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CHEM 254 Course Notes
Introduction to Chemical Thermodynamics

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Abstract

These notes are intended as a resource for myself; past, present, or future students of this course, and anyone interested in the material. The goal is to provide an end-to-end resource that covers all material discussed in the course displayed in an organized manner. These notes are my interpretation and transcription of the content covered in lectures. The instructor has not verified or confirmed the accuracy of these notes, and any discrepancies, misunderstandings, typos, etc. as these notes relate to course's content is not the responsibility of the instructor. If you spot any errors or would like to contribute, please contact me directly.

1 January 7, 2019

1.1 Introduction of thermodynamics

Definition 1.1 (Thermodynamics)**. Thermodynamics** refers to the macroscopic scale: only bulk properties of matter (e.g. pressure, temperature, volume) are needed for a complete thermodynamic description.

Definition 1.2 (Statistical Thermodynamics)**. Statistical Theormodynamics**, also known as **Statistical Mechanics**, uses atomic and molecular properties to calculate therodynamic properties of bulk matter.
For example, heat capacity of substance is determined by available motional states of its constituent ules, such as rotational and vibrational states.

Example 1.1. Suppose initial temperature of a cup of coffee is $T_{initial} = 85C$.
The temperature would decay *exponentially* until it reaches the equilibrium temperature: the temperature of the room.
The temperature of the room would be trivially increased and thus can be treated constant.

1.2 Ideal gas law

For a gas, we need only three macroscopic variables: P (pressure), V (volume), and T (temperature).
We refer to a piston model: pressure is the force due to the mass pushing down on the piston divided by the area of the piston (force per area). Force in our piston model would simply be $F = mg$ where m is the mass of the weight and g is the gravitational constant $9.8s^{-2}$.
In **equilibrium** the external pressure P_{ext} is equivalent to the pressure of the gas P.
Note that for a given particle of the gas in equilibrium, the particle with momentum with component mv_x perpendicular to the piston should be reflected and repelled, ultimately travelling with $-mv_x$ momentum. This implies that $\Delta p_{wall} = 2mv_x$ (initial momentum absorbed and additional mv_x exerted onto particle to reflect it).
From statistical mechanics we know that $\frac{3}{2}kT = \frac{1}{2}mv^2$, so the higher the velocity the higher the temperature of the gas.
The total change in pressure of the wall is $\Delta p_{total} = 2mv_x N_{coll}$ where N_{coll} the number of colliding particles. This is simply

$$N_{coll} = \frac{\text{\# of particles}}{\text{total volume}} V_{coll} \frac{1}{2}$$

where the $\frac{1}{2}$ since half the particles are directed towards the wall and V_{coll} is the volume space for collisions.
$V_{coll} = Av_x \Delta t$ where A is the area of the wall and v_x is the velocity of the particles.
We let N be the number of particles per unit volume (our fraction above).
Thus we have

$$\Delta p_{total} = mNAv_x^2 \Delta t$$

Note that force simply change in momentum over change in time or

$$F_{wall} = \frac{\Delta p_{total}}{\Delta t} = mNAv_x^2$$

Finally pressure is simply the force divided by area thus

$$P_{wall} = mv_x^2 N$$

We observe that $v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$ so

$$P_{wall} = \frac{mv^2 N}{3}$$

Recall that $\frac{3}{2}kT = \frac{1}{2}mv^2$ so $mv^2 = 3kT$ therefore

$$P_{wall} = NkT = \frac{nN_A kT}{V}$$

where N_A is Avogadro's number (number of particles per mole) and n is the number of moles. If we define $N_A k = R$ to be the **ideal gas constant**, we note that this is exactly the **ideal gas law**

$$P = \frac{nRT}{V}$$

2 January 9, 2019

2.1 Definition of a system

We can define the **type of a system** in terms of how it exchanges energy and matter:

Type	Exchange of energy	Exchange of matter
isolated	no	no
open	yes	yes
closed	yes	no

NB: it is not possible to exchange matter without exchanging energy.
Some examples include

System	Type
animal	open
airtight room containing beaker with boiling water	closed
incadescent light bulb	closed
lake	open
greenhouse	closed
the earth	open

2.2 Properties of barriers

There are certain properties of barriers we care about:

moveable vs rigid allow/not allow P, V to change

adiabatic vs diathermal thermally insulating vs thermally conducting

permeable vs impermeable allow/not allow transport of matter

In order from most adiabatic to most diathermal, we have **vacuum**, **cork**, **glass**, **copper**.

2.3   Equilbriums

We define **thermal equilibrium** when two systems A, B are at the same temperature i.e. $T_A = T_B$ (e.g. two closed systems in thermal contact).
We define **thermodynamic equilbrium** when $T_A = T_B$, $P_A = P_B$ and $x_A = x_B$ where x_j is the mole fraction (concentration) (e.g. two open systems in contact).
Once equilbrium is established systems do not spontaneously "unequilibriate".
The **Zeroth law of Thermodynamics** states that if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$ i.e. two systems that are separately in thermal equilibrium with a third system are also in thermal equilbrium with each other.
Examples of equilbriums reached for two systems $1, 2$ wherein all properties are not equivalent:

rigid, diathermal, impermeable wall $T_1 = T_2$ but $P_1 \neq P_2$ and $x_1 \neq x_2$

movable, adiabatic, impermeable wall $P_1 = P_2$ but $r_1 \neq T_2$ and $x_1 \neq x_2$

permeable, rigid, diathermal wall $T_1 = T_2$, $P_1 \neq P_2$, $x_1 \neq x_2$ (depends on which species it is permeable to)

2.4   Partial pressure

For a mixture of (ideal) gases, the total pressure is simply the sum of the partial pressures:

$$P = \sum_i P_i = \sum_i \frac{n_i RT}{V}$$

Note that since $\frac{P_i}{P} = \frac{n_i}{n} = x_i$ (mole fraction) we have $P_i = x_i P$. This assumes that the pressures of the individual gases are independent.
For real gases, the **van der Walls** equation of state tries to approximate the ideal gas law for real gases

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

where a account for the attractive interaction and b accounts for the finite molecular size (determined empirically).

3   January 11, 2019

3.1   Ideal gas law examples

Example 3.1 (Q1.14)**.** Note the mass of a He atom is smaller than that of an Ar atom. At the same molar density, volume, and temperature, does the Ar gas exert more pressure than the He gas?

Answer. No, they exert the same pressure. We know that from statistical mechanics ($kT = mv_x^2$) for a fixed temperature the Ar atoms would have a lower velocity squared.
Therefore the pressure is solely determined by temperature not by the mass and thus the ideal gas law applies to any (ideal) gas regardless of atomic/molecular species.

Example 3.2 (Q1.3)**.** Give an example of based on molecule-molecule interactions illustrating how the total pressure upon mixing two *real* gases could be different from the sum of partial pressures.

Answer. If molecules from two gases form **hydrogen bonds** (attractive interaction) then total pressure will be *lower* than sum of partial pressures (and vice versa for repulsive interactions).

Example 3.3 (P1.5). There is a gas mixture of ethane and butane in a sealed container having $230 cm^3$ capacity filled to a pressure of $97.5 \times 10^3 Pa$ at $23.1 C$. If the total mass of the gas is $0.3554 g$ what is the mole % of butane in the mixture?

Solution. Note that $n = n_1 + n_2 = \frac{PV}{RT} = 9.1 \times 10^{-3} mol$ where n_1 and n_2 are the number of moles of ethane and butane, respectively.
We also know that $n_1 M_1 + n_2 M_2 = 0.3554 g$. Solving the system of two equations (two unknowns) we have

$$n_2 = \frac{9.1 \times 10^{-3} mol - \frac{0.3554 g}{M_1}}{1 - \frac{M_2}{M_1}} = 2.915 \times 10^{-3} mol$$

Therefore the mol % of butane is $\frac{n_2}{n_1 + n_2} = 0.32$ or 32%.

Example 3.4 (P1.29). A balloon filled with $11.5 L$ of Ar at $18.7 C$ and $1 atm$ rises to height in the atmosphere where pressure is $207 Torr$ and the temperature is $-32.4 C$. What is the final volume of the balloon? Assume pressure inside and outside are the same.

Solution. Note that

$$\frac{P_i V_i}{P_f V_f} = \frac{nRT_i}{nRT_f}$$

$$\Rightarrow V_f = \frac{P_i T_f}{P_f T_i} V_i$$

where $T_i = 18.7 C = 291.9 K$, $T_f = -32.4 C = 240.8 K$, $P_i = 1 atm$, $P_f = 207 Torr = 0.272 atm$. Solving for V_f we get $34.8 L$.

3.2   First law of thermodynamics

The **first law of thermodynamics** states that the *internal energy U* of an *isolated system* is **constant**: energy is conserved.
That is isolated system = system of interest + surroundings where

$$\Delta U_{total} = \Delta U_{system} + \Delta U_{surroundings} = 0$$
$$\Rightarrow \Delta U_{system} = -\Delta U_{surroundings}$$

3.3   Energy, work and heat

Note **energy** can be thought of as capacity of one physical system to do **work** on another physical system. **Work** is defined as

$$w = \int_{y_i}^{y_f} \vec{F} \cdot d\vec{y}$$

one can always model work as raising a mass m up or down in Earth's gravitational field by height Δh or $mg\Delta h$. For example, a gas expanding and moving a piston of mass m of area A up (which exerts $P_{external} = \frac{mg}{A}$) does work

$$w = \int_{y_i}^{y_f} \vec{F} \cdot d\vec{y} = -\int_{y_i}^{y_f} P_{external} A \, dy = -\int_{y_i}^{y_f} P_{external} \, dV = -mg\Delta y$$

Where did the energy come from to do the work? This may be from a heat source that heated up the gas to cause it to expand.

Heat is defined as the energy that flows across the system/surrounding boundary because of a *temperature difference* between the system and surroundings.

Remark 3.1. Work is the transfer of energy as a result of force acting *through a distance.*

Note that both **heat** and **work** are **transitory**: in equilibrium states one cannot quantify heat or work but only the energy.

Restating the first law, we note that beyond chemical reactions, the change in internal energy is only a function of work and heat:

$$\Delta U = \Delta U_{system} = q + w = -\Delta U_{surroundings}$$

where q is the heat and w is the work associated with a process.

Note that $q > 0$ is when the system temperature is **raised** and $w > 0$ denotes work done **on the system**.

4　January 14, 2019

4.1　Calculating work (at constant P, V, T) example

Note the following terms are used for descripting constant properties:

isochoric constant volume

isothermal constant temperature

isobaric constant pressure

Example 4.1. A 1.5 mole sample of ideal gas at $28.5C$ exapnds isothermally from an initial volume of $22.5dm^3$ to a final volume of $75.5dm^3$. Calculate w for this process for expansion against an external pressure of $0.498 \times 10^5 Pa$

Solution. Note that $P_{external}$ is constant to integrating over the change in volume we have

$$w = -P_{external}(V_f - V_i) = -0.498 \times 10^5 Pa(75.5 - 22.5) \times 10^{-3} m^3 = -2.64 \times 10^3 J$$

(NB: $dm = 10^{-1}m$ so $(dm)^3 = 10^{-3}m^3$).

4.2　Heat capacity

How much does a certain heat flow change affect the temperature of a system? We define

$$\begin{aligned} C &= \lim_{\Delta T \to 0} \frac{q}{T_f - T_i} \\ &= \frac{dq}{dT} \end{aligned}$$

C is an **extensive** property (depends on molar amount), so usually the *molar heat capacity C_m* (units $JK^{-1}mol^{-1}$) (**intensive**) is used in calculations. Note that $C = C(T)$ in general depends on *temperature.*
C depends on the material and on the conditions which it is measured. We define

$C_{V,m}$ molar heat capacity at constant volume

$C_{P,m}$ molar heat capacity at constant pressure

We can calculate heat flow into/out of a system at constant volumes or pressures e.g.

$$q_P = \int_{T_i}^{T_f} C_P(T)\, \mathrm{d}T$$

$$q_V = \int_{T_i}^{T_f} C_V(T)\, \mathrm{d}T$$

Let us look at the **microscopic origin** of heat capacity. A small molecule have a number of ways to store energy/heat:

1. Putting electrons into higher energy levels (quantum mechanical excited states)

2. Vibration (CO (carbon monoxide) has one vibrational degrees of freedom (DOF), stretch along bond axis)

3. Rotation (CO has two rotation DOFs: rotation axes perpendicular to bond axis)

4. Translate (3 DOFs)

Energy can be stored into each DOF. Each DOF of translate and rotation contributes $\approx R/2$ heat capacity (R is the ideal gas constant). For vibration, if $\frac{\Delta E}{kT} < 0.1$ (low excitation) then it contributes $\approx R$; if $\frac{\Delta E}{kT} > 10$ then it contributes ≈ 0 heat capacity (high energy excitation).

For energy states, we know that the relative probability of being in state i and j is

$$\frac{Pr(E_i)}{Pr(E_j)} = e^{-\frac{E_i - E_j}{kT}}$$

notice that if $E_i \approx E_j$ then $Pr(E_i) \approx Pr(E_j)$.

Molecules exchange energy by **collisions** where a colliding molecule gain or loses $\approx kT$ energy.

4.3   Heat transfer for isothermal ideal gases

Note that ΔU is proportional to ΔT so in an isothermal process $\Delta T = 0$ thus $\Delta U = 0$. If work is done by an ideal gas e.g. expansion) then we know that $q = \Delta U - w \neq 0$.

So while a process is isothermal and $\Delta T = 0$, $q \neq 0$ (for an ideal gas) since heat is transferred from an external thermal reservoir to maintain the temperature.

4.4   Heat capacity vs temperature and phase

For solids, it is much easier to measure $C_{P,m}$. Note that in the solid-state energy can be taken up in **lattice vibrations (phonons)**. As temperature increases the number of phonon states *increases*.

Liquids have even a greater heat capacity: in addition to local vibrational modes it also has additional *low energy modes* and more degrees of freedom.

$C_{P,m}$ drops for gas since a lattice no longer exists (no phonons).
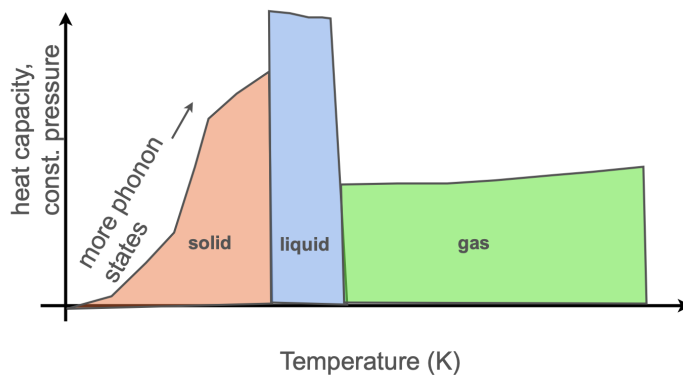
4.5 Difference in C_P and C_V for a gas

At *constant pressure*, work is done on the surrounds where $\Delta U = q + w$ (piston can move). On the contrary at *constant volume*, no work is done so $\Delta U = q$, so the energy is transferred into heat that is stored in the molecules. In other words for a given heat flow dq we have $dT_P < dT_V$ (change in temperature when pressure is constant is less than change in temperature when volume is constant).

We must conclude that $C_P > C_V$ (we will prove that $C_{P,m} - C_{V,m} = R$ for an ideal gas).

4.6 Heat capacity example

Example 4.2. An electric motor connected to drilling machinery can heat $11.6kg$ of ice water $(T = 273K)$ to $T = 355K$ in 2.5 hours. Assuming the same rate of work how high could the same motor raise a $225kg$ weight in 2.5 minutes? Assume the heat specific heat capacity of water is $4.18JK^{-1}g^{-1}$.

Solution. We first calculate the rate of energy from the motor

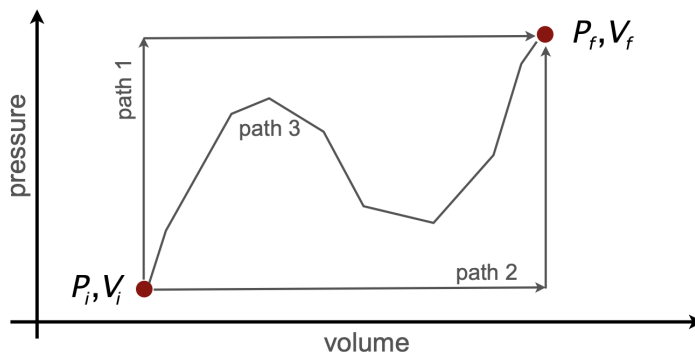$$\text{rate(energy/s)} = \text{power} = \frac{C_P m_{H_2O} \Delta T}{2.5 \text{hours}} = 442Js^{-1}$$

now relating the work done in 2.5 minutes to the potential of gravity

$$mgh = 442Js^{-1} \cdot 150s \Rightarrow h = 30m$$

4.7 State functions vs path functions

A system can take many paths in moving from an initial state to a final state

A **state function** only depends on the initial and final states, *not* on the path taken.
For example, **internal energy** U is a **state function** where $U = U(P, V)$ and

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

If the second partial derivatives are symmetric

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial U}{\partial V}\right)_P\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial P}\right)_V\right)_P$$

it can be proven that dU is an exact *differential* where

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

thus U and ΔU are **state functions** (Note that U is not easily measureable whereas ΔU is).
Note that work w is a **path function** since we integrate over the change in volume of time $(w = -\int P_{ext}\, dV)$.
Consider path 1 and path 2 in the figure above:

$$\text{path 1: } w_1 = -\int P_{ext}\, dV = -P_f \delta V$$

$$\text{path 2: } w_2 = -\int P_{ext}\, dV = -P_i \delta V$$

since volume changes when $P_{ext} = P_f$ for path 1 and when $P_{ext} = P_i$ for path 2, thus $w_1 \neq w_2$.
Since w is not a state function, then q is not a state function since $q = \Delta U - w$.

5   January 16, 2019

5.1   Review of calculus

Coverage: integration, partial derivatives, and the **total differential**, defined as

$$df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy$$

As previously stated if the second partial derivatives are symmetric i.e. $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ then f is a **state function**.

6   January 18, 2019

6.1   Cyclic integrals

Note that there are no quantities q_i, q_f, w_i, w_f (initial and final states of heat or work) as discussed before (they are transitory).
We define the **cyclic integral** corresponding to a *cyclic path* where the initial state is equal to the final state.
Note that for any **state function** e.g. U its cyclic integral is always zero i.e.

$$\oint dU = 0$$

But the above *may not hold* for **path functions** like w or q i.e.

$$\oint \mathrm{d}w \neq 0 \qquad \oint \mathrm{d}q \neq 0$$

6.2   Specifying state functions P, V, T

Note that for any system of a fixed mass any state can be characterized by any two of the three P, V, T: e.g. internal energy U can be expressed as only $U(V, T), U(P, T)$ or $U(P, V)$.
This however does not hold for path functions like heat q or work w.

6.3   Reversibility

In thermodynamics we assume the system and surroundings are *separately* in **internal equilbrium** (otherwise they may not have unique values of P, V, T,etc.).
Hence any process we consider must be a **quasi-static process** i.e. the system moves through succession of equilbrium states.
We ask ourselves: are all such processes **reversible** i.e. can the system **and** surroundings return to the initial state)?
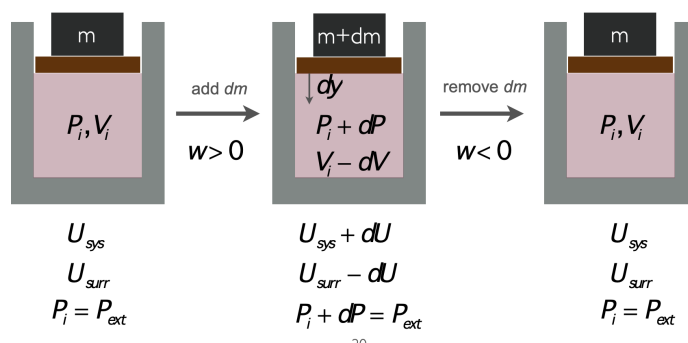

Figure 6.1: A piston with mass m containing some ideal gas where we apply an additional $\mathrm{d}m$ *small* weight then remove it. Note that this system is reversible. NB: The $w > 0$ and $w < 0$ in the diagram should be $\mathrm{d}w > 0$ and $\mathrm{d}w < 0$.

In a **reversible isothermal** $(\mathrm{d}T = 0)$ cyclic process we have

$$\oint \mathrm{d}w = 0$$

i.e. no net work was done on the system. That is in the above example $w_{compression} = -w_{expansion}$.

Remark 6.1. In a reversible process, the system and external pressures *must be the same* i.e. $P = P_{ext}$.

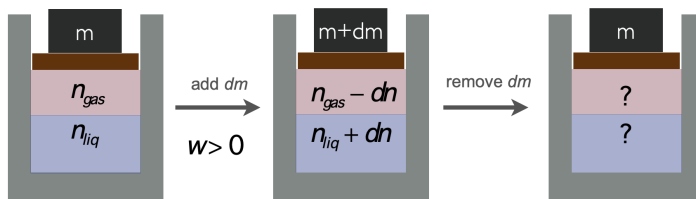Consider the following isothermal process with both liquid and gas forms:

Figure 6.2: An irreversible process since we have both gases and liquids which causes change in phase.

Note that isothermal compression causes some of the gas to **condense** to liquid state: this reduces the internal pressure so $P \neq P_{ext}$. Thus this is an **irreversible processs**: we expect n_{gas} to not necessarily return to its original value (we will see later condensation is not quite reversible).
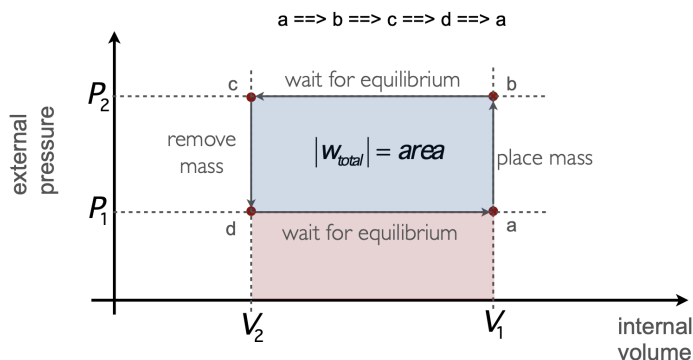
6.4   Example of irreversible piston

Consider the following process
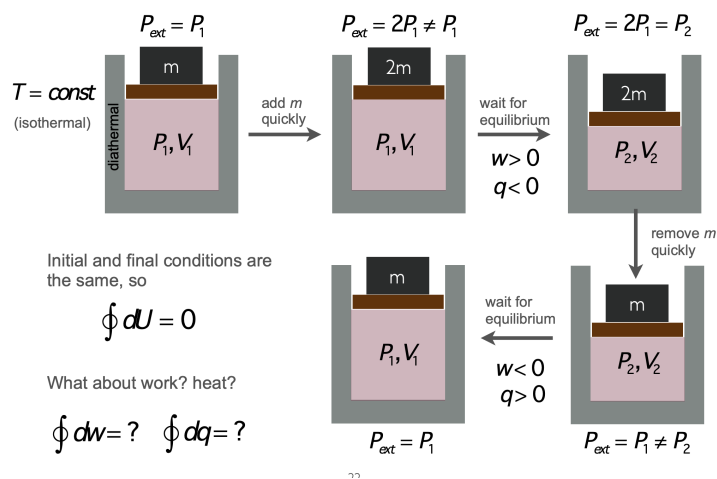
Note that while $\oint dU = 0$ (the initial and final state of the *system* is the same), we show that work is done on the system and heat flows out of the system.

We examine an **indicator diagram** of the process which maps the change in pressure and volume during each stage:

Note that

$$w_{tatal} = \sum_i -P_{ext}\Delta V_i = -P_2(V_2 - V_1) - P_1(V_1 - V_2)$$

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

so net work is done on the system.

Remark 6.2. The reason why this example is irreversible is because there is a long enough time period where $P_{ext} \neq P$!

Aside. The work corresponds to the area inside the rectangle. Note if the process was performed the other way (i.e. mass removed then placed back) then $w < 0$.

Note that since $\Delta U = q_{total} + w_{total} = 0$, then $q_{total} = -w_{total} < 0$ so heat flows out of the system.

6.5 Reversible expansion and compression

For a reversible process note that $P = P_{ext}$. Let $V_2 < V_1$, then

$$w_{compress} = -\int P_{ext}\, dV$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

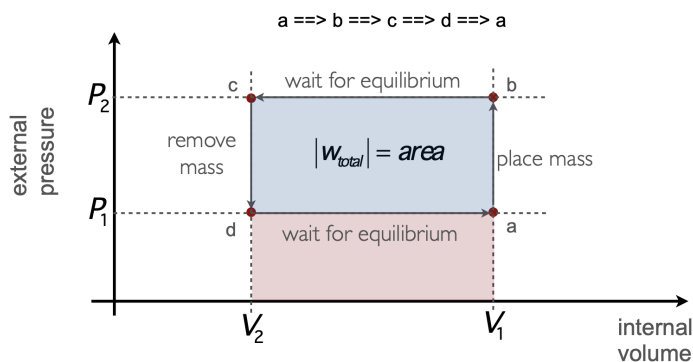$$= -nRT \ln\left(\frac{V_2}{V_1}\right) > 0$$

so $w_{compress} > 0$. similarly

$$w_{expand} = -nRT \ln\left(\frac{V_1}{V_2}\right) = -w_{compress} < 0$$

so $w_{expand} < 0$. Therefore reversible expansion then compression results in

$$\oint dw = 0$$

6.6 Example of reversible vs irreversible process

Consider the following reversible isothermal expansion and **two-step irreversible isothermal expansion**:

Note that

$$\text{reversible: } w_{rev} = -\int P_{ext}\,dV = -nRT\ln\left(\frac{V_3}{V_1}\right)$$

$$\text{irreversible: } w_{irrev} = -P_2(V_2 - V_1) - P_3(V_3 - V_2)$$

Suppose we plug in $n = 1mol, P_1 = 10bar, P_3 = 1bar, V_1 = 3L, V_2 - V_1 = (V_3 - V_1)/2$. Solving we get $w_{rev} = -6.907kJ$ and $w_{irrev} = -3.8kJ$.

Notice that

1. Work is negative in both cases (expansion does work on surroundings)

2. $|w_{irrev}| < |w_{rev}|$: geometrically the area of the irreversible rectangles is strictly smaller than the area of the reversible process).

We could have approximated a reversible process with small irreversible steps:
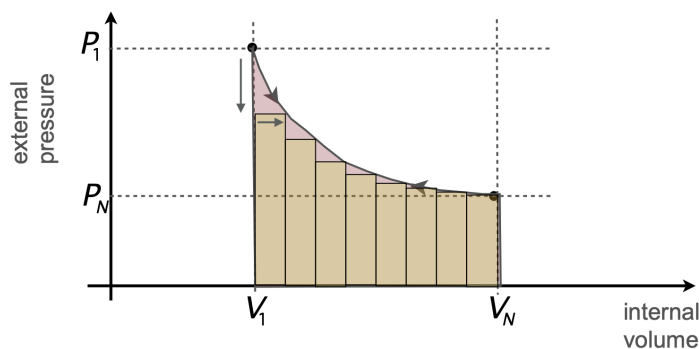
7   January 21, 2019

7.1   Change in internal energy

Recall we can write U in terms of two variables for a fixed amount of ideal gas (we can use the ideal gas law to solve for P afterwards)

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

For an isochoric process (constant volume) we can simplify to

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

which we know simplifies to $dU = dq = C_V\,dT$.

Question 7.1. Does this hold in non-constant volume processes? For an **ideal gas** we know the molecules do not interact so it should not depend on volume anyways, thus

$$dU = C_V\,dT$$

holds as well.

7.2 Enthalpy

We define the **enthalpy** of a process as

$$H = U + PV$$

thus in general the *change in enthalpy* is

$$\Delta H = \Delta U + \Delta(PV)$$

We consider two cases:

Constant volume Under constant volume we know that $w = 0$ (since $\Delta V = 0$) so $\Delta U = q = C_V \Delta T$ (for an ideal gas or in general).

Thus $\Delta H = q + V \Delta P$.

Constant pressure From above we have $\Delta H = \Delta U + \Delta(PV)$. Since pressure is constant and we assume it is reversible ($P = P_{ext}$) then $\Delta H = q - P_{ext}\Delta V + P_{ext}\Delta V = q = C_P \Delta T$.

That is the change in enthalpy is equal to the heat transfer for a reversible constant pressure process.

For an ideal gas, we have the simplification

$$\Delta H = \Delta U + \Delta(PV) = C_V \Delta T + \Delta(nRT) = C_P \Delta T$$

since $C_P - C_V = nR$.

Remark 7.1. In **constant volume** processes, heat flow q_P is exactly ΔU.
In **constant pressure** processes, heat flow q_V is exactly ΔH.

Recall that we have $C_P - C_V = nR$ and $C_{P,m} - C_{V,m} = R$ (molar heat capacity).

7.3 Change calculations in internal energy, enthalpy, heat and work example

Example 7.1. Given the following indicator diagram:
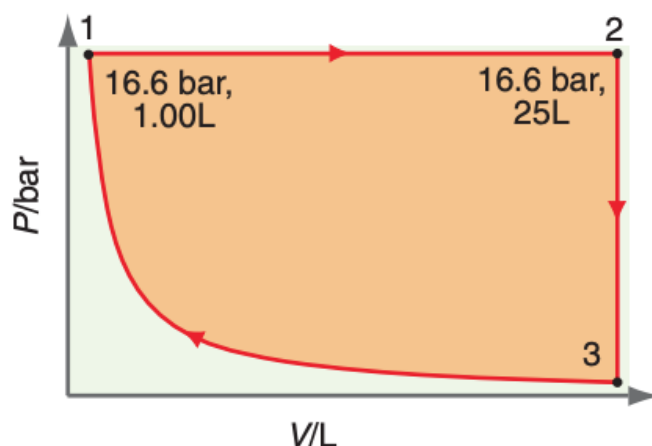
where there is $2.5 mol$ of an ideal gas with $C_{V,m} = 20.79 J mol^{-1}K^{-1}$. Also $T_1 = T_3$.
Find $q, w, \Delta U, \Delta H$ for each segment.

Solution. We have

	$\Delta U(kJ)$	$\Delta H(kJ)$	$q(kJ)$	$w(kJ)$
isobaric: $1 \to 2$	99.6	139.4	139.4	-39.8
isochoric: $2 \to 3$	-99.6	-139.4	-99.6	0
isothermal: $3 \to 1$	0	0	-5.35	5.35
total	0	0	34.5	-34.5

where we have since $1 \to 2$ is constant pressure

$$\Delta U_{12} = nC_{V,m}(T_2 - T_1)$$
$$= nC_{V,m}\left(\frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR}\right)$$
$$= \frac{20.79 \, Jmol^{-1}K^{-1}}{0.08314 \frac{L \cdot bar}{K \cdot mol}} \cdot 16.6 bar(25L - 1L)$$
$$= 99.6 kJ$$

Also note that

$$w_{12} = -\int P_{ext} \, dV = -16.6 bar \frac{10^5 Pa}{bar}(25 \times 10^{-3}m^3 - 1 \times 10^{-3}m^3) = -39.8 kJ$$
$$q_{12} = \Delta U - w_{12} = 99.6 kJ - (-39.8 kJ) = 139.4 kJ$$
$$\Delta H_{12} = \Delta U_{12} + \Delta(PV) = 99.6 kJ - (P_2 V_2 - P_1 V_1) = (C_V + nR)(T_2 - T_1) = 139.4 kJ$$

note that $\Delta H = q$ which make sense since $1 \to 2$ is isobaric.
For $2 \to 3$ we note it is constant volume so

$$\Delta H_{23} C_P \delta T = -139.4 kJ$$

Also we have

$$\Delta U_{23} = C_V \Delta T = C_V\left(\frac{P_2 V_2 - P_3 V_3}{nR}\right) = -99.6 kJ$$

and $\Delta U = q$ so $q = -99.6 kJ$.
Finally for $3 \to 1$ where the temperature is constant, we have $T_1 = T_3 = \frac{P_1 V_1}{nR} = 73.3 kJ$

$$w_{31} = -\int P_{ext} \, dV = -\int_{V_3}^{V_1} \frac{nRT}{V} \, dV$$
$$= -nRT \ln\left(\frac{V_1}{V_3}\right)$$
$$= -(2.5 mol)(8.314 Jmol^{-1}K^{-1}) \cdot 73.3 \times 10^3 J \cdot \ln\left(\frac{1L}{25L}\right)$$
$$= 5.35 kJ$$

7.4   Reversible adiabatic expansion

For an adiabatic process there is *no heat flow*: that is $q = 0$ and thus $\Delta U = w$.
For an ideal gas we have $dU = C_V \, dT$, regardless of the path (i.e. even if $q = 0$). Therefore $C_V \, dT = -P_{ext} \, dV$.
Since the process is reversible we have $P = P_{ext}$ and thus $C_V \, dT = -nRT\frac{dV}{V}$.

Taking the integral from initial to final we have

$$\int C_v \frac{dT}{T} = -NR \int \frac{dV}{V}$$

$$\Rightarrow C_V \ln\left(\frac{T_f}{T_i}\right) = -nR \ln\left(\frac{V_f}{V_i}\right)$$

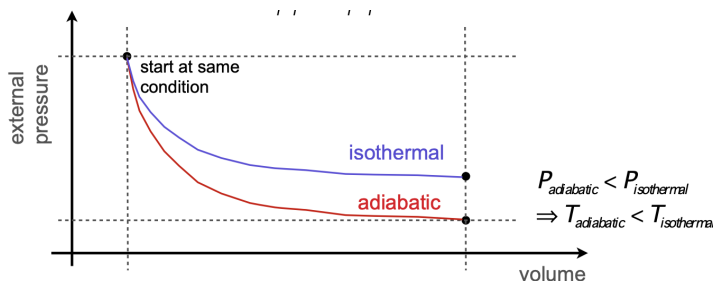$$\Rightarrow \frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{\frac{-nR}{C_V}}$$

Note that for an ideal gas $C_P - C_V = nR$ so we define $\gamma = \frac{C_P}{C_V} > 1$, thus

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

or if we substitute $\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i}$ then

$$P_i V_i^\gamma = P_f V_f^\gamma$$

Since $\gamma > 1$ we see that as volume increases, pressure must decrease proportionally faster in an adiabatic process than in a isothermal process

We also note that during example we see $V_f > V_i$ and thus $T_f < T_i$ so an adiabatic expansion actually **cools** the gas (compression raises T).

Remark 7.2. For an adiabatic process even though there is no heat flow, temperature changes!

7.5   Irreversible adiabatic expansion

Let's assume an adiabatic expansion isagainst a constant external pressure that is $P \neq P_{ext}$ so it is an irreversible process.

We still have $C_V \, dT = -P_{ext} \, dV$. Suppose C_V is also constant then

$$C_V \int_{T_i}^{T_f} dT = -P_{ext} \int_{V_i}^{V_f} dV$$

$$\Rightarrow C_V (T_f - T_i) = -P_{ext}(V_f - V_i) = -P_{ext}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$

rearranging we have

$$T_f\left(C_V + P_{ext}\frac{nR}{P_f}\right) = T_i\left(C_V + P_{ext}\frac{nR}{P_i}\right)$$

So we can solve for the final temperature if the initial and final pressures are known.

Question 7.2. What happens if a gas expands in a vacuum? ($P_{ext} = 0$). Note that $P_{ext} = 0$ thus $dT = 0$ so it is actually an isothermal process!

7.6 Internal energy of ideal gases and volume vs temperature

Note for $U(V,T)$ the differential is

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

note for a constant volume process we've seen

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

In chapter 5 of the text the following is derived

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

so we have

$$dU = C_V \, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

Question 7.3. Does ΔU depend more strong on temperature or volume?
Note for an ideal gas

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\partial nRT/V}{\partial T}\right)_V - P = \frac{nRT}{V} - P = 0$$

therefore $dU = C_V \, dT$ or $U = U(T)$ as shown before.
In general for real/van der Waal gases $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$, however it is still small compared to C_V, i.e. $\Delta U_{T=const} <<$ $\Delta U_{V=const}$ for a real gas.
What about solids and liquids?
Typical dV is small for a liquid or solid (density does change much over range of pressure these phases are stable) hence

$$\Delta U_T = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV \approx \left(\frac{\partial U}{\partial V}\right)_T \Delta V \approx 0$$

since $\Delta V \approx 0$.

Remark 7.3. In nearly *all circumstances* for any phase of matter it is a good approximation to take

$$\Delta U = \int_{T_i}^{T_f} C_V \, dT = n \int_{T_i}^{T_f} C_{V,m} \, dT$$

7.7 Enthalpy as a function of temperature and pressure

Note the total differential of $H(T,P)$ is

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

Let us consider two cases:

Constant pressure $dP = 0$ We've already showed that $\Delta H = q_P$, therefore

$$dH = dq_P = \left(\frac{\partial H}{\partial T}\right)_P dT$$

therefore

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

therefore C_P can be obtained by measuring heat flow at constant pressure.

Constant temperature $dT = 0$ We need to calculate $\left(\frac{\partial H}{\partial P}\right)_T$ which is (derivation in section 3.6)

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

What about for an ideal gas? We note that $V = \frac{nRT}{P}$ thus

$$\left(\frac{\partial H}{\partial P}\right)_T = V - \frac{nRT}{P} = 0$$

thus $dH = 0$ for an *isothermal process involving an ideal gas*! (it is only a function of pressure).

Remark 7.4. The lack of intermolecular interactions in ideal gases means enthalpy does not depend on pressure when temperature is fixed.

7.8 How are C_P and C_V related?

From 1st law of thermodynamics we have

$$dQ = dU - \underset{\sim}{w}$$
$$\Rightarrow dq_P = \left(C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right) - (-P\, dV)$$
$$\Rightarrow C_P\, dT = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P\, dV$$
$$\Rightarrow C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$
$$\Rightarrow C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$
$$\Rightarrow C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

where the last line follows from $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ as previously mentioned before (proved in chapter 5). This can be rewritten as

$$C_P = C_V + TV\frac{\beta^2}{\kappa}$$

where the **isobaric volumetric thermal expansion coefficient** β is defined as

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

If temperature increases ($\partial T > 0$) volume also increases ($\partial V > 0$) then $\beta > 0$ so it measures expansion due to increase in thermal energy. One can think of β as the *percent increase in volume* due to an infinitessimal increase in T.

Also **isothermal compressibility** κ is defined as

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

If when pressure increases ($\partial P > 0$) volume decreases ($\partial V < 0$) then $\kappa > 0$ so it measure "compressibility". Similar to β one can think of κ as the *percent decrease in volume* due to infinitessimal increase in pressure.

Remark 7.5. Note that there is a $+$ in $C_P = C_V + TV\frac{\beta^2}{\kappa}$ even though κ has a $-$ sign since we use the *cylic or triple product rule* here where

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

Note that for an ideal gas

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{PV} = \frac{1}{T}$$
$$\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{nRT}{P^2V} = \frac{1}{P}$$

therefore

$$C_P - C_V = TV\frac{\beta^2}{\kappa} = \frac{TPV}{T^2} = nR$$

Thus we have derived $C_P - C_V = nR$ or $C_{P,m} - C_{V,m} = R$ for an **ideal gas**.

Remark 7.6. For *solids and liquids* $\beta V = \left(pderivVT\right)_P$ is much smaller than a gas (i.e. does not expand as much when temperature increases) so $C_P \approx C_V$.

7.9   Example of change in enthalpy calculations

Example 7.2. Calculate the change in enthalpy when $124g$ of liquid methanol initially at $1bar$ and $298K$ undergoes a change of state to $2.5bar$ and $425K$. Use the following: density of liquid methanol $= 0.701gcm^{-3}$, and $C_{P,m} = 81.1JK^{-1}mol^{-1}$.

Solution. Note that for liquids we have

$$\mathrm{d}H = C_P\,\mathrm{d}T + V\,\mathrm{d}P$$

and since ΔH will be the same for any path we have:

$$\Delta H = n\int_{298K}^{425K} C_{P,m}\,\mathrm{d}T + \int_{1bar}^{2.5bar} V\,\mathrm{d}P$$
$$\approx nC_{P,m}\Delta T + V\Delta P$$
$$= 39.9kJ + 26.6J$$

note that the contribution from the change in T is much larger than ΔP.

7.10   Joule-Thompson experiment

We want to measure $\left(\frac{\partial U}{\partial V} \right)_T$ which we know is 0 for ideal gases but non-zero for real gases.

That is: how much does the internal energy change if we expand the gas at constant temperature?

The *original Joule experiment* involved releasing gas through a valve into a second chamber and measuring the change in temperature in the surrounding water bath:
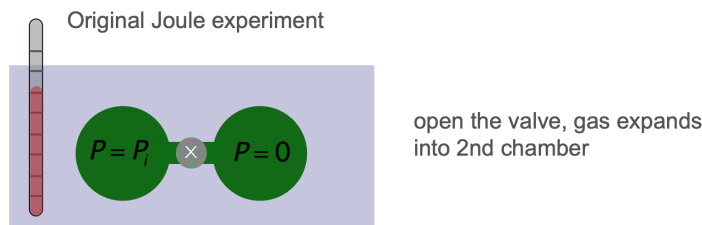
Joule noted $\mathrm{d}T_{water} = 0$ so he concluded $\left(\frac{\partial U}{\partial V} \right)_T = 0$. However the experimental sensitivity was not good enough (since the heat capacity of waterloo was 1000 times that of the gas).

The **Joule-Thompson experiment** improves on the sensitivity by measuring $\left(\frac{\partial H}{\partial P} \right)_T$ instead, from which we can obtain $\left(\frac{\partial U}{\partial V} \right)_T$:
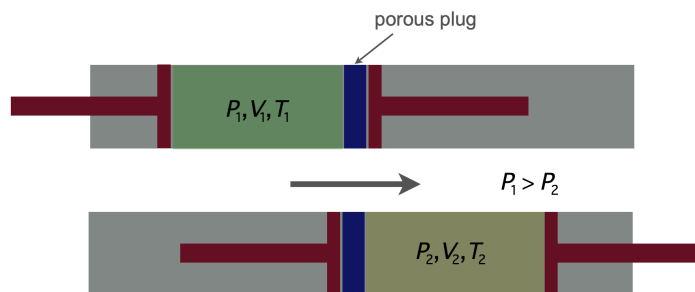
The experiment pushes a gas at constant pressure P_1 adiabatically ($q = 0$) through a *porous plug* into a chamber maintained at constant pressure P_2, where $P_1 > P_2$.

The total work done is thus

$$ w = - \int_{V_1}^{0} P_1 \, \mathrm{d}V - \int_{0}^{V_2} P_2 \, \mathrm{d}V = P_1 V_1 - P_2 V_2 $$

and since $q = 0$, we have $\Delta U = U_2 - U_1 = w$.

Combining the above we have $U_2 + P_2 V_2 = U_1 + P_1 V_1$: **enthalpy is constant (isenthalpic)!**

Since we know $\Delta P = P_2 - P_1$ and we can measure ΔT experimentally, we define the **Joule-Thompson coefficient** as

$$ \mu_{JT} \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P} \right)_H = \left(\frac{\partial T}{\partial P} \right)_H $$

Thus we have

$$\mathrm{d}H = 0 = C_P\,\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P$$

$$\Rightarrow C_P\left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P = 0$$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P = -C_P\mu_{JT}$$

thus we can measure $\left(\frac{\partial H}{\partial P}\right)_T$ directly.

Finally to derive $\left(\frac{\partial U}{\partial V}\right)_T$ from above:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P\mu_{JT} + V}{\kappa V} - P$$

Consider the following cases of μ_{JT}:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H > 0 \qquad \text{for negative } \mathrm{d}P \text{ (expansion) }, \mathrm{d}T \text{ is also negative (cooling)}$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H < 0 \qquad \text{for negative } \mathrm{d}P \text{ (expansion) }, \mathrm{d}T \text{ positive (heating)}$$

$$\mu_{JT} = 0 \qquad \text{true for ideal gas; expansion no change in } T$$

It can be shown for *van der Waal* gases in the limit of zero pressure

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

where $\mu_{JT} > 0$ reflects dominance in *attractive* potential (constant a) and $\mu_{JT} < 0$ reflects dominance of *repulsive* potential (constant b).

We note that real gases have inversion points where μ_{JT} reverses signs:
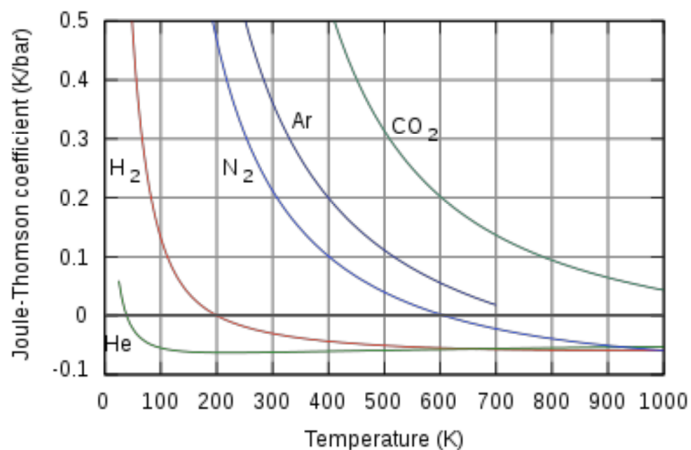
What is the intuition behind μ_{JT}? When $\mu_{JT} < 0$ molecules have enough kinetic energy (high temperature) so repulsive forces dominant. As gas expands isenthapically average separation between particles increase so part of potential energy converted to kinetic energy (gas warms).

Vice versa, when $\mu_{JT} > 0$ attractive potential dominates so part of the kinetic energy is converted to potential energy as gas expands (gas cools).

In fact we can use the **Joule-Thompson effect** to liquefy gases:
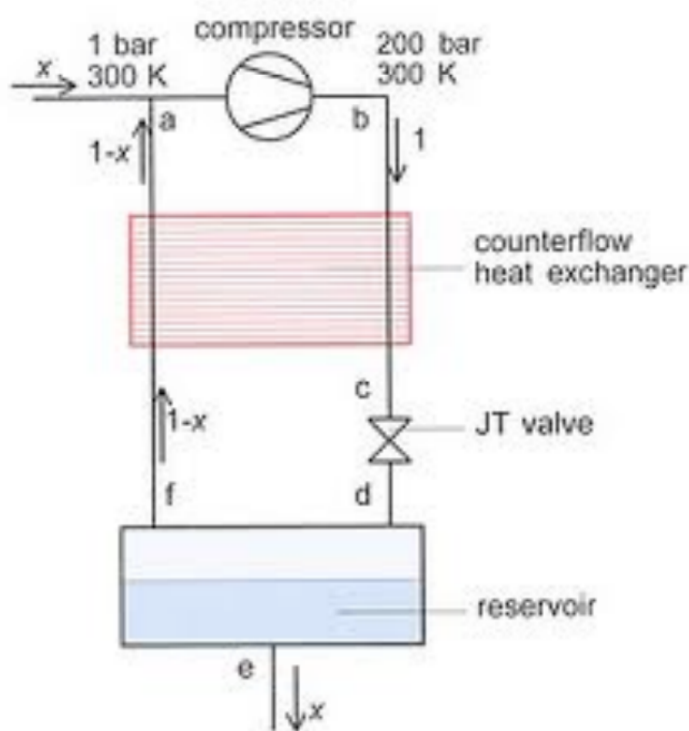
When the gas is below its inversion point ($\mu_{JT} > 0$) prior to reaching the JT valve, it is possible to liquefy. Liquid Ar, N_2 and O_2 are produced this way.

8   January 28, 2019

8.1   Thermochemistry

So far we have looked at thermodynamics without chemical reactions.

Learning how energy and enthalpy changes upon breaking and forming chemical bonds can tell us whether certain reactions will occur under given conditions and how much a reaction can produce.

Note that reactions carried out at *constant volume* implies $\Delta U = q_V$.
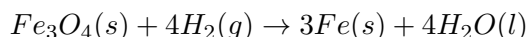
Reactions carried out at *constant pressure* implies $\Delta H = q_P$.

Some terminology:

endothermic heat flows from surroundings *into system* $(q > 0)$

exothermic heat flows *out of system* $(q < 0)$

When writing down reactions we must always specific phase (s, l, g) e.g.

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(l)$$

Note that the **standard state** of all chemical reactions is $P = 1bar$ and $T = 298.15K$, where ΔH^o and ΔU^o denotes change in H and U at standard pressure $P = 1bar$.

We define the follow terminology:

enthalpy of reaction $\Delta H_R = q_P$ at fixed P, T

standard enthalpy of reaction ΔH_R^o enthalpy reaction **per mole** at standard state $(P = 1bar, T = 298.15K)$

standard enthalpy of formation ΔH_f^o: this is exactly ΔH_R^o if the reactants are pure elements *in their mmost stable form* and **one mole** of the species is formed under standard state e.g.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$
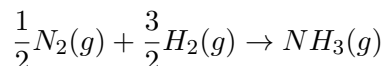
Note that $\Delta H_f^o = 0$ for a pure element in its standard state: this is our **standard reference state** (e.g. at $P = 1bar, T = 298.15K$ for 1 mole of $N_2(g)$).

9   January 30, 2019

10   February 1, 2019

10.1   Bomb calorimeter

10.2   Entropy

Imagine the molecules in a glass of water have all their velocities align upwards simultaneously causes the volume of water to be ejected from the gas.Although this does not violate the first law (conservation of energy), the probability of this intuitively seems surely 0.

Similarly we never observe hot molecules (high velocity) and cold molecules (low velocity) segregate themselves to form a spontaneous temperature gradient.

We never observe such spontaneous changes but they do not violate the conservation of energy. However, we do observe that temperature of the whole volume reaches a thermal equilibrium.

We first define **entropy**. Recall q and w are not state functions: recall for dq:

$$\mathrm{d}q = \mathrm{d}U - \mathrm{d}w = C_V \, \mathrm{d}T + P \, \mathrm{d}V$$

this is not an exact differential since

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \qquad \text{heat capacity independent of volume}$$

but

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

In order to make this an exact differential and hence a state function, we divide by T:

$$\frac{\mathrm{d}q}{T} = \frac{C_V}{T} \, \mathrm{d}T + \frac{P}{T} \, \mathrm{d}V$$

where we confirm it is an exact differential

$$\left(\frac{\partial C_V / T}{\partial V}\right)_T = 0$$
$$\left(\frac{\partial P / T}{\partial T}\right)_V = 0$$

11   Assignment 1 notes

Pressure in *bar* and volume in L When calculating things, pressure may be given in *bar* and volume in L.

Note to calculate energy in J, we need to convert each to SI units where $1bar = 10^5 Pa$ and $1L = 10^{-3} m^3$.

Remark 11.1. NB: when given a in $bar L^2 mol^{-2}$, remember to convert L to m^3 where

$$1000L = 1m^3 \Rightarrow 1L = 10^{-3} m^3$$

Ideal isothermal problems We know $\Delta U = 0$ so $q = -w$.

Calculat work first. Find V_i from ideal gas law $V_i = \frac{nRT}{P_i}$. Since $\Delta T = 0$, then $P_i V_i = P_f V_f$ to calculate V_f. Now if *reversible*, then we substitute in $P_{ext} = P = \frac{nRT}{V}$ then solve the integral. If P_{ext} constant, then it's trivial.

q follows from $q = -w$.

ΔH should be 0 since $\Delta U = 0$ and $\Delta(PV) = nR\Delta T = 0$.

Real isothermal reversible problems $\Delta U \neq 0$ but instead we use

$$\mathrm{d}U = C_V \, \mathrm{d}T + \frac{an^2}{V^2} \, \mathrm{d}V$$

since isothermal we drop $C_V \, \mathrm{d}T$ i.e. $\mathrm{d}U = \frac{an^2}{V^2} \, \mathrm{d}V$ (then we inteegrate).

Calculate work next where

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

so we integrate. V_f and V_i are usually given.

Heat is simply $q = \Delta U - w$.

ΔH is more involved: suppose

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

note that $H = U + PV$, thus

$$\frac{\partial H}{\partial V} = \frac{\partial U}{\partial V} + \frac{\partial PV}{\partial V}$$
$$= \frac{\partial U}{\partial V} + \frac{\partial\left(nRT\frac{V}{V-nb} - \frac{an^2}{V}\right)}{\partial V}$$
$$= \frac{\partial U}{\partial V} + \left(\frac{-n^2 RTb}{(V - nb)^2} + \frac{an^2}{V^2}\right)$$
$$= \frac{\partial U}{\partial V} - \frac{n^2 RTb}{(V - nb)^2} + \frac{an^2}{V^2}$$

Integrating both sides with respect to V we get

$$\Delta H = \int dU - \int \frac{-n^2 RTb}{(V - nb)^2}\, dV + \int \frac{an^2}{V^2}\, dV$$
$$= -\int \frac{-n^2 RTb}{(V - nb)^2}\, dV + \int \frac{2an^2}{V^2}\, dV$$

since $C_V\, dT = 0$.

Total differential To check if an expression is a total differential, simply take the partial derivation with respect to the other variable, e.g.

$$(2y + 1/y)\, dx + (2x - x/y^2)\, dy$$

note that $\frac{\partial 2y + 1/y}{\partial y} = 2 - 1/y^2$ and $\frac{\partial 2x - x/y^2}{\partial x} = 2 - 1/y^2$ so it is a total differential.

Ideal adiabatic problems We know that $q = 0$. We simply calculate work as in the isothermal case.

$\Delta_U = w$ as well.

For ΔH, we need to find $\Delta(PV) = nR\Delta T$. To find T_f and T_i we use either the reversible or irreversible adiabatic equations below.

Reversible adiabatic ideal gas We have

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

which we use to solve for T_f then for $dU = C_V\, dT$.

Irreversible adiabatic ideal gas We have

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

Ideal ΔU calculations We can either use $\Delta U = q + w$, some property of the process (e.g. isothermal implies $\Delta U = 0$) or in general

$$dU = C_V\, dT$$

Enthalpy at constant pressure We note that

$$\mathrm{d}H = C_P\,\mathrm{d}T$$

which is derived from the total differential of $\mathrm{d}H$ in terms of pressure (which is constant) and volume.

C_P, q_p **vs** C_V, q_V Note that $q_P \neq q_V$! To convert between the two, we note the conversion

$$C_P - C_V = nR$$