Chapter 2. The First Law of Thermodynamics

2A.1 Heat, Work, and Energy

Newton's first law: The velocity is conserved in magnitude and direction in the absence of an external force: $E_k = \frac{1}{2}mv^2$ is conserved.

Newton's second law:

$$F = m\frac{dv}{dt} = ma$$

If a body moves a distance *dx* through a force field *F*(*x*), the change of the kinetic energy is

$$\int_{x_1}^{x_2} F(x)dx = m\int_{x_1}^{x_2} \frac{dv}{dx}dx = m\int_{v}^{v} vdv = \frac{1}{2}m(v_2^2 - v_1^2)$$

so

$$\int_{x_1}^{x_2} F(x)dx = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 = E_{k_2} - E_{k_1}$$

This change is the work done on the body by outside forces:

$$w = \int_{x_1}^{x_2} F(x)dx$$

If this force is a function of x alone, not of time, the force can be related to a potential energy function $U(x)$:

$$F = -\frac{dU(x)}{dx}$$

$$E_{k_2} + U(x_2) = E_{k_1} + U(x_1)$$

The total energy, the sum of **the kinetic energy plus the potential energy**, is conserved.

$$C \equiv \frac{\text{đ}Q}{dT}$$

2A.4(b) Heat Capacity

Heat: Extensive Property
Temperature: Intensive Property

For electrical heat,

$q = I^2 Rt$: Joule's law of electrical heating

$C \equiv \dfrac{q}{\Delta T}$: **Heat Capacity** **[Meaning and Definition]**

$C(T)$: The heat capacity is a function of temperature.

$$C(T) = \frac{dq}{dT}$$

Explanation of Eq. (2A.14) not right.

$C_V \equiv \left(\frac{dq}{dT}\right)_V$: heat capacity **<u>at constant volume - *Theoretician*</u>**

$C_p \equiv \left(\frac{dq}{dT}\right)_p$: heat capacity **<u>at constant pressure - *Experimentalist*</u>**

$C_{V,m} = \frac{1}{n}\left(\frac{dq}{dT}\right)_V$: molar heat capacity at constant volume

$C_{p,m} = \frac{1}{n}\left(\frac{dq}{dT}\right)_p$: molar heat capacity at constant pressure

2A.2 Internal Energy Function, *U*

System: Some part of the world that we are interested, and plan to describe thermodynamically.

Surroundings: The rest of the world outside the system.

Closed System: In which the transfer of matter to and from the surroundings is forbidden. Energy may be exchanged between a closed system and the surroundings.

Isolated System: When a closed system cannot work nor exchange heat with its surroundings.

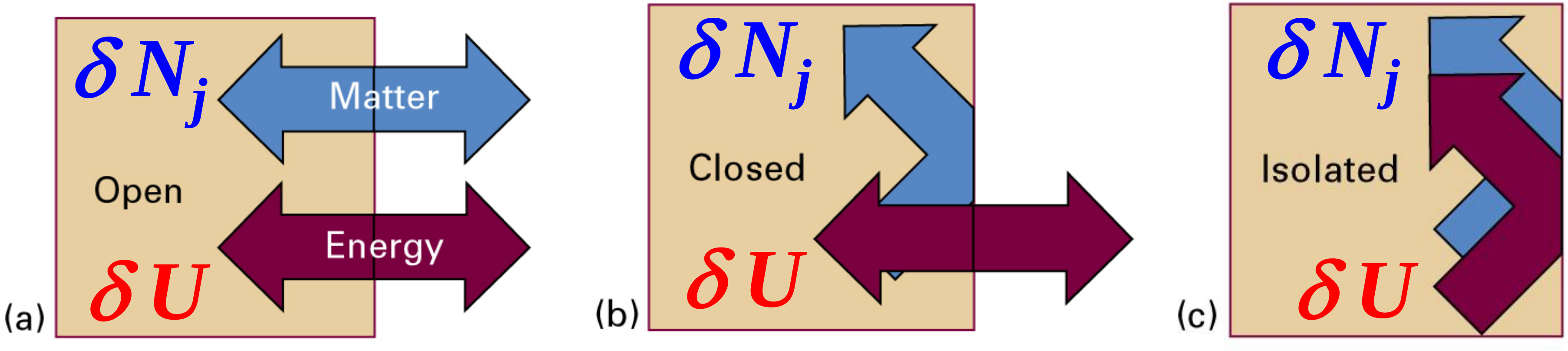


Figure 2A.1

(a) An open system can exchange matter and energy with its surroundings.

(b) A closed system can exchange energy with its surroundings, but it cannot exchange matter.

(c) An isolated system can exchange neither energy nor matter with its surroundings.

U: internal energy function
w: an amount of work
q: heat

The First Law: $dU = đq + đw$ **(2A.2)**

Reversible or Irreversible

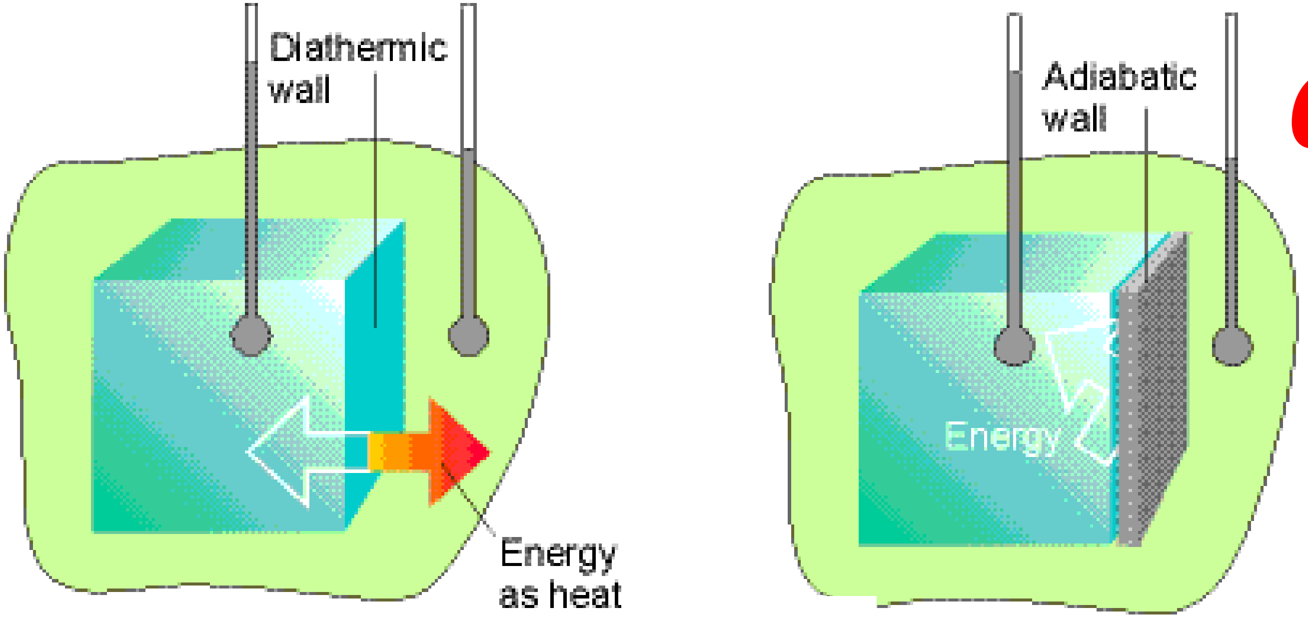
The sign convention
(+): flow into the system
(–): flow out from the system

James P. Joule:
- Combined mechanics and caloric theory
- Heat is simply another form of energy.
- The total energy of an isolated system is conserved.

Energy
- nuclear binding energy
- mass energy (Einstein's mc^2)

adiabatic

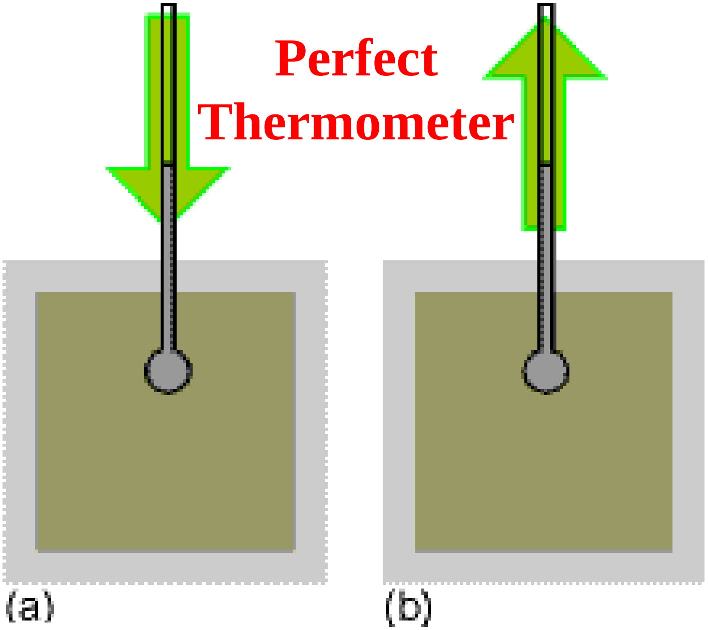
$$\text{đ}q = 0$$



(a) (b)

(a) A diathermic system is one that allows energy to escape as heat through its boundary if there is a difference in temperature between the system and its surroundings **(‘dia’ = through).**

(b) An **adiabatic** system is one that does not permit the passage of energy as heat through its boundary even if there is a temperature difference between the system and its surroundings.



Perfect Thermometer

adiabatic

during reaction

= not in equilibrium

Endothermic Reaction

Exothermic Reaction

Figure 2A.2

(a) When an endothermic reaction occurs in an adiabatic system, the temperature falls.

(b) If the reaction is exothermic, then the temperature rises.

2A.3 Work

If the position moves from a position x_1 to x_2

against an opposing force *F*, the work will be:

$$w = -\int_{x_1}^{x_2} F dx$$

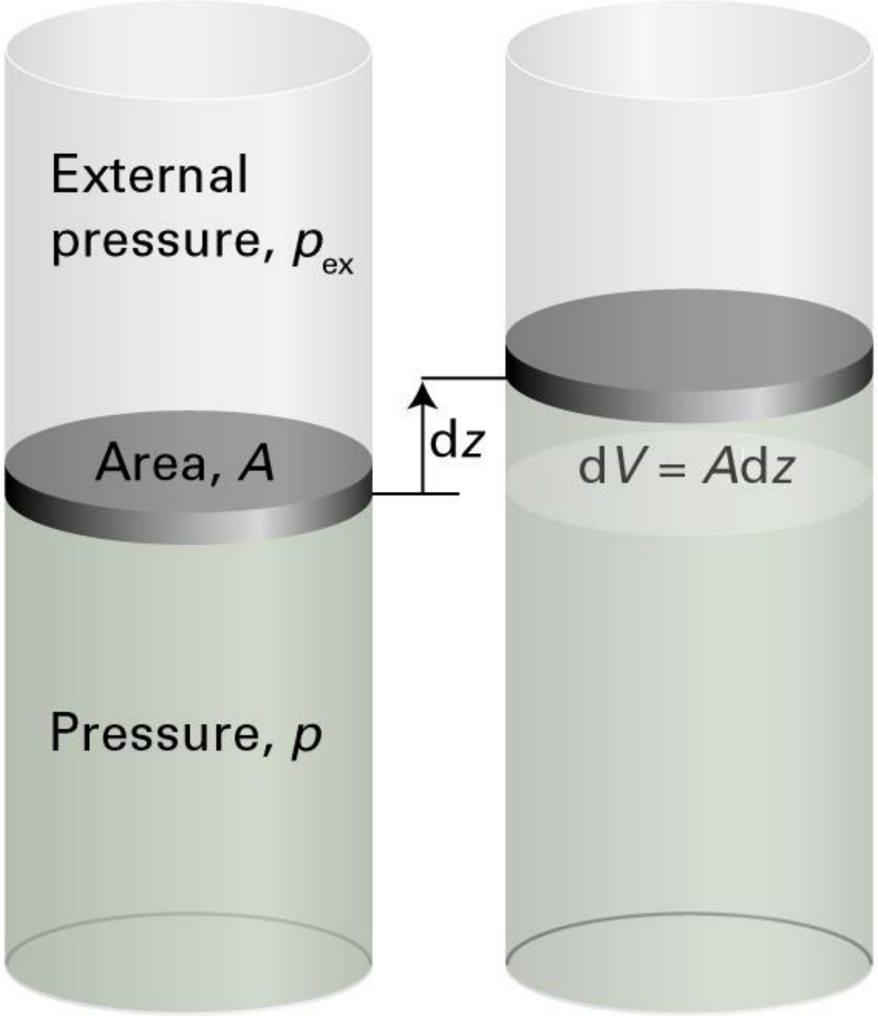
The negative sign in this equation confirms to our stated convention that work done by the gas is negative.

The opposing pressure: $p_{ex} = \frac{F}{A}$

Expansion work

$$w = -\int_{x_1}^{x_2} F dx = -\int_{x_1}^{x_2} p_{ex} A dx = -\int_{V_1}^{V_2} p_{ex} dV, \ \ where \ \ dV = Adx$$

$$dw = -p_{ex} dV$$



$$work = -p_{ex}\Delta V$$

Figure 2A.5
When a piston of area A moves out through a distance dz, it sweeps out a volume $dV = A\,dz$. The external pressure, p_{ex}, is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

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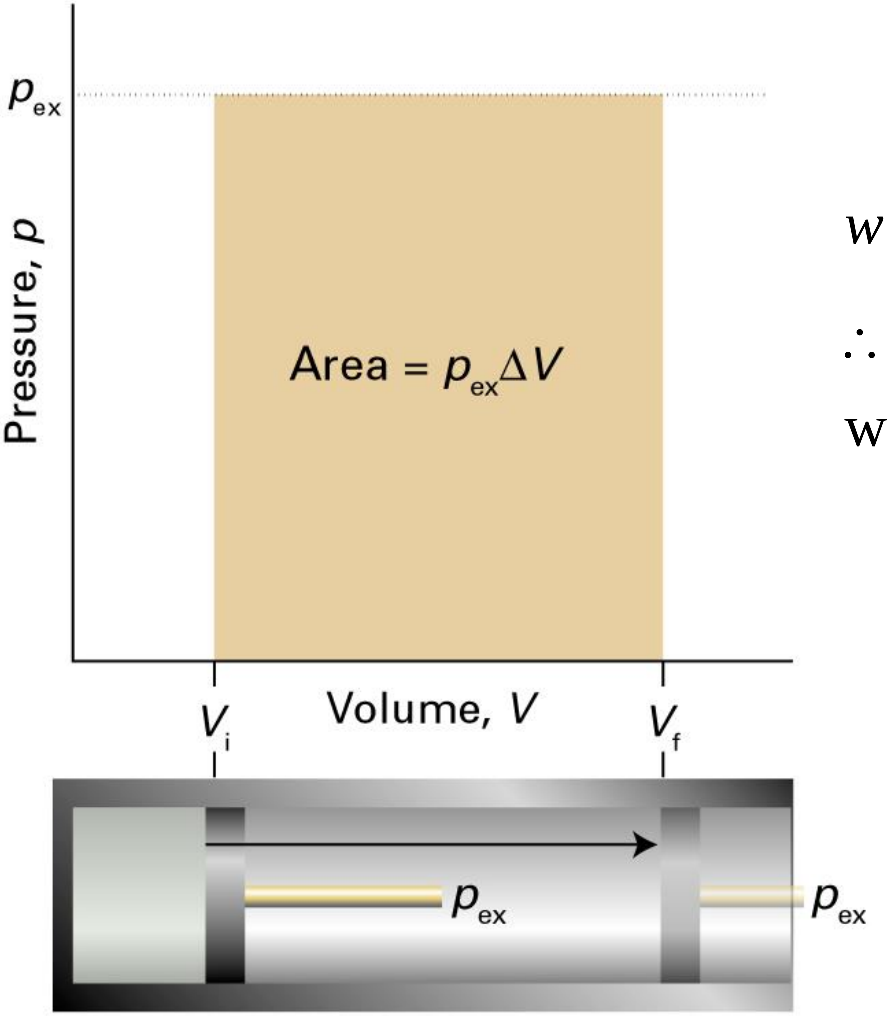

$$w = -\int_{V_i}^{V_f} p_{ex} dV = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i)$$

$\therefore$ The work done on the system is

$$w = -p_{ex}\Delta V$$

Figure 2A.6
The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

Table 2A.1

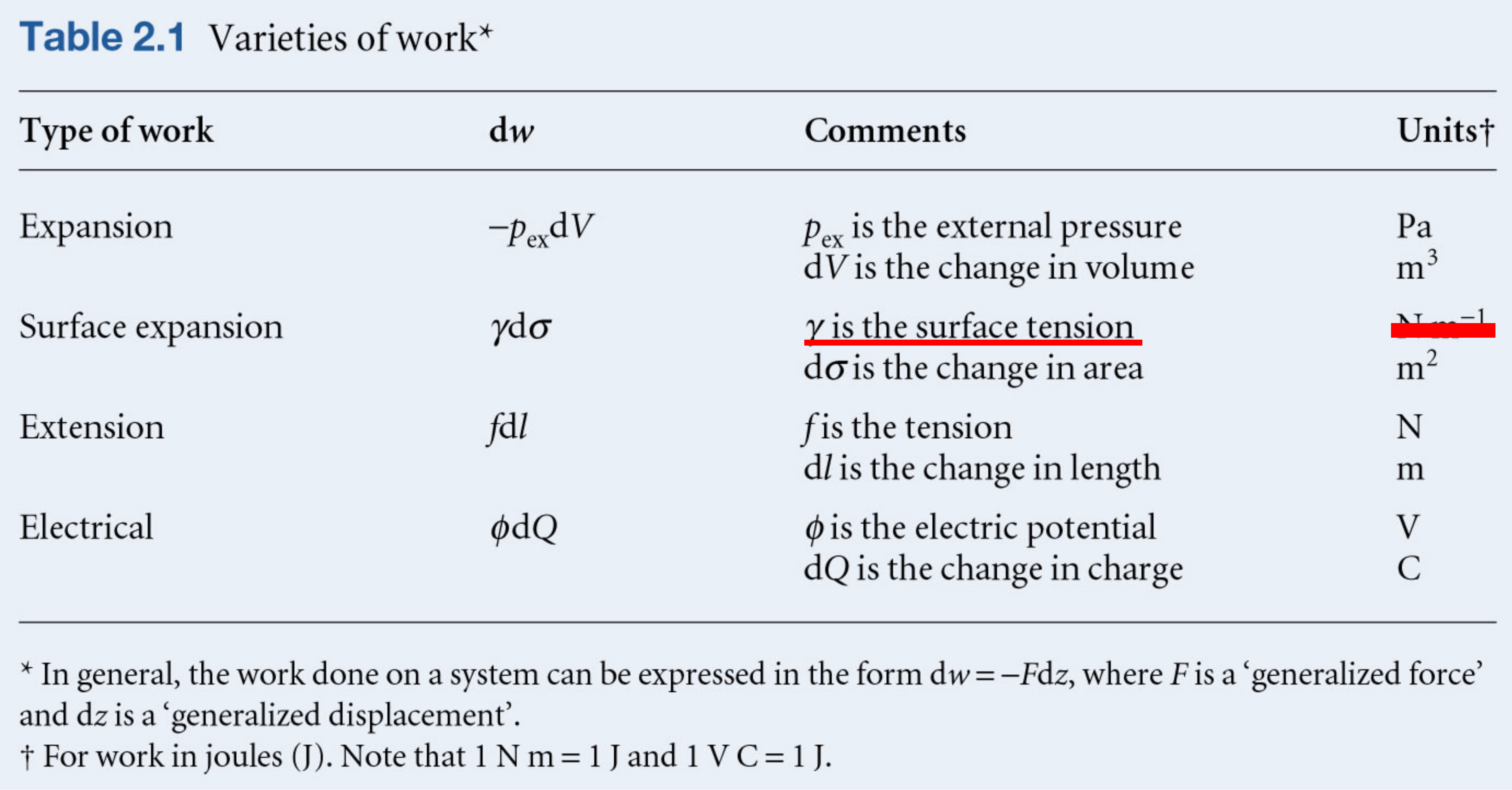

Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}\mathrm{d}V$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma \mathrm{d}\sigma$	γ is the surface tension dσ is the change in area	~~N m^{-1}~~ m^2
Extension	$f\mathrm{d}l$	f is the tension dl is the change in length	N m
Electrical	$\phi \mathrm{d}Q$	ϕ is the electric potential dQ is the change in charge	V C

* In general, the work done on a system can be expressed in the form $\mathrm{d}w = -F\mathrm{d}z$, where F is a 'generalized force' and dz is a 'generalized displacement'.

† For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.

Surface Tension = Interfacial Free Energy

2A.3(c) Reversible Expansion **Equilibrium**

In thermodynamics, a reversible change is one that can be reversed **by an infinitesimal modification** of a variable.

$$\underline{p_{ex} \approx p_{in}}$$

$$dw = -p_{ex}dV = -p_{in}dV \qquad \textbf{(2A.8a)}$$

$$w = -\int_{V_i}^{V_f} p_{in}dV$$

where p_{in} may be a function of volume.

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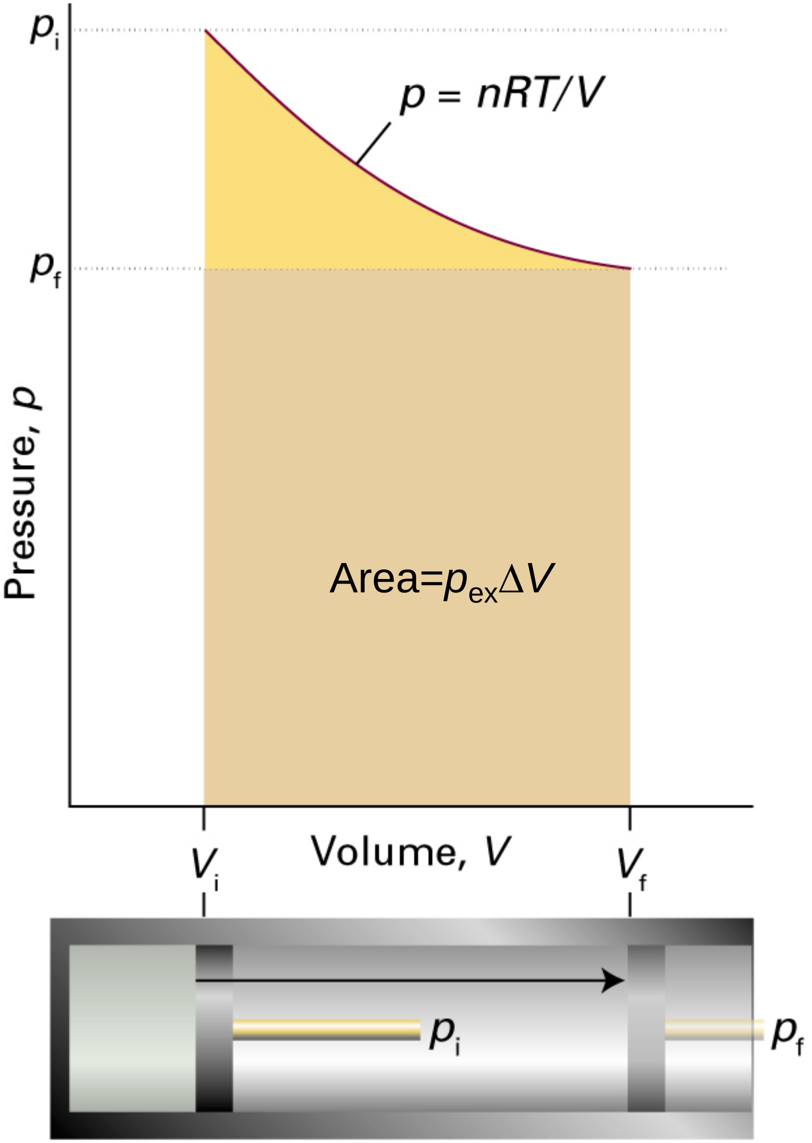
One example of reversibility: $$\underline{T_{ex} = T_{in}}$$

Thermal equilibrium of two systems with the same temperature.

Isothermal Reversible Expansion



For ~~isothermally reversible~~ process,

$$p_{ex} \approx p_{in}$$

$$dw = -p_{ex}dV = -p_{in}dV$$

$$w = -\int_{V_i}^{V_f} p_{in}dV$$

(Perfect Gas)

$$pV = nRT \quad \text{(ideal gas)}$$

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V}dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\ln\frac{V_f}{V_i}$$

Figure 2A.7

The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$.

The work done during the **irreversible** expansion against the same final pressure is equal to the rectangular area (shown darker).

$$P_{ex} \neq P_{in}$$

$$T_{ex} = T_{in}$$

Note that the reversible work is greater than the irreversible work.

Isothermal Reversible or Irreversible Expansion

$P_{ex} \neq P_{in}$
$T_{ex} = T_{in}$

$$w = -\int_{V_1}^{V_2} p_{ex} dV$$

Expansion work

The larger the opposing pressure (for a given ΔV), the more work will be done. There is a limit to how large p_{ex} can be, of course, since if it is greater than the pressure of the driving gas (p), no expansion will occur at all. How can the work be maximized?

Consider an ideal gas in a cylinder with a movable piston, with the pressure p_i = 10 *atm* and volume V_i = 1 m^3. Let us assume that the opposing pressure (also 10 *atm* at the start) consists of 1 *atm* due to the air outside and 9 *atm* due to nine weights sitting on the piston (each exerting 1 *atm* pressure). **If all the weights are removed at once**, the gas will expand against the constant p_i = 1 *atm* until its pressure is 1 *atm* – that is, until it reaches equilibrium. If the expansion is isothermal, its final volume will be 10 m^3, and the work done is:

$$dw = -(1\,atm)(10-1)\,m^3 = -9\,m^3 atm$$

2A.4 Heat

As a function of two independent parameters

(1 Component)

$U(T,V)$: internal energy

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

Reversible

State Function

Exact Differential

From the first law,

Reversible or Irreversible

$$dU = dq + dw = dq - \underbrace{p_{ex}dV}_{pV\text{ work}} + \underbrace{\cancel{d}w_e}$$

any other work
(e.g. electrochemical)

At **constant volume**, no other work

$$dU = dq$$

$$C(T,t) \equiv \frac{dq}{dT}$$

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

Derivation of Eq. (2A.14)

Never Definition

교재 error

$U = U(T,V)$ vs. $U = U(T,V,time)$

Equilibrium ***Nonequilibrium***

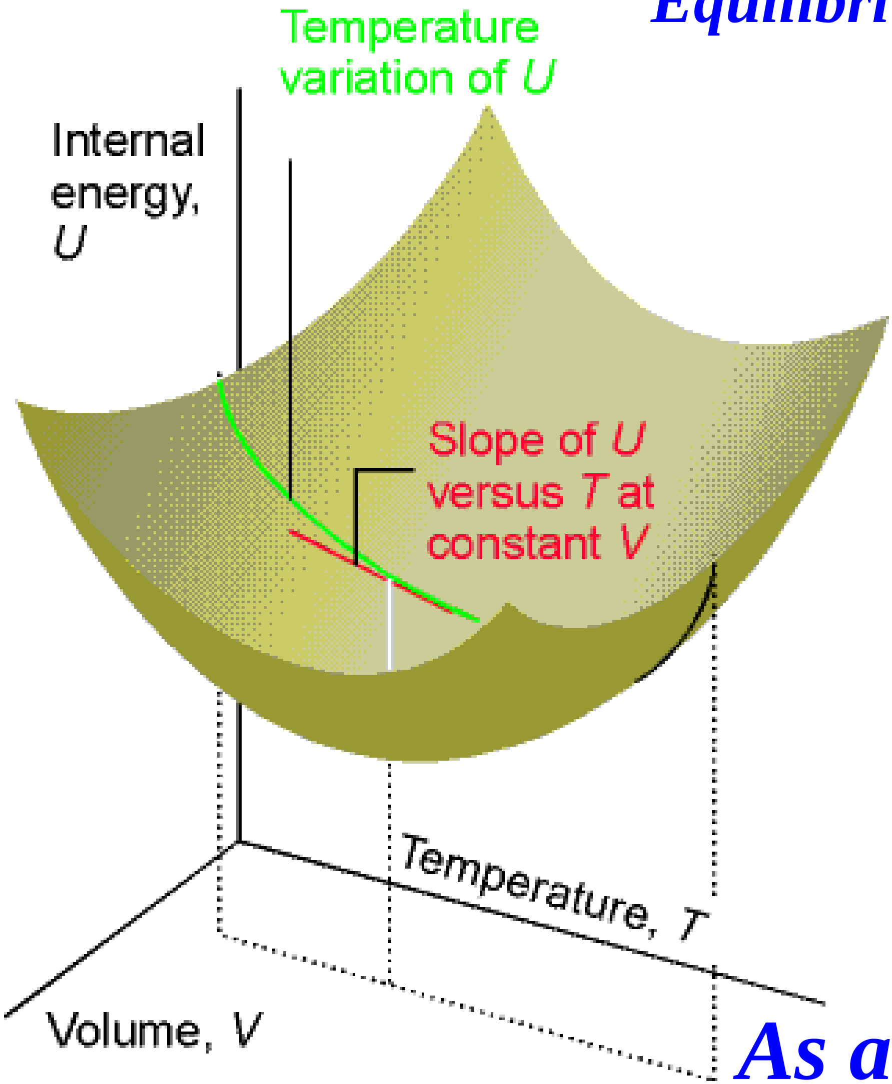


Fig. 2A.10

The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface.

The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to *T*.

The slope of this curve at any point is the partial derivative $(\partial U/\partial T)_V$.

As a function of two independent parameters

(1 Component)

2A.1 Work and Heat

Internal energy is stored in molecular bonds: in molecular **translation, rotation, and vibration**, and the energy of **mutual interactions** of molecules.

In molecular terms, the process of ***heating*** is the transfer of energy that makes use of the differences in **thermal motion** - the **random motion** of molecules - between the system and the surroundings.

In summary, heat stimulates **random motion** (of either the system or the surroundings).

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In molecular terms, ***work*** is the transfer of energy that makes use of **organized motion**. When a weight is raised or lowered, its atoms move in an organized way.

The electrons in an electric field move in an orderly direction (drift velocity).

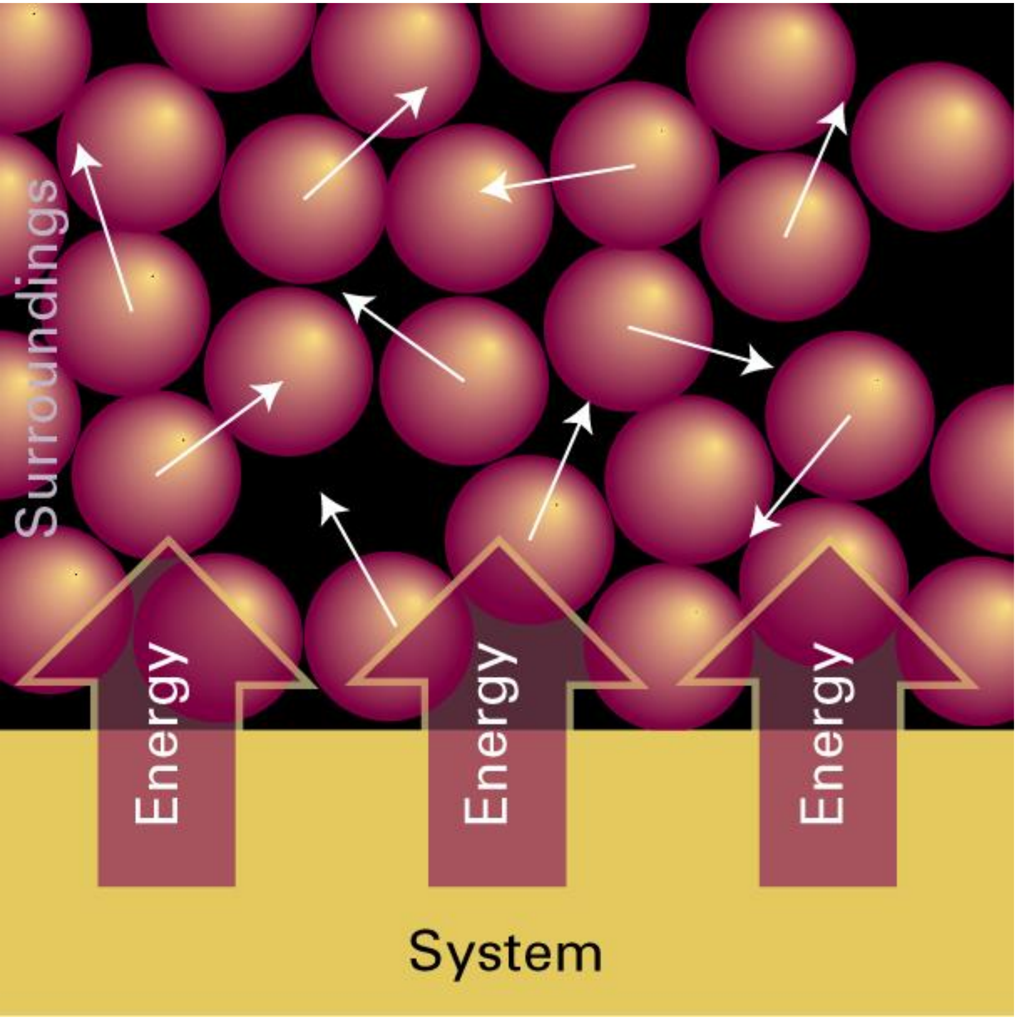


Figure 2A.3

When energy is transferred to the surroundings as heat, the transfer stimulates disordered motion of the atoms in the surroundings.

Transfer of energy from the surroundings to the system makes use of **disordered motion (thermal motion)** in the surroundings.

2B Enthalpy

In many cases, it is more convenient to use temperature and pressure, rather than temperature and volume, as independent variables.

$$U(p,T)$$

$$dU(p,T) = \underbrace{\left(\frac{\partial U}{\partial T}\right)_p}_{\text{not heat capacity}} dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

For me
For convenience

Define a new function called **the Enthalpy *H***

$$H \equiv U + pV$$

$$H + dH = (U + dU) + (p + dp)(V + dV)$$

$$= U + dU + pV + Vdp + pdV + \overset{0(\because \text{doubly infinitestimal})}{\cancel{dpdV}}$$

$$H + dH = U + pV + dU + Vdp + pdV$$

$$= H + dU + Vdp + pdV$$

$$dH = dU + pdV + Vdp$$

$$= dU + d(pV) \qquad (*)$$

$$dU = dq - pdV \qquad (**)$$

Reversible or Irreversible

(The First Law)

By combining eqs (*) and (**), one obtains

$$dH = dq - pdV + pdV + Vdp$$

$$= dq + Vdp$$

Reversible or Irreversible

Now impose the condition that pressure is kept constant,

$$(dH)_p = (dq)_p$$

The increase in the property *H* is equal to the amount of heat added to a system at constant pressure.

$$\therefore C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

2B.2 Calculation of C_p–C_V

$$H = U + pV$$

$$C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial U}{\partial V}\right)_T \right]$$ **General (derivation on white board)**

$$C_p - C_V = nR$$ **Ideal Gas** **(2B.9)**

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_p [p + \left(\frac{\partial U}{\partial V}\right)_T$$

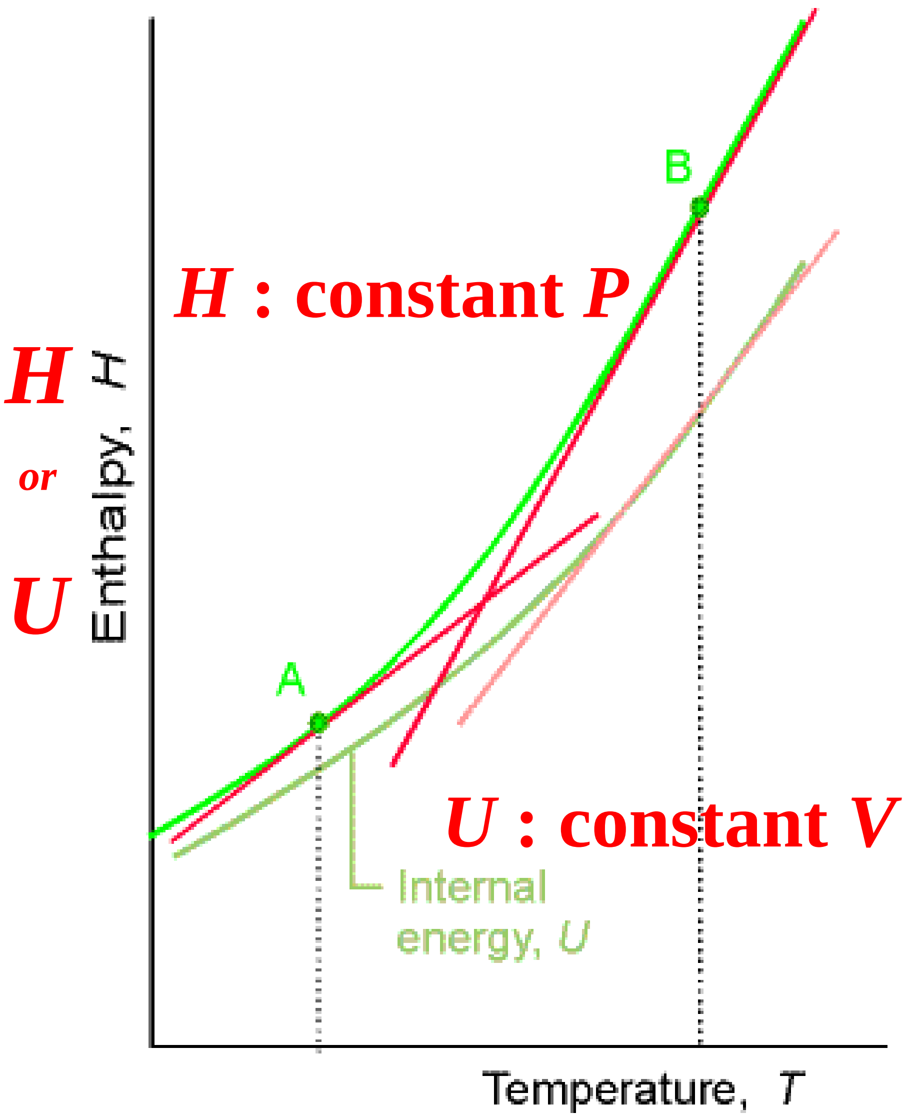


Figure 2B.3

The slope of a graph of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity.

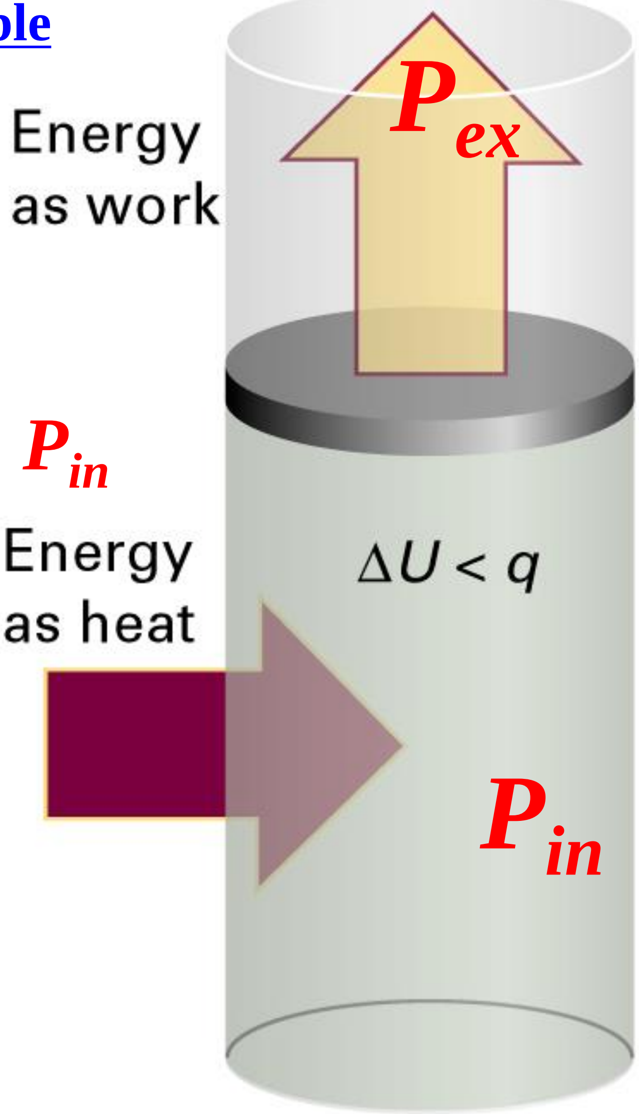
The slope of the graph may change with temperature, in which case the heat capacity may varies with temperature.

For gases, **the slope of the graph of enthalpy vs. temperature is steeper than that of the graph of internal energy versus temperature, and C_p is larger than C_V.**

[Positive Thermal-Expansion Coefficient]

Reversible

$$P_{ex} = P_{in}$$



$$C_p - C_V = nR$$

Ideal Gas

Weight Lifting

Figure 2B.1

When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work.

In such a case, the change in internal energy is smaller than the energy supplied as heat.

$$P\,V = N\,k_B\,T$$

$$P\,dV = N\,k_B\,dT$$

2E.1 Reversible Adiabatic Expansion (Perfect Gas)

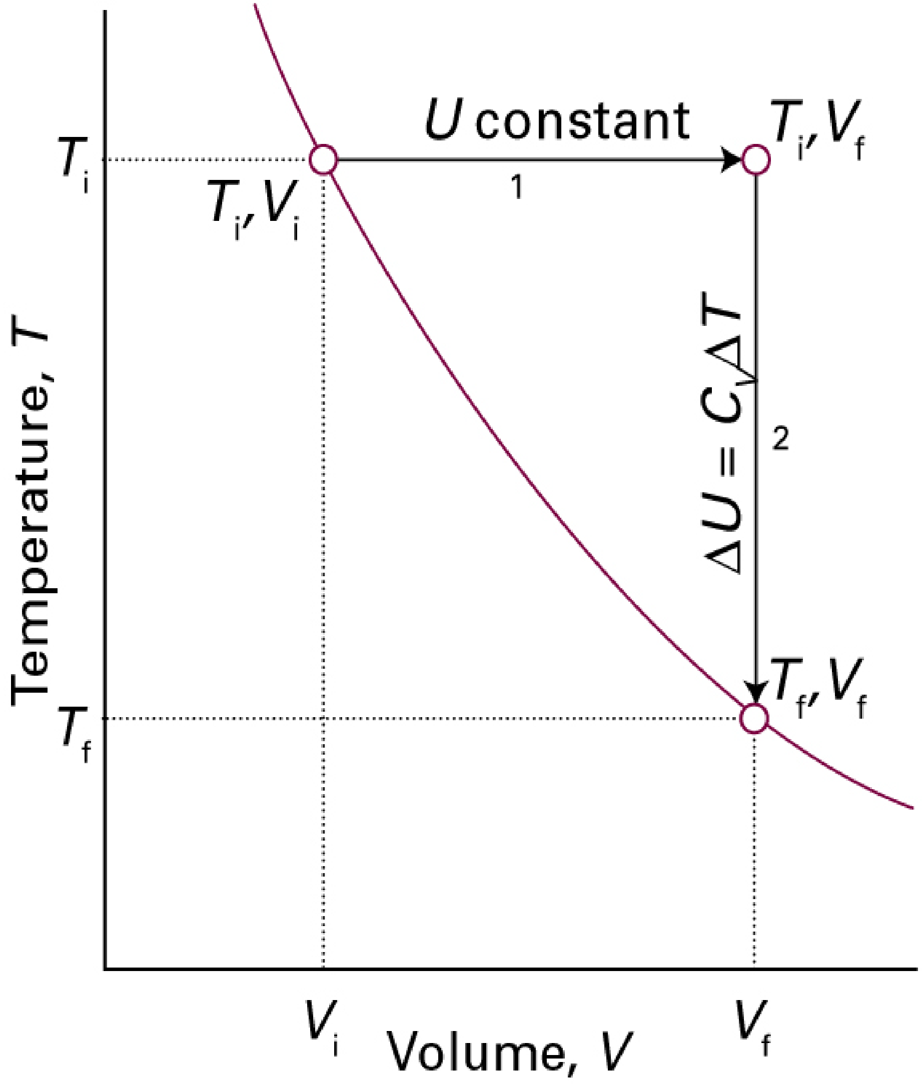


Figure 2E.1

To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps.

In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas.

In the second step, the temperature of the system is decreased at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

2E.1 Reversible Adiabatic Changes

Perfect Gas

The work of adiabatic change

$$T_i, V_i \rightarrow T_f, V_f$$

$$dU = dq + dw$$

$$dq = 0 \quad (\because adiabatic)$$

$$\therefore dU = dw$$

$$\therefore w = \int_{initial\ state}^{final\ state} (dU)_V = \int_{T_i}^{T_f} C_V dT_V = C_V(T_f - T_i)_V = C_V \Delta T_V$$

Note that C_V is dependent only on the temperature for ideal gas.

$$p_{ex} \approx p_{in}$$

$$dU = dq + dw$$

2E.1 Reversible Adiabatic Expansion of a Perfect Gas

$$dq = 0$$

$$\therefore dU = dw = -pdV$$

$U(T)$ = Perfect Gas

$U(T,V)$ or $U(T,P)$ = Real Gas

$$dU = C_V dT$$

Combining the two equations,

$$C_V dT = -pdV$$

On inserting $pV = nRT$, the last equality becomes

$$C_V dT = -\frac{nRT}{V} dV$$

$$C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

$$\text{Let } c = \underline{\frac{C_V}{nR}} = \frac{C_{V,m}}{R}$$

C = 3/2 for monoatomic ideal gas

$$\left(\frac{T_f}{T_i}\right)^c = \left(\frac{V_i}{V_f}\right)$$

(Ideal + Adiabatic + Reversible)

(2E.2b)

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C = 3/2 for monoatomic ideal gas

$$V_f T_f^c = V_i T_i^c$$ **(2E.2b)**

We can predict the temperature of a gas that has expanded adiabatically and reversibly from a volume V_i and temperature T_i to a volume V_f.

$$T_f = \left(\frac{V_i}{V_f}\right)^{\frac{1}{c}} T_i$$

(Ideal + Adiabatic + Reversible)

The work done on the ideal gas as it expands adiabatically and reversibly from V_i to V_f becomes

$$\Delta U = w = C_V \Delta T = C_V \left(T_f - T_i\right) = C_V \left[\left(\frac{V_i}{V_f}\right)^{\frac{1}{c}} T_i - T_i\right]$$

$$= C_V T_i \left\{\left(\frac{V_i}{V_f}\right)^{\frac{1}{c}} - 1\right\}$$

(Ideal + Adiabatic + Reversible)

2E.2 *p-V* Relation for Perfect Gas (Adiabatic Changes)

Derivation: Justif. 2E.2 [Homework] p. 101

γ = 5/3

for monoatomic ideal gas

Defining $\underline{\gamma = \frac{C_p}{C_V}}$, we obtain

(Ideal + Adiabatic + Reversible)

$$\underline{pV^{\gamma} = \text{constant}}$$

(skip)

$$p_f V_f^{\gamma} = p_i V_i^{\gamma}$$

$$w = C_V T_i \left\{ \left(\frac{V_i}{V_f} \right)^{\frac{1}{c}} - 1 \right\}, \quad \frac{1}{c} = \gamma - 1$$

$$c = \frac{C_{V,m}}{R}$$

$$\frac{1}{c} = \frac{R}{C_{V,m}} = \frac{C_{p,m} - C_{V,m}}{C_{V,m}}$$

$$= \frac{C_{p,m}}{C_{V,m}} - 1 = \gamma - 1$$

Combining the above two equations,

$$w = C_V T_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right\}$$

Since $\gamma > 1$ for all gases, the pressure *p* falls off faster with volume ($p \propto \frac{1}{V^{\gamma}}$: the curve is called an adiabat) than in the case of isothermal expansion ($p \propto \frac{1}{V}$).

Reversible

Ideal Gas

$\gamma = 5/3$

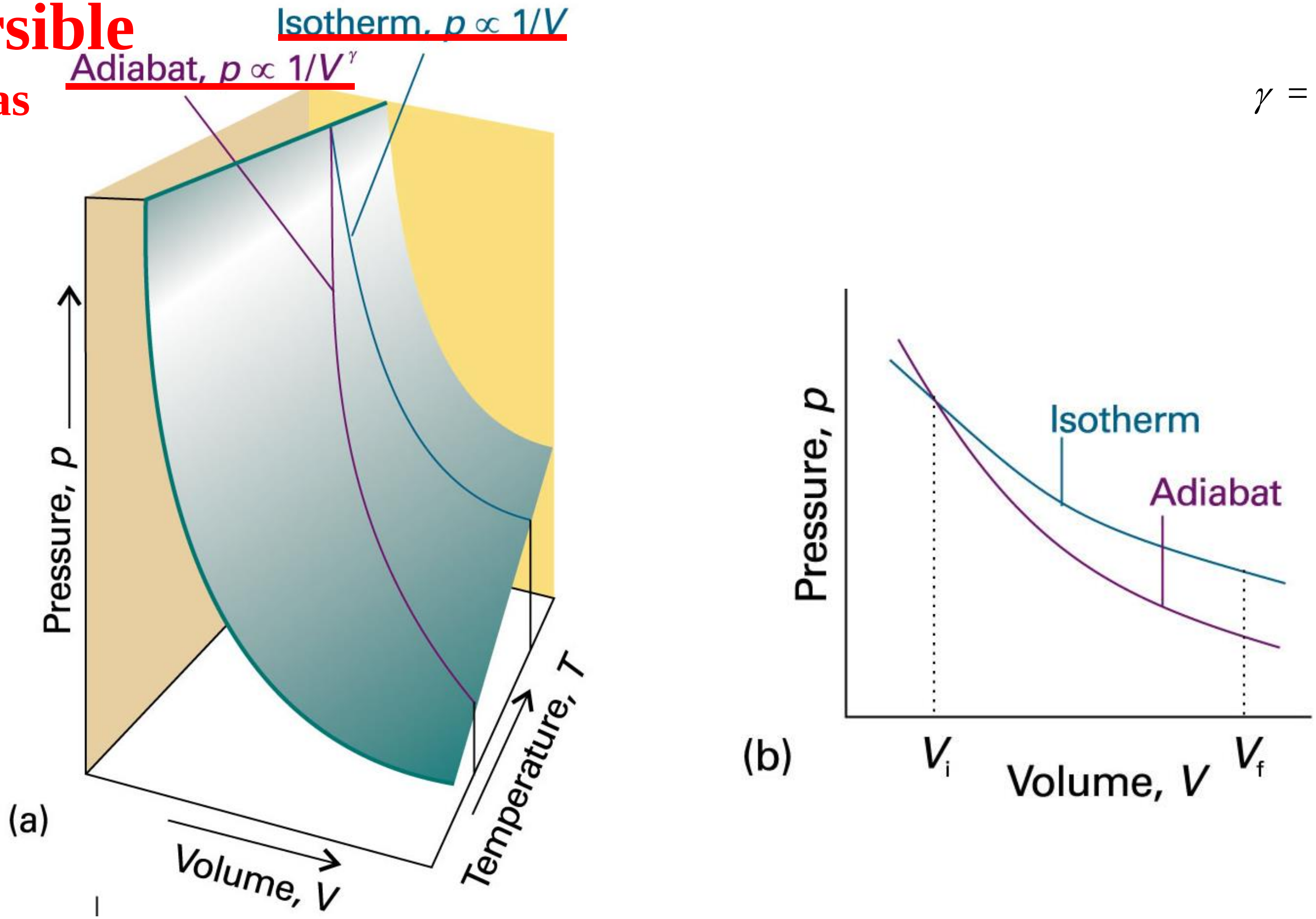


Figure 2E.2 An adiabat depicts the variation of pressure with volume when a gas expands **reversibly** and adiabatically.

(a) An adiabat for a perfect gas.

(b) Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

Molecular Interpretation of Internal Energy (Ideal Gas)

Consider the case of **a monatomic gas** at a temperature *T*. We know that the kinetic energy of one atom of mass *m* is

$$E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \qquad \text{(A)}$$

According to **the equipartition theorem**, the average energy of each term is $\frac{1}{2}kT$, where *k* is the Boltzmann constant. Therefore, the mean energy of the atoms is $\frac{3}{2}kT$ and the total energy of the gas (there being no potential energy contribution) is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$. We can therefore write

$$U_m = U_m(0) + \frac{3}{2}RT \qquad \text{(B)}$$

Monatomic Gas (B)

where $U_m(0)$ is the molar internal energy at *T*=0, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of atoms. This equation shows that the internal energy of **a perfect gas** increases linearly with temperature.

(Only in Classical Physics)

Since the heat capacity at constant volume is:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{(C)}$$

the heat capacity of a monatomic perfect gas can be calculated by inserting the equation (B) into equation (C). That is,

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_m = \frac{3}{2}R \qquad \text{(D)}$$

For a linear molecule, we must consider rotational contributions in addition to translational contributions. Linear molecule has two rotational modes of motion, each contributing a term $\frac{1}{2}kT$ to the internal energy.

$$U_m(T) = U_m(0) + \frac{5}{2}RT$$

Chap. 0

Quantized Energy Level

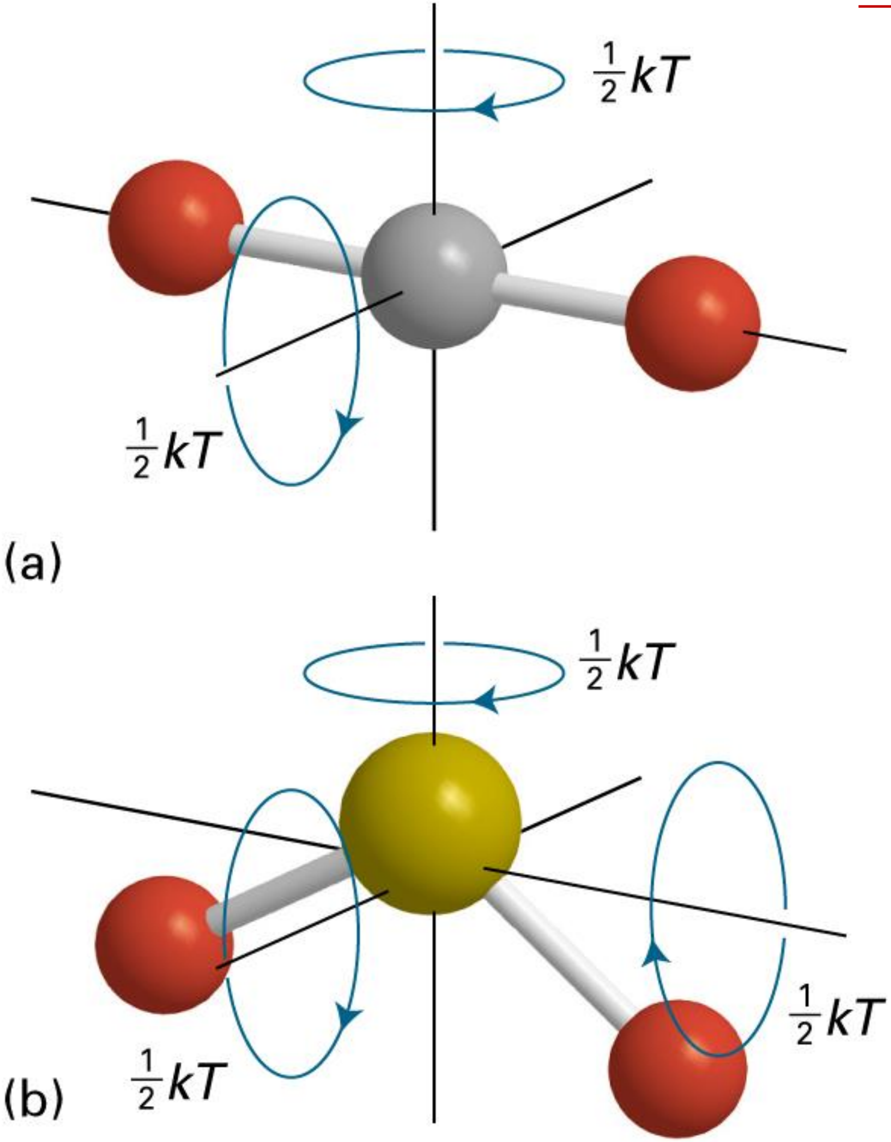
Fig. A.2

Translation < Rotation < Vibration < Electronic

Fig. B.3

(Ideal Gas)

Equipartition Theorem



$$U_m(T) = U_m(0) + \frac{5}{2}RT$$

Fig. A.2 A non-linear molecule can rotate around three axes and therefore the mean rotational energy is $\frac{3}{2}kT$, and there is a rotational contribution of to the molar internal energy.

$$U_m(T) = U_m(0) + 3RT$$

(Only in Classical Physics)

For any kind of expansion of any kind of material, the work done on the system as it changes from V_i to V_f is given by

$$w = -\int_{V_i}^{V_f} p_{ex}\, dV$$

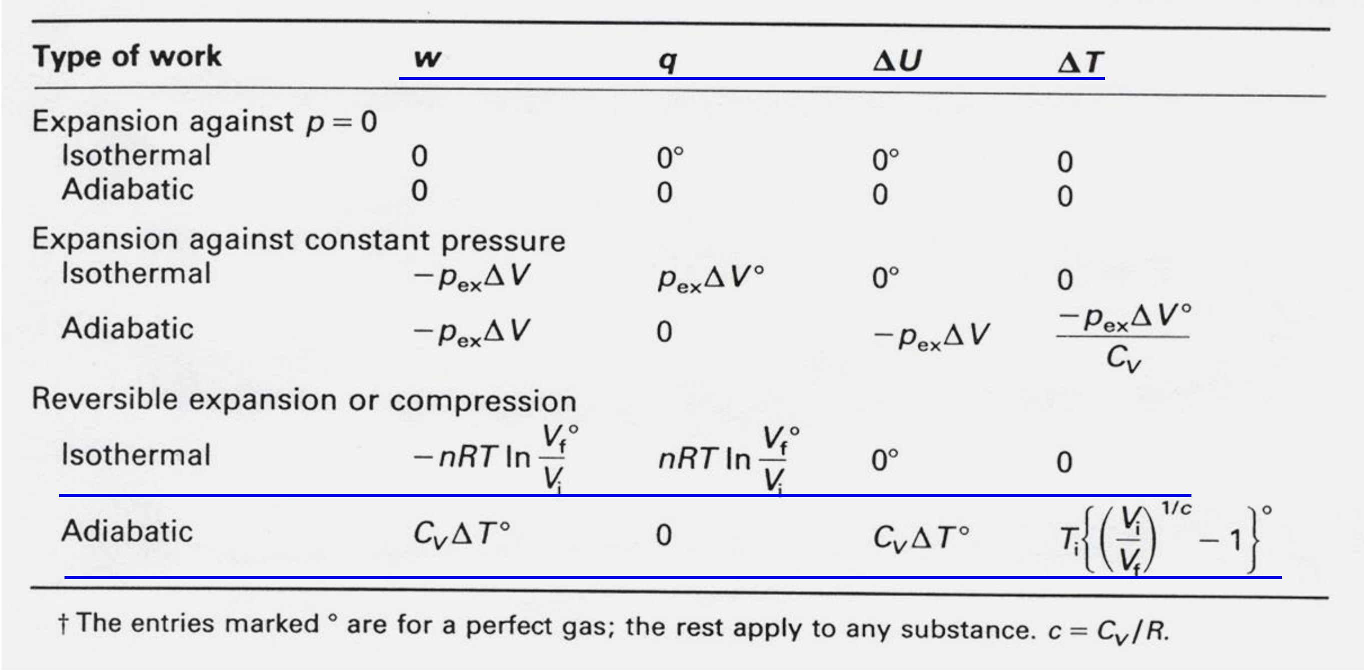
where p_{ex}, the external pressure, depends upon how the change is organized.

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

0 **0** ***ideal gas***

isothermal

(Ideal Gas)



Type of work	w	q	ΔU	ΔT
Expansion against $p = 0$				
Isothermal	0	0°	0°	0
Adiabatic	0	0	0	0
Expansion against constant pressure				
Isothermal	$-p_{ex}\Delta V$	$p_{ex}\Delta V^\circ$	0°	0
Adiabatic	$-p_{ex}\Delta V$	0	$-p_{ex}\Delta V$	$\frac{-p_{ex}\Delta V^\circ}{C_V}$
Reversible expansion or compression				
Isothermal	$-nRT \ln \frac{V_f^\circ}{V_i}$	$nRT \ln \frac{V_f^\circ}{V_i}$	0°	0
Adiabatic	$C_V \Delta T^\circ$	0	$C_V \Delta T^\circ$	$T_i\left\{\left(\frac{V_i}{V_f}\right)^{1/c} - 1\right\}^\circ$

† The entries marked ° are for a perfect gas; the rest apply to any substance. $c = C_V/R$.

2C Thermochemistry (p. 80)

ΔH : + or -

Thermochemistry: the study of the heat produced or required by chemical reaction

Reaction enthalpy $\Delta U = \Delta Q_V, \quad \Delta H = \Delta Q_p$

2C.1 Standard Enthalpy Changes

Absolute enthalpies of substances are not known. Still, enthalpies relative to an arbitrary standard state may be used, provided the same standard state is used for the reactants and products.

The standard enthalpy change, ΔH^o: the change in enthalpy for a process in which the initial and final substances are in their standard states. Here the standard state of some substance is its most stable form **under 1 *bar* (≈ *atm*) and at the temperature specified**.

***Reactant* (*Equilibrium or Metastable*) + ΔH → *Product* (*Equilibrium*)**

Examples of standard enthalpy change

1. standard enthalpy of **Vaporizatoin**

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H^\circ_{vap}(373K) = +40.66 kJ/mol$

2. standard **Reaction** enthalpy

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ(298K) = -890 kJ/mol$

Enthalpies of physical changes

1. standard enthalpy of **Vaporization** ΔH°_{vap}
2. standard enthalpy of **Fusion**

~0.5 eV/atom

$Si(s) \rightarrow Si(l)$ $\Delta H^\circ_{fus}(273K) \approx +50 kJ/mol$

3. standard enthalpy of **Sublimation**

$C(s, \text{graphite}) \rightarrow C(g)$ $\Delta H^\circ_{sub}(298K) = +716.69 kJ/mol$

Reactant (Equilibrium or Metastable) + ΔH → Product (Equilibrium)

A change in **enthalpy** is **independent of the path** between the two states:

$$\mathrm{A}(s) \rightarrow \mathrm{A}(g) \qquad \Delta H^{\circ}_{sub}(T)$$

$$\mathrm{A}(s) \rightarrow \mathrm{A}(l) \qquad \Delta H^{\circ}_{fus}(T)$$

$$\mathrm{A}(l) \rightarrow \mathrm{A}(g) \qquad \Delta H^{\circ}_{vap}(T)$$

overall: $\mathrm{A}(s) \rightarrow \mathrm{A}(g)$

$$\therefore \Delta H^{\circ}_{sub}(T) = \Delta H^{\circ}_{fus}(T) + \Delta H^{\circ}_{vap}(T)$$

A consequence of ***H*** being **a state function** is that the standard enthalpy of a forward process and its reverse must be equal and opposite:

$$\Delta H^{o}(\text{reverse}) = -\Delta H^{o}(\text{forward})$$

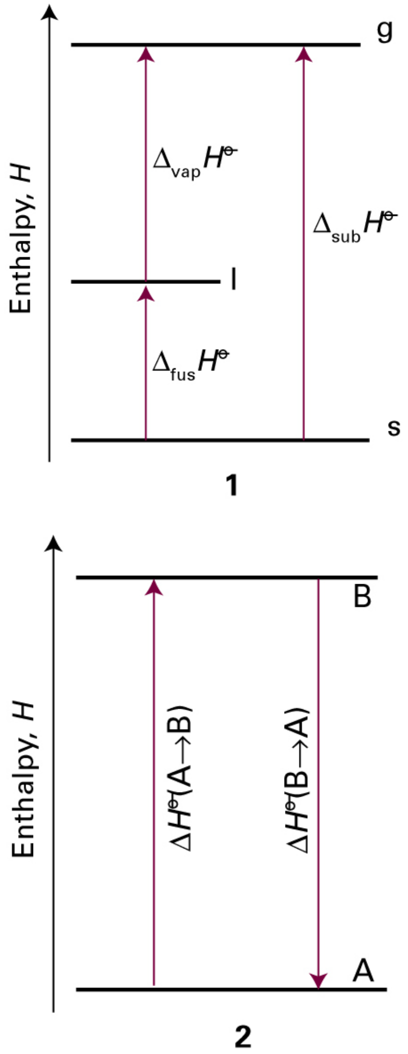


Fig. 2C.1

2C.1(b) Enthalpies of Chemical Changes

1. standard enthalpy of combustion ΔH_c°

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta H_c^\circ(298K) = -2{,}808 kJ/mol$$

Glucose 포도당

2. enthalpy of hydrogenation

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3 \quad \Delta H^o(298\text{K}) = -132 \text{ kJ/mol}$$

$$\text{Benzene} + 3H_2 \rightarrow C_6H_{12} \quad \Delta H^o(298\text{K}) = -246 \text{ kJ/mol}$$

$$|-246| < |-3\times132|$$

Why is the enthalpy of hydrogenation of benzene is less than the value of three times of enthalpy of hydrogenation of ethylene?

Because of resonance stabilization of benzene.

2C.1(c) Hess's Law

The enthalpy change of any reaction may be expressed as the sum of the enthalpy changes of a series of reactions into which the overall reaction may formally be divided.

$$\mathrm{CH_2{=}CH(CH_3)}(g)+\mathrm{H_2}(g) \rightarrow \mathrm{CH_3CH_2CH_3}(g) \qquad \Delta H^{o} = -124\ \mathrm{kJ/mol}$$

$$\mathrm{CH_3CH_2CH_3}(g)+5\mathrm{O_2}(g) \rightarrow 3\mathrm{CO_2}(g)+4\mathrm{H_2O}(l) \qquad \Delta H_c^{\circ} = -2220 kJ/mol$$

$$\mathrm{CH_2{=}CH(CH_3)}(g)+\frac{9}{2}\,\mathrm{O_2}(g) \rightarrow 3\mathrm{CO_2}(g)+3\mathrm{H_2O}(l) \qquad \Delta H_c^{\circ} = ?$$

$$\mathrm{CH_2{=}CH(CH_3)}(g)+\mathrm{H_2}(g) \rightarrow \mathrm{CH_3CH_2CH_3}(g) \qquad -124\ \mathrm{kJ/mol}$$

$$\mathrm{CH_3CH_2CH_3}(g)+5\mathrm{O_2}(g) \rightarrow 3\mathrm{CO_2}(g)+4\mathrm{H_2O}(l) \qquad -2220\ \mathrm{kJ/mol}$$

$$\mathrm{H_2O}(l) \rightarrow \mathrm{H_2}(g)+\frac{1}{2}\mathrm{O_2}(g) \qquad +286\ \mathrm{kJ/mol}$$

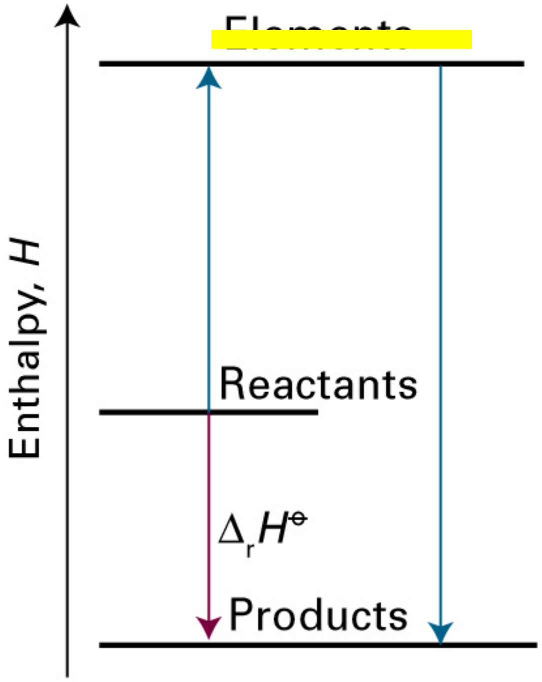
$$\mathrm{CH_2{=}CH(CH_3)}(g)+\frac{9}{2}\,\mathrm{O_2}(g) \rightarrow 3\mathrm{CO_2}(g)+3\mathrm{H_2O}(l) \qquad \Delta H_c^{\circ} = -2060 kJ/mol$$

$H\ (T,P,N_j)$: State Function ***Reversible***

Cohesive Energy ≈ Enthalpy of Formation ≈ Enthalpy of Sublimation

2C.2(a) Enthalpy of Formation

Reference Point



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The standard enthalpy of formation ΔH_f° of a substance is **the standard reaction enthalpy for its formation from elements** **in their reference states**.

$$6\mathrm{C}(\underline{s}, \underline{\mathrm{gr}}) + 3\mathrm{H}_2(\underline{g}) \rightarrow \mathrm{C}_6\mathrm{H}_6(\underline{l})$$

$$\Delta H_f^\circ(\mathrm{C}_6\mathrm{H}_6, l) = +49.0 kJ/mol$$

It is convenient to adopt the convention that the enthalpy of every element in its standard state is zero.

The reaction can be regarded as proceeding by decomposing the reactants into elements and then forming those elements into products.

Cohesive Energy ***= Energy required to form separate neutral atoms in their ground state from the solid at 0 K at 1 atm***

Si(*s*) = 4.6 eV/atom

Charles Kittel
“Introduction to Solid State Physics”

The reaction enthalpy in terms of enthalpies of formation

In general,

$aA+bB + \Delta H = cC+dD$

$\Delta H = cC+dD-aA-bB$

$$\Delta H^\circ = \{c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)\} - \{a\Delta H_f^\circ(\mathrm{A}) - b\Delta \mathrm{H}_f^\circ(\mathrm{B})\} \qquad \textbf{(2C.5a)}$$

$$\Delta H^\circ = \sum_J \nu_J \Delta H_f^\circ(J)$$

2C.3 The Variation of Enthalpy with Temperature

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad dH = C_p dT$$

$$C_p = C_p(T)$$

$$dH = C_p(T)dT$$

$$\therefore \underline{H(T_f) - H(T_i) = \int_{T_i}^{T_f} C_p(T)dT}$$

Reversible = Time Independent

This expression applies to every species involved in the reaction, and so the reaction enthalpies at T_f and T_i are related by the Kirchhoff's Law:

$$\Delta H(T_f) = \Delta H(T_i) + \int_{T_i}^{T_f} \Delta C_p(T)dT$$

(2.36)

where $\Delta C_p = \sum_J v_J C_{p,J} = (cC_{p,C} + dC_{p,D}) - (aC_{p,A} - bC_{p,B})$

for $aA + bB \rightarrow cC + dD$

$$\underline{\Delta H = H(\text{prod.}) - H(\text{react.})}$$

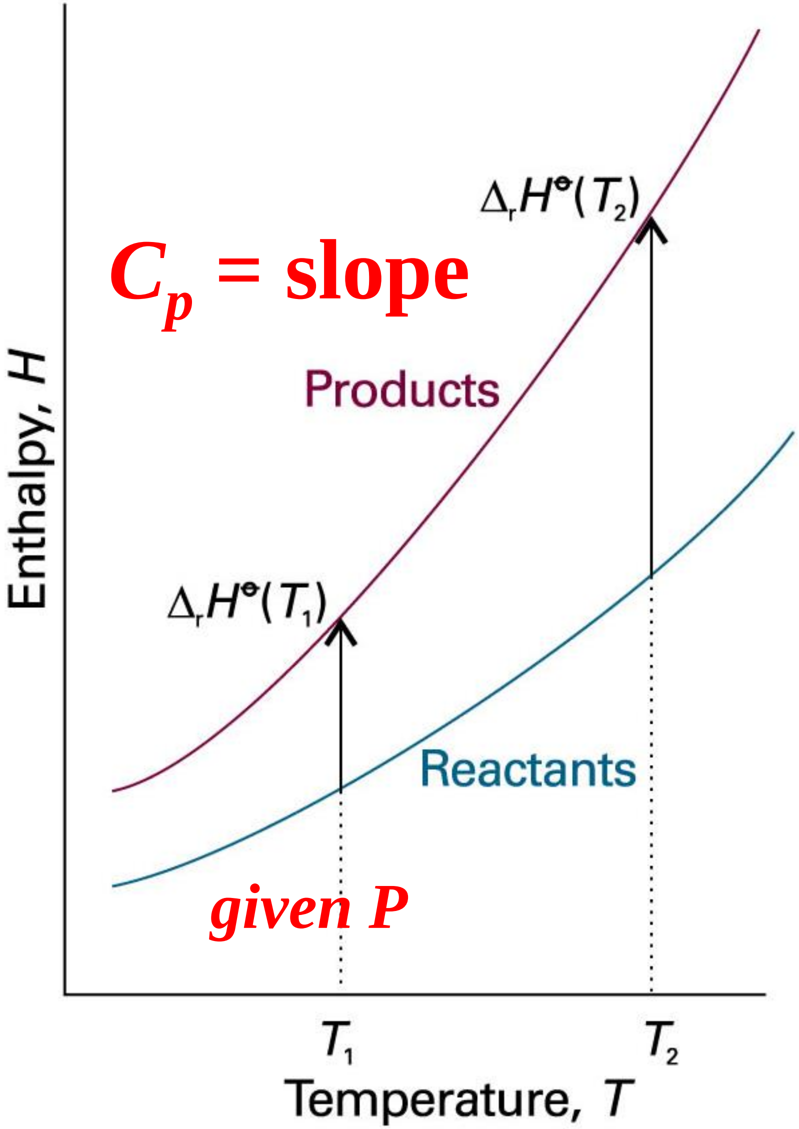


Figure 2C.2

An illustration of the content of Kirchhoff's law.

When the temperature increases, the enthalpies of the products and the reactants both increase, but may do so to different extents.

In each case, the change in enthalpy depends on the heat capacities of the substances.

The change in reaction enthalpy reflects the difference in the heat capacities.

$\Delta H = H$ (product) – H (reactant)

The Relation between ΔH and ΔU

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + [pV](\text{prod}) - [pV](\text{react})$$

For liquids and solids, $[pV](\text{prod}) - [pV](\text{react}) \approx 0.$

$$\therefore \Delta H \approx \Delta U$$

In the case of reactions involving gases, assuming that the gas behaves as an ideal gas, $pV=nRT$.

$$\begin{aligned}\Delta H &= \Delta U + pV(\text{prod}) - pV(\text{react})\\ &= \Delta U + nRT(\text{prod}) - nRT(\text{react})\end{aligned}$$

Since $\Delta n_{gas} = n_{gas}(\text{prod}) - n_{gas}(\text{react})$

$$\therefore \Delta H = \Delta U + \Delta n_{gas}RT$$

Ex. $CH_2{=}CH(CH_3)(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$

2D State Functions and Differentials (p. 90)

State Function: Properties that are determined only by the present state of the system, and are independent of how that state has been prepared.

e.g., internal energy, volume, pressure, temperature, density, refractive index, etc. **In Equilibrium**

Path Function: Properties that are related to what is happening to the system when changes are in progress.

e.g., work, heat, etc.

(p. 91)

Exact and Inexact Differentials

***U*, *V*: state function**

$$\int_a^b dU = U_b - U_a$$

Since the integral is path independent, the differential of a state function is called an **exact differential**.

***q*, *w*: path function**

The integrals of their differentials in going from state *a* to *b* depend upon the path chosen. Therefore, their differentials are called **inexact differentials**.

$$\int_a^b dw = w \neq w_b - w_a$$

$$\Delta U = \int_{U_i}^{U_f} dU = U_f - U_i$$

dU: complete or exact differential

$U(T,V)$

$U(T,P)$

or

$U(V,\varepsilon)$

$$q = \int_{path} dq$$

$d\,w$ or $d\,q$: incomplete or inexact differential

1. q is not a state function, and the heat added cannot be expressed in the form of $q_f - q_i$.
2. The path of integration should be specified because q depends on the path selected.

Example 2D.1 **(Reversible + Ideal Gas)** $T_{ex} = T_{in}$ $P_{ex} = P_{in}$

$T_i, V_i \rightarrow T_i, V_f$: Expansion of an ideal gas

1. Path 1: Free (reversible) expansion against zero external pressure.

2. Path 2: Reversible, isothermal expansion accompanied by the appropriate influx of heat

Find *w*, *q* and *dU* for each path.

Solution:

$$(path\,1)\;\; w = -p\Delta V = 0$$

$$(path\,2)\;\; w = -\int_{V_i}^{V_f} p\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\ln\frac{V_f}{V_i}$$

dU=0 for an expansion of an ideal gas **($T_i = T_f$)** $\because \left(\frac{\partial U}{\partial V}\right)_T = 0$

$$(path\,1)\;\; q = 0\;(\because q = -w)$$

$$(path\,2)\;\; q = nRT\ln\frac{V_f}{V_i}$$

칠판 그림 필요

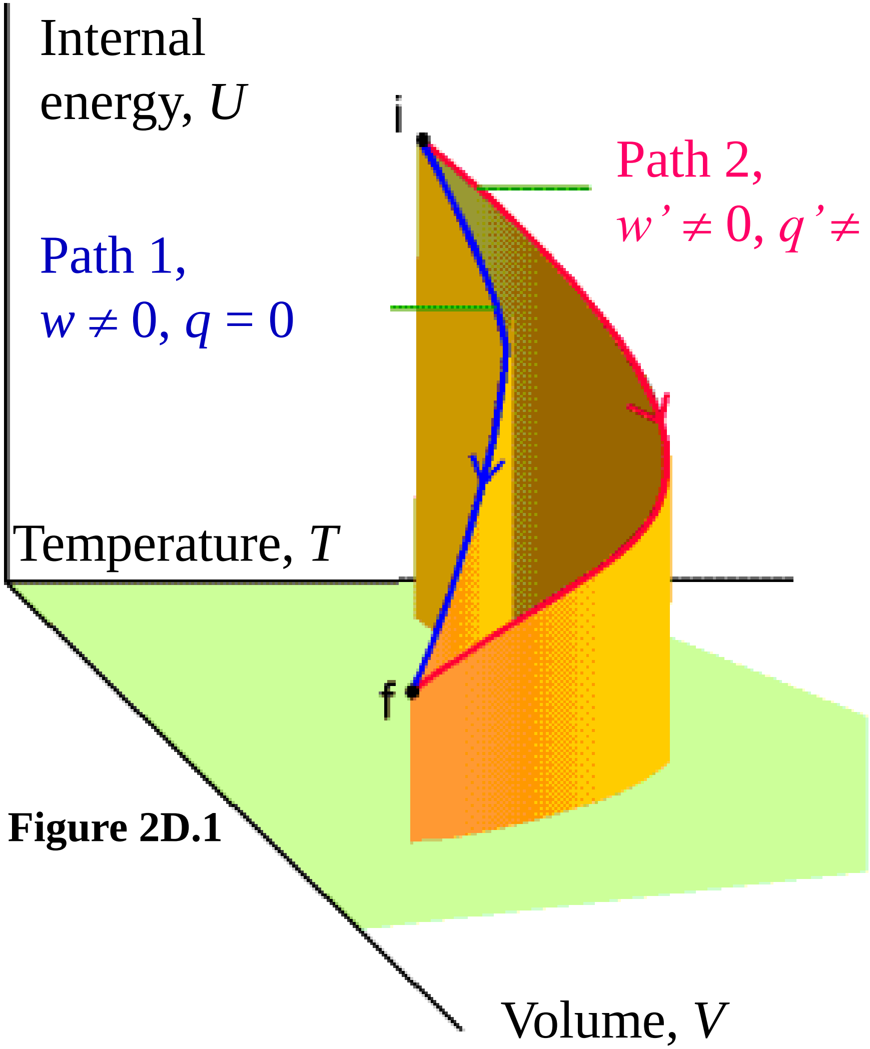


Figure 2D.1

$U(T,V)$ or $U(T,P)$

Figure 2D.1

As the volume and temperature of a system change, the internal energy changes.

An adiabatic and a non-adiabatic path are shown as path 1 and 2, respectively:

They correspond to different values of q and w, but to the same value of ΔU.

$$dU = đq + đw$$

The sum of two inexact differentials can be an exact differential.

-190325(월)

2D.2 Changes in Internal Energy *U*: *State Function*

$$U = U(V,T)$$

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

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

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

The internal energy at ($V + dV$, $T+dT$) differs from that at (V , T) by an infinitesimal amount, which we write dU.

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

The rate of change of the internal energy as the volume of the system is changed isothermally

$$\left(\frac{\partial U}{\partial V}\right)_T \equiv \Pi_T \qquad \text{(2D.4)}$$

Definition of 'internal pressure'

Manipulating the First Law

$$dU = dq + dw \quad U = U(V,T)$$

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

$$H = U + pV \quad H = H(T,p)$$

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

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

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

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

State Function

Exact differential

(2D.3)

(2D.13)

How the Internal Energy Varies with Volume

$$\left(\frac{\partial U}{\partial V}\right)_T \equiv \Pi_T$$

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

$$\Rightarrow \quad \left(\frac{\partial U}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}$$

the rate of change of volume with
increase of temperature

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

The isobaric thermal-expansion coefficient **(2D.6)**

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \alpha V \left(\frac{\partial U}{\partial V}\right)_T$$ **(2D.3)**

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

Definition of 'internal pressure'

$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_{\mathrm{T}} \qquad p = \frac{RT}{V_m - b} - \frac{a}{V_m{}^2}$$

$\left(\frac{\partial U}{\partial V}\right)_T$ is a measure of how the interactions change when the volume of the sample is changed isothermally.

This is supported by noting that the case of a van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

(derivation on ppt 2-60)

We expect that the coefficient is smaller for gases than for solids because we know that molecular interactions are not very important in gases.

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_\mathrm{T}$$

Definition of ‘internal pressure’

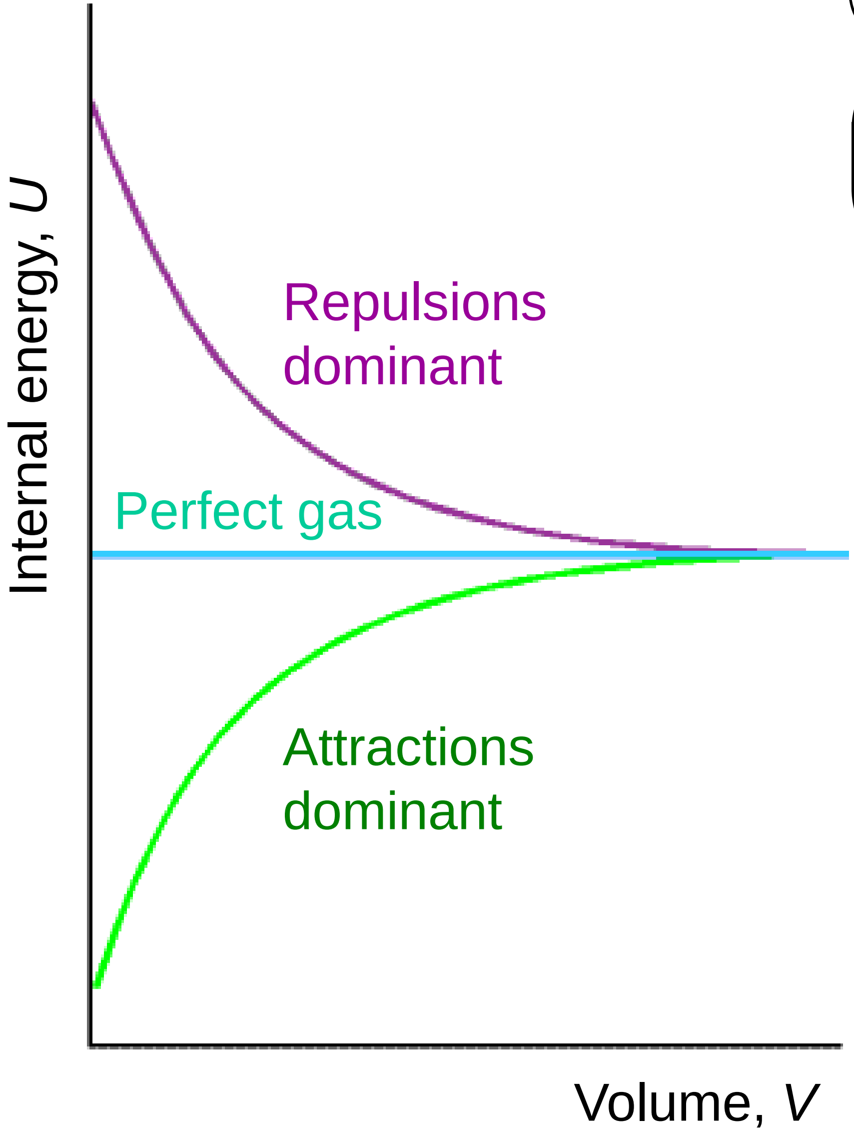


Figure 2D.4

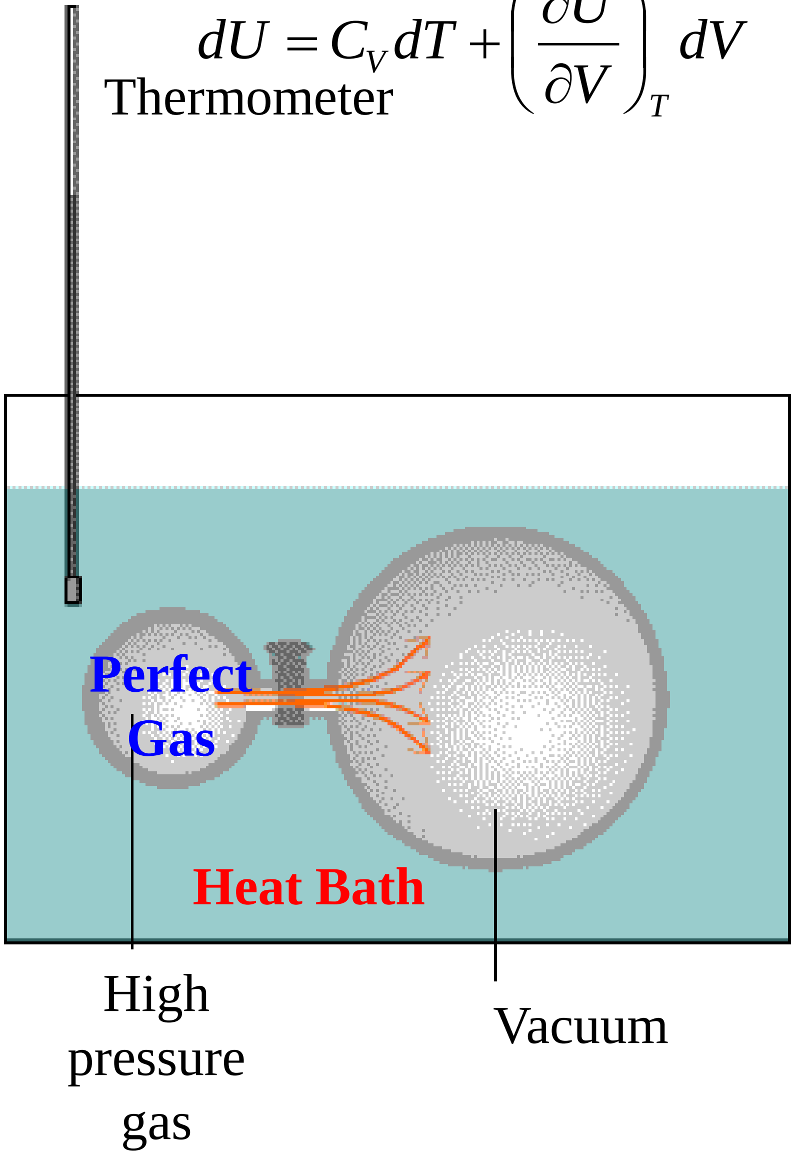
For a perfect gas, the internal energy is independent of the volume (at constant temperature).

If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become further apart on average.

If repulsions are dominant, the internal energy decreases as the gas expands.

$$dU = \delta q + \delta w$$

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



Problem:

Heat capacity of the apparatus is huge.

Joule Experiment

$w = 0$ (expansion into the vacuum)

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$ **Perfect Gas**

$$\Delta U = 0$$

$q = 0$ (The bath temp. does not change.)

Figure 2D.5

A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands into a vacuum.

The heat absorbed by the gas is proportional to the change in temperature of the bath.

He observed no change in temperature.

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

Exercise:

Will be proved in Chap. 3.

Use equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ to prove that $\left(\frac{\partial U}{\partial V}\right)_T$ of an ideal gas is zero: that is, evaluate the right-hand side using $p = \frac{nRT}{V}$.

Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for the van der Waals equation.

Solution:

For an ideal gas, $\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V} - p = p - p = 0$$

van der Waals Gas

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

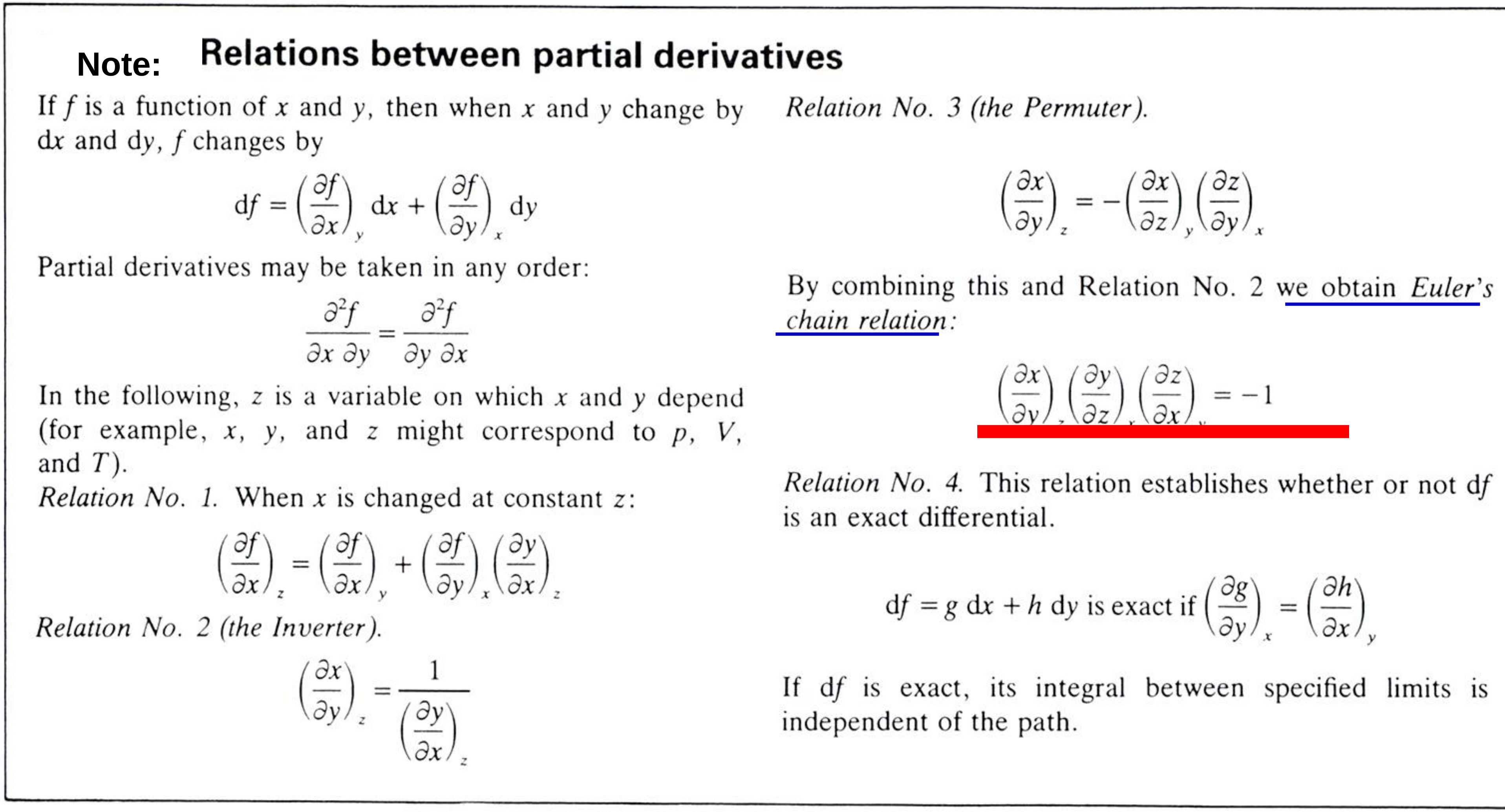
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m - b} \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{RT}{V_m - b} - p = \frac{RT}{V_m - b} - \frac{RT}{V_m - b} + \frac{a}{V_m^2} = \frac{a}{V_m^2}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$$

Definition of 'internal pressure'

The van der Waals constant *a* is directly related to the attractive forces between the molecules, as is the internal pressure.



Note:

Relations between partial derivatives

If f is a function of x and y, then when x and y change by $\mathrm{d}x$ and $\mathrm{d}y$, f changes by

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

Partial derivatives may be taken in any order:

$$\frac{\partial^2 f}{\partial x\,\partial y} = \frac{\partial^2 f}{\partial y\,\partial x}$$

In the following, z is a variable on which x and y depend (for example, x, y, and z might correspond to p, V, and T).

Relation No. 1. When x is changed at constant z:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Relation No. 2 (the Inverter).

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

Relation No. 3 (the Permuter).

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

By combining this and Relation No. 2 we obtain *Euler's chain relation*:

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

Relation No. 4. This relation establishes whether or not $\mathrm{d}f$ is an exact differential.

$$\mathrm{d}f = g\,\mathrm{d}x + h\,\mathrm{d}y \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

If $\mathrm{d}f$ is exact, its integral between specified limits is independent of the path.

2D.3 Temperature Dependence of Enthalpy

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

State Function

Exact differential

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

αV

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

Thermal-Expansion Coefficient

the change of volume under the influence of pressure at constant temperature

Isothermal Compressibility

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

Negative sign, because κ is convenient positively.

(2D.7)

2D.3 The Joule-Thompson Effect

Thermal-Expansion Coefficient

Isothermal Compressibility

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

$$\downarrow$$

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

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

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

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

How do you measure $\left(\frac{\partial T}{\partial p}\right)_H$? **(2D.13)**

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

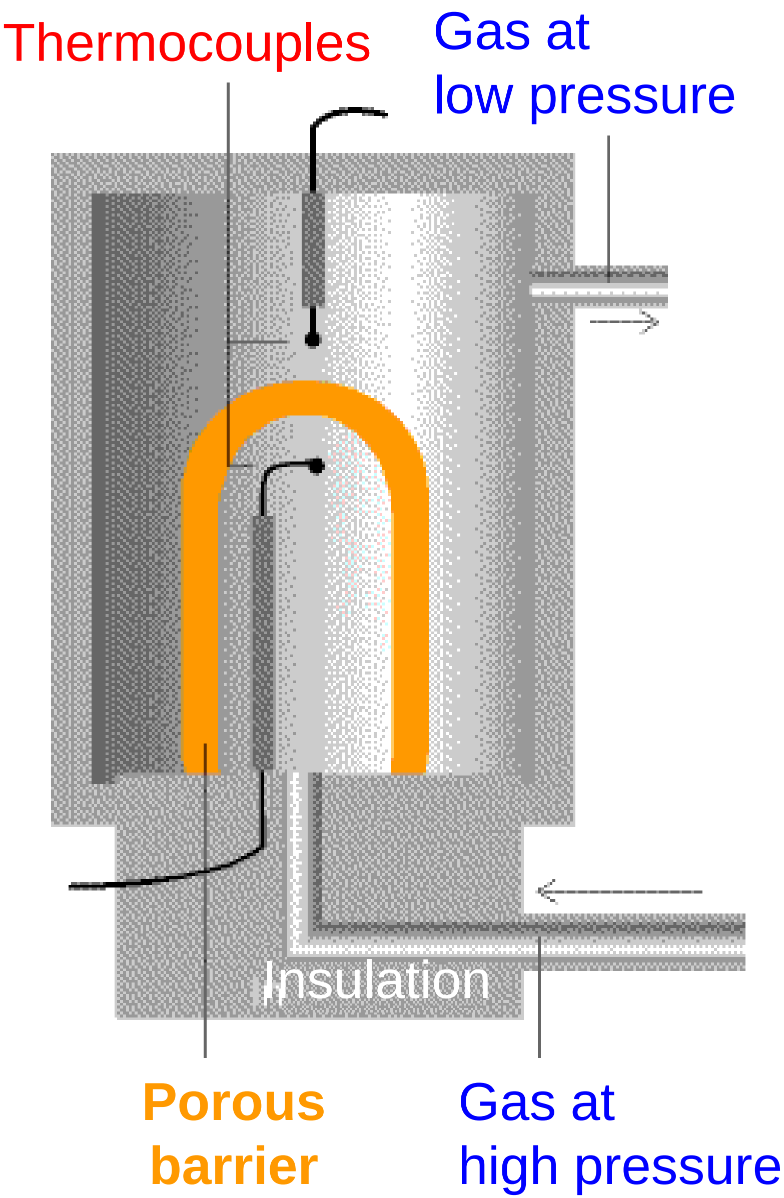


Figure 2D.6

A diagram of the apparatus used for measuring the Joule-Thomson effect.

The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated.

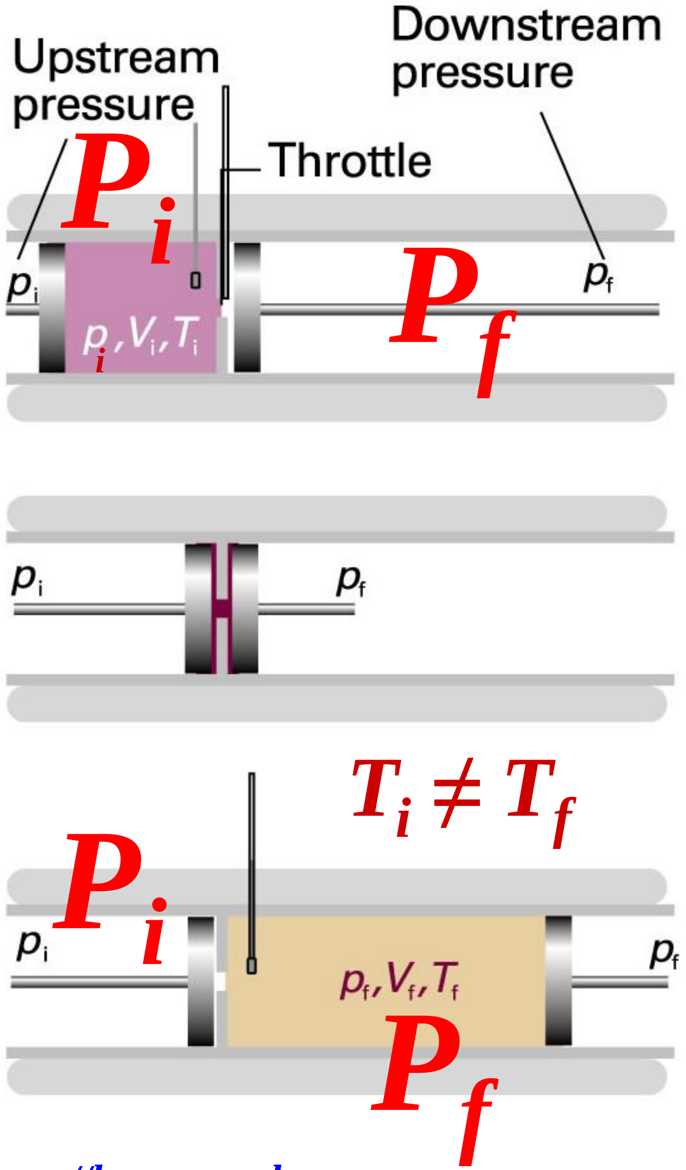
As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy)

Whether the expansion results in a heating or a cooling of the gas depends on the conditions.

Justification 2D.3 Joule-Thomson Effect

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

$$\Delta q = 0$$



~~isothermal~~ compression: the work done on the gas (left side) $= -p_i(0 - V_i) = p_i V_i$

~~isothermal~~ expansion: the work done on the gas (right side) $= -p_f(V_f - 0) = -p_f V_f$

the total work on the gas $= p_i V_i - p_f V_f$

∴ the change in internal energy

$$U_f - U_i = p_i V_i - p_f V_f$$

$$\therefore \underline{U_f + p_f V_f = U_i + p_i V_i}$$

$\therefore H_f = H_i$ (no change in enthalpy, isenthalpic)

Figure 2D.7 A diagram representing the thermodynamic basis of Joule-Thomson expansion. The pistons represent the upstream and downstream gases, which maintain **constant pressures** either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \quad : \text{Joule-Thompson coefficient} \qquad \left(\frac{\partial T}{\partial p}\right)_H ? \qquad \textbf{(2D.14)}$$

$\mu_{JT} > 0$: if $dT < 0$ and $dp < 0$, the gas cools on expansion.

(skip) $\mu_{JT} < 0$: if $dT > 0$ and $dp < 0$, the gas is heated by expansion.

Gases showing heating effects ($\mu_{JT} < 0$) show a cooling ($\mu_{JT} > 0$) effect when their temperature has been lowered beneath their inversion temperature.

Below its inversion temperature a gas is cooled on expansion. For a sufficiently large pressure drop, the cooling may drop the temperature below the boiling point of the gas, when the liquid will form. This principle is applied to making refrigerator.

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_H C_p = -\mu_{JT} C_p$$

$$\left(\frac{\partial H}{\partial T}\right)_V = C_p + \left(\frac{\alpha}{\kappa}\right)\left(\frac{\partial H}{\partial p}\right)_T = C_p + \left(\frac{\alpha}{\kappa}\right)\left(-\mu_{JT} C_p\right) \qquad \textbf{(2D.15)}$$

$$= \left(1 - \frac{\alpha \mu_{JT}}{\kappa}\right) C_p$$

(skip)

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

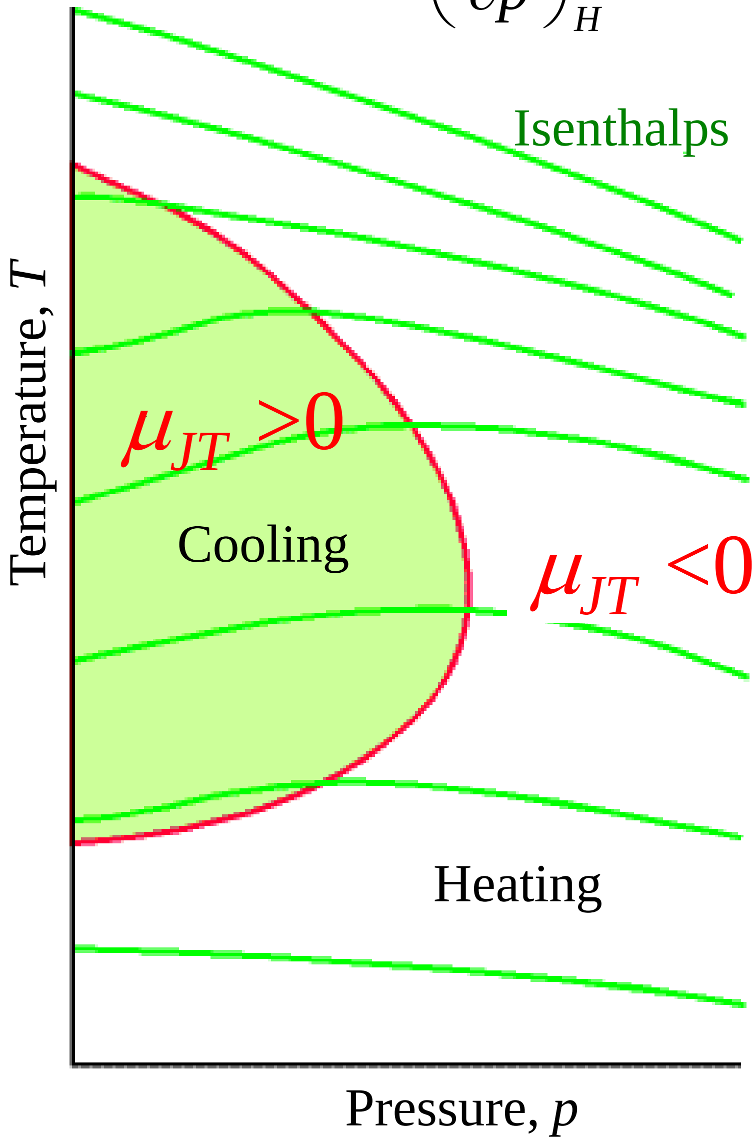


Figure 2D.10

The sign of the Joule-Thomson coefficient, μ_{JT}, depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the inversion temperature of the gas at that pressure.

For a given pressure, the temperature must be below a certain value if cooling is required. However, if it becomes too low, the boundary is crossed again and heating occurs.

Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy.

The inversion temperature curve runs through the points of the isenthalps where their slopes change from negative to positive.

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

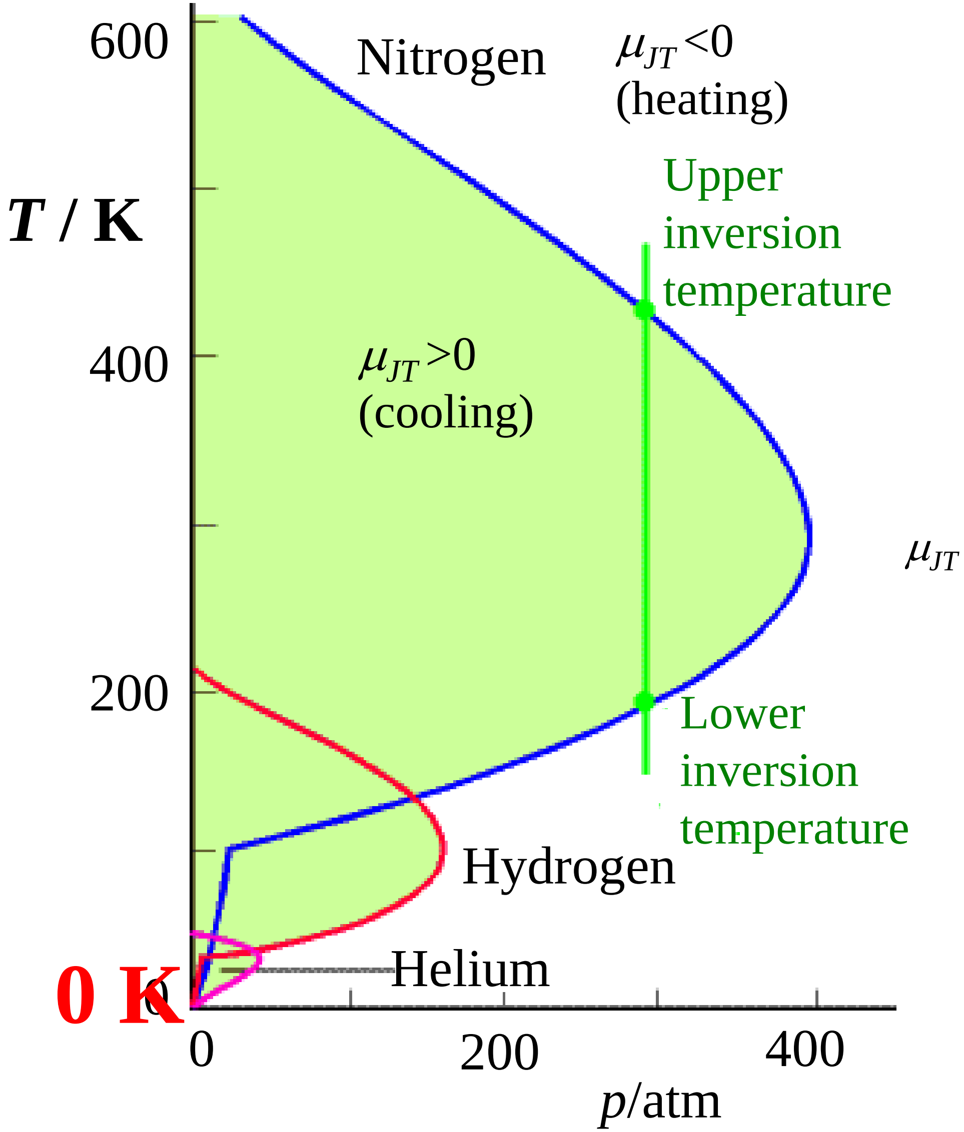


Figure 2D.11

The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.

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

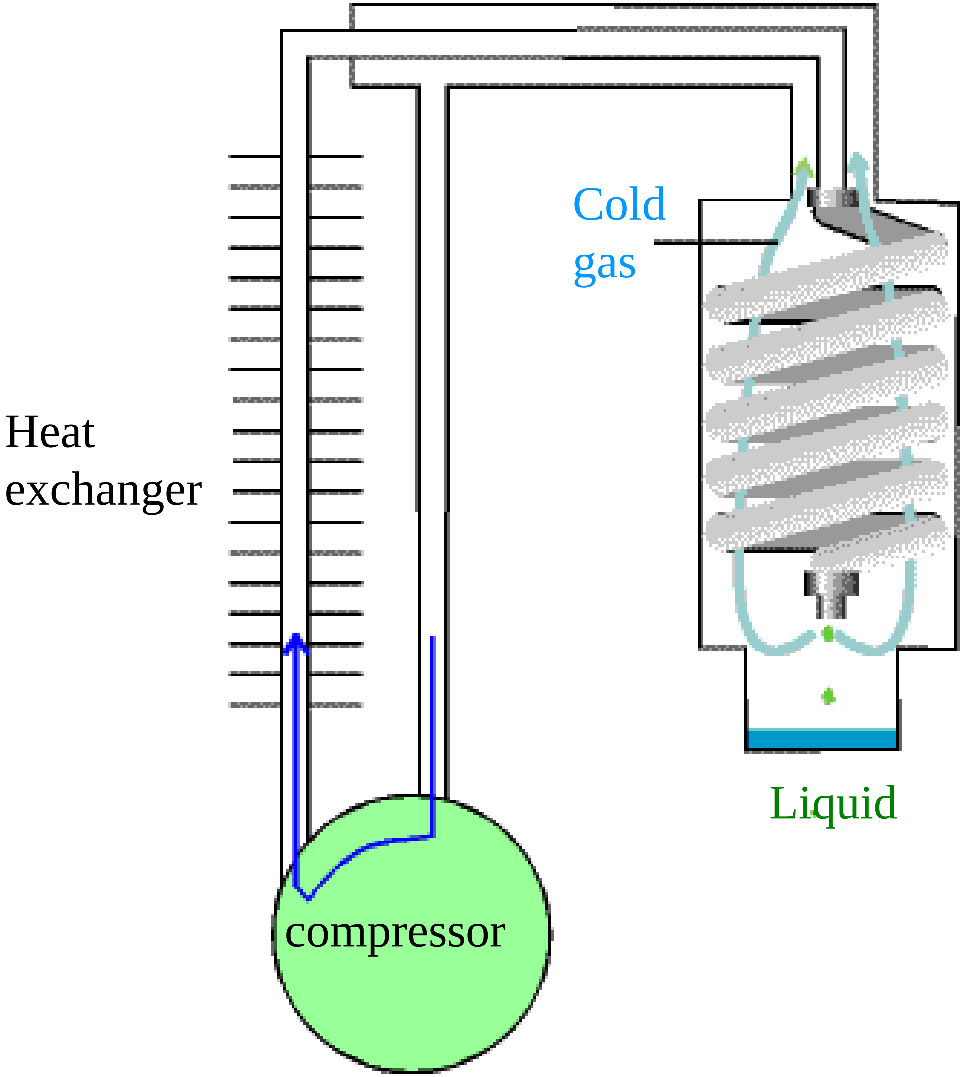


Figure 2D.12

The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated and, so long as it is beneath its inversion temperature, it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.

[Derivation on the white board]

The Exact Relation between C_V and C_p

ppt 2-23

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

$$H = U + pV$$

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

$$\left(\frac{\partial U}{\partial T}\right)_V \longrightarrow C_V$$

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

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

$$\therefore C_p - C_V = \alpha V\left(\frac{\partial U}{\partial V}\right)_T + p\alpha V$$

$$= \alpha V\left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\}$$

Definition of 'internal pressure'

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

thermal-expansion coefficient

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

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

(Derivation in Chap. 3) **ppt 2-59**

↓

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

ppt 2-63

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

thermal-expansion coefficient

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

compressibility

$$\begin{aligned}
\therefore C_p - C_V &= \alpha V\left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \\
&= \alpha V\left\{p + T\left(\frac{\partial p}{\partial T}\right)_V - p\right\} \\
&= \alpha V T\left(\frac{\partial p}{\partial T}\right)_V = \alpha V T\left(\frac{\alpha}{\kappa}\right)
\end{aligned}$$

$$\underline{C_p - C_V = \left(\frac{\alpha^2}{\kappa}\right) T\, V}$$

General

For an ideal gas, $pV = nRT$.

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

thermal-expansion coefficient

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

compressibility

$$\therefore C_p - C_V = \left(\frac{\alpha^2}{\kappa}\right)TV = \frac{\frac{1}{T^2}}{\frac{1}{p}}TV = \frac{p}{T^2}TV = \frac{nRT}{T} = nR$$

Problems from Chap. 2

2A.2(b) 2A.3(b) 2A.4(b) 2A.4

2B.2 2B.3(b) 2B.4

2C.1(b) 2C.3(b) 2C.7(b)

2D.3(b) 2D.4(b) 2D.4

2E.2(b) 2E.3(b)