible Expansion: $p_{\text{external}} = p$

The mass holding down the piston is gradually reduced in small increments (*e.g.*, 1 mg). p_{external} is only infinitesimally smaller than the gas pressure p. The gas pressure in the cylinder and the external pressure are balanced. The small mass increments can be replaced, reversing the expansion.



Irreversible Expansion: $p_{\text{external}} < p$

All of the mass holding down the piston is suddenly removed. The gas expands against a lower external pressure. To reverse the process, the mass would have to be lifted to the top of the piston, requiring additional work – ***not reversible***.