CHEE 210 THERMODYNAMIC PROPERTIES OF FLUIDS

Winter 2012

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http://www.chemeng.queensu.ca/courses/CHEE210/

CHEE 210 Information

Class Times

Tuesday	8:30 AM	Stirling Hall A
Wednesday	9:30 PM	Stirling Hall A
Friday	8:30 AM	Stirling Hall A

Tutorials:	Fri.	Grp B	14:30 AM	Dupuis Room 217
	Mon.	Grp A	13:30 PM	Ellis Room 324

Teaching Assistants:

- Devproshad Paul (PhD Student)
- Jessica Cui (PhD Student)
- Todd Allward (MSc Student, EngChem 2010)

(Note that email addresses for Tas are on the course website)

Course Information and Logistics

Midterms (2) each 20%, Final Exam 55%, Marked Assignments 5%

Exact date of midterms to be confirmed.

Midterm 1 week of Feb 13-17
Midterm 2 week of Mar 19-23

Reminder of departmental policy regarding passing of independent work.

"Students must pass the individual examination component (comprised of quizzes, midterms and the final exam) of a course to receive a passing grade. If a student does not pass the designated laboratory/project/assignment component, he/she will fail the entire course and be allocated a mark of FR (40-49%). With this mark, the student may be eligible to write the supplemental exam in September."

http://chemeng.queensu.ca/PDF/DepartmentalpoliciesRevJanuary2012.pdf

Course Information and Logistics

Midterms (2) each 20%, Final Exam 55%, Marked Assignments 5%

Exact date of midterms to be confirmed.

Midterm 1 week of Feb 13-17
Midterm 2 week of Mar 19-23

Reminder of departmental policy regarding missing a midterm.

"For students who miss a midterm test or quiz for legitimate reasons and provide the required supporting documentation (see Appendix A at link below), the weight of the midterm/quiz will be reassigned to the final exam. Otherwise, a missed midterm test or quiz will be given a grade of zero. No make-up midterm tests or quizzes will be provided."

http://chemeng.queensu.ca/PDF/DepartmentalpoliciesRevJanuary2012.pdf

Course Information and Logistics

NEW DESIGN PROJECT PLAN (APSC200)

Only CHEE and ENCH students do the design project

It is part of APSC200 and involves both CHEE210 and CHEE223 material.

Exact details of design project are still being established. Current plan is to design a combined heat and power system for the new Engineering building that is currently being planned using an Organic Rankine Cycle or similar System.

Global Course Objectives

- Build on concepts presented in APSC 131, 132
- Extend many of the concepts presented in CHEE 221 to other properties beyond mass and energy (Mining Engineers should review mass and energy balances from your process course).
- Develop a deeper understanding of how the thermodynamic properties of fluids relate to processes such as:
  - the production of useful work as in turbine generators and power cycles
  - pumps and compressors
  - refrigeration and the production of liquified gases.

Global Course Objectives

- A more meaningful understanding of the non-ideal behaviour of gases, generalized equations of state that represent the P-V-T behaviour of both liquids and gases, phase diagrams and the importance of "critical state" will be attained.
- The ability to apply the concepts introduced in lectures and through tutorials to the optimization of a power plant.

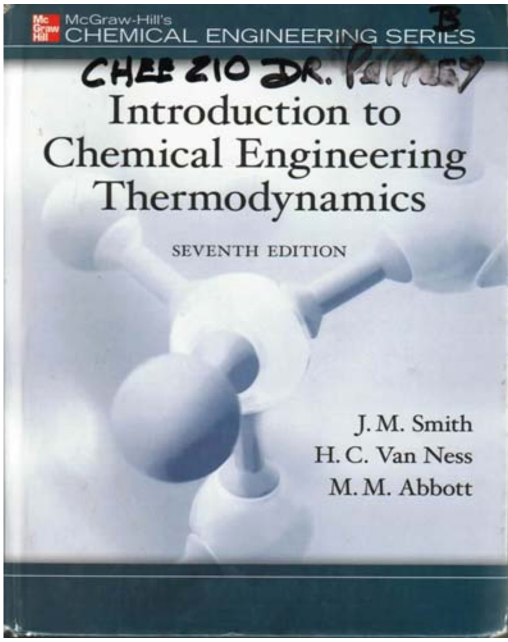
Comment: This course deals with equations of state and the properties of fluids but does not involve chemical change. (e.g., no enthalpy of reaction, enthalpy of formation, etc.)

One Way to Look at the Course

The first half of Smith, Van Ness and Abbott.

CHEE 210 covers most of the material in the first half of the text. The one criterion is that we avoid the chemical aspects of fluid thermodynamics. No reaction and no heats of mixing.

CHEE 311 covers most of the material in the second half of the text and covers heats of reaction etc.



The Final Exam is probably open book. The midterms may be open book depending on the layout of the tutorial rooms.

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Contents

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We will zip through Chapters 1 and 2 as most of it should be review. Section 2.12 on mass and energy balances for open systems is very important.

Chapter 3 is challenging. You should learn to solve cubic equations on your calculator.

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Only Section 4.1 and 4.2 are needed for CHEE 210.

Ch. 5 is challenging and requires hard work and thinking.

Ch. 6 builds on Ch. 3.
Ch. 6 involves derivations.

Ch. 7 and 8 are the basis for the design project.
Ch. 9 is important Chemical Engineering knowledge.

Ch. 9 is the last chapter covered in CHEE 210

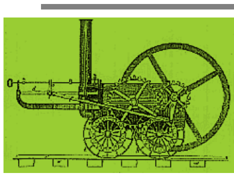
You will, however, need data from Appendices A, B, C, E, F and G

Motivation and Review

OBJECTIVES

- Origins and Motivations for Studying Thermodynamics
- Review and revisit some fundamental concepts
  - » Thermodynamic systems
  - » Equilibrium and Steady State
  - » Thermodynamic Properties and the Importance of Units
  - » Processes and Cyclic Processes (Cycles)
  - » Work, Heat and Other Forms of Energy
  - » Thermodynamic Concept of Heat and Heat Transfer
    - Zeroth Law of Thermodynamics
  - » Develop the Principle of Conservation of Energy
  - » Introduce Enthalpy and Heat Capacity

Richard Trevithick created the need for CHEE 210



Richard Trevithick's is considered the inventor of the tramway locomotive even though his original invention was designed for a road and not for a railroad. However, Trevithick's accomplishments were many and the inventor did not fully receive the credit he was due during his lifetime. "I have been branded with folly and madness for attempting what the world calls impossibilities, and even from the great engineer, the late Mr. James Watt, who said to an eminent scientific character still living, that I deserved hanging for bringing into use the **high-pressure** engine. This so far has been my reward from the public; but should this be all, I shall be satisfied by the great secret pleasure and laudable pride that I feel in my own breast from having been the instrument of bringing forward and maturing new principles and new arrangements of boundless value to my country. However much I may be straitened in pecunary circumstances, the great honour of being a useful subject can never be taken from me, which to me far exceeds riches". - Richard Trevithick in a letter to Davies Gilbert

Thermodynamic Properties of Fluids

The critical question that arose during the development and improvement of the steam engine was "Just how much work can be generated from a given amount of heat?". The pursuit of the answer to this question has led to the development of modern thermodynamics.

One of the key concerns of CHEE 210 is knowing the thermodynamic state of a **<u>system</u>** at **<u>equilibrium</u>**. A concise (mathematical) description of the system's state at different conditions allows us to determine quantitatively:

- heat and work effects associated with a process
- the maximum work obtained or minimum work required for such a transformation
- whether a process can occur spontaneously

Steam locomotives? Should you care?

Thermodynamics is concerned with the development of mathematical relationships between thermodynamic properties such as pressure, volume and temperature that define a system at equilibrium. These relationships are of critical importance in all aspects of **<u>engineering</u>** and are used in the design and specification of:

- Automobiles (engines, pumps, air conditioners)
- Power Stations (turbines, compressors, pumps)
- Aircraft (jet engines, cabin pressure, emergency oxygen)
- Spacecraft (rocket engines, fuel cells, life support)
- Bio-Medical Devices(life-support systems, artificial organs)
- Chemical Plants (pumps, compressors, ejectors, and much more)

Engineering and Thermodynamics of Fluids

- Automobiles (engines, pumps, air conditioners)
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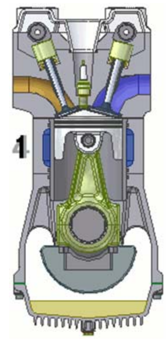
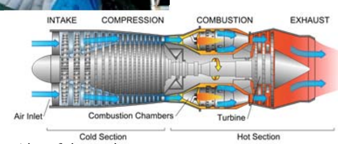


Rotor from steam turbine

Apollo vintage
space suit life support

Heart and Lung Machine



Aircraft jet engine

Dimensions and Units

678 *APPENDIX A. Conversion Factors and Values of the Gas Constant*

Table A.1: Conversion Factors

Quantity	Conversion
Length	1 m = 100 cm = 3.28084(ft) = 39.3701(in)
Mass	1 kg = 10^3 g = 2.20462(lb_m)
Force	1 N = 1 kg m s^{-2} = 10^5(dyne) = 0.224809(lb_f)
Pressure	1 bar = 10^5 kg m^{-1} s^{-2} = 10^5 N m^{-2} = 10^5 Pa = 10^2 kPa = 10^6(dyne) cm^{-2} = 0.986923(atm) = 14.5038(psia) = 750.061(torr)
Volume	1 m^3 = 10^6 cm^3 = 10^3 liters = 35.3147$(ft)^3$ = 264.172(gal)

Pressure! Various units and conversion factors! Gas constant critical!
Pressure usually in atmospheres or bar.
Possibly torr (=mmHg) or kPa

Usually m^3 or L or mL or cm^3 but all conversions are simple factors of 10.

* Gimli Glider

Dimensions and Units

Density	$1\ g\ cm^{-3} = 10^3\ kg\ m^{-3}$
	$= 62.4278 (lb_m)(ft)^{-3}$
Energy	$1\ J = 1\ kg\ m^2\ s^{-2} = 1\ N\ m$
	$= 1\ m^3\ Pa = 10^{-5}\ m^3\ bar = 10\ cm^3\ bar$
	$= 9.86923\ cm^3 (atm)$
	$= 10^7 (dyne)\ cm = 10^7 (erg)$
	$= 0.239006 (cal)$
	$= 5.12197 \times 10^{-3} (ft)^3 (psia) = 0.737562 (ft)(lb_f)$
	$= 9.47831 \times 10^{-4} (Btu) = 2.77778 \times 10^{-7}\ kWhr$
Power	$1\ kW = 10^3\ W = 10^3\ kg\ m^2\ s^{-3} = 10^3\ J\ s^{-1}$
	$= 239.006 (cal)\ s^{-1}$
	$= 737.562 (ft)(lb_f)\ s^{-1}$
	$= 0.947831 (Btu)\ s^{-1}$
	$= 1.34102 (hp)$

Very important!
Energy almost always measured in joules sometimes as kWh (= 3,600,000 J) or calories. You should understand all of these and their conversion

Very important!
Be sure you understand the difference between power and energy. A watt is the power produced when one joule per second is generated. Power always involves a unit of time in the denominator as it is the rate of energy generation or consumption (not energy itself)

Table A.2: Values of the Universal Gas Constant

$R = 8.314\ J\ mol^{-1}\ K^{-1} = 8.314\ m^3\ Pa\ mol^{-1}\ K^{-1}$
$= 83.14\ cm^3\ bar\ mol^{-1}\ K^{-1} = 8{,}314\ cm^3\ kPa\ mol^{-1}\ K^{-1}$
$= 82.06\ cm^3 (atm)\ mol^{-1}\ K^{-1} = 62{,}356\ cm^3 (torr)\ mol^{-1}\ K^{-1}$
$= 1.987 (cal)\ mol^{-1}\ K^{-1} = 1.986 (Btu)(lb\ mole)^{-1}(R)^{-1}$
$= 0.7302 (ft)^3 (atm)(lb\ mol)^{-1}(R)^{-1} = 10.73 (ft)^3 (psia)(lb\ mol)^{-1}(R)^{-1}$
$= 1{,}545 (ft)(lb_f)(lb\ mol)^{-1}(R)^{-1}$

Sample Problem: Energy and Power Units

Each morning Dr. Peppley wakes up, gets dressed in a dashing athletic outfit and works out for 20 minutes on his Infiniti elliptical trainer equipped with a watt meter and cumulative calorie meter. On a typical day, Dr. Peppley generates power at a rate of 180 watts during the workout and the calorie accumulator registers that 320 calories of energy have been produced at the end of 20 minutes.

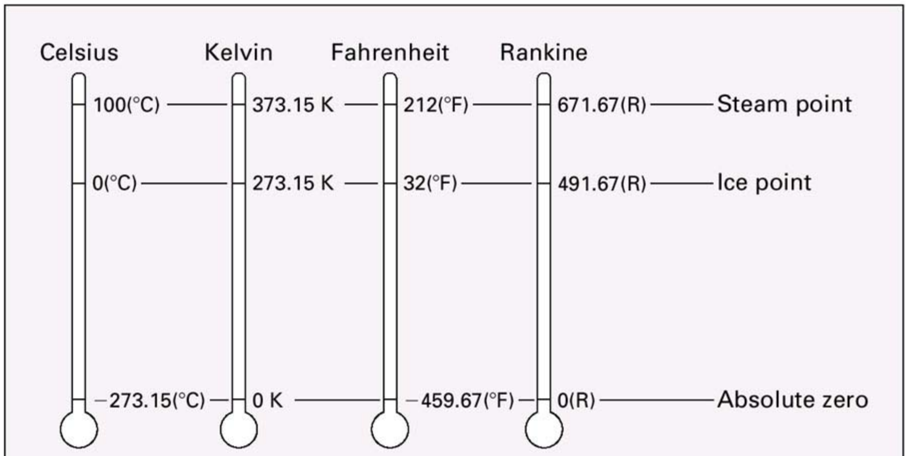
How many joules of energy did Dr. Peppley actually generate in the 20 minute period based on the watt meter?

A calorie is approximately equivalent to 4.18 J. Is the calorie accumulator correct? What should it read?

During the months of December and January last year Dr. Peppley's electrical bill indicated that 1650 kWh were consumed over a 60 day period. Assuming on average each student would generate 180 W, how many CHEE 210 students would need to be on the trainer for one hour per day (every day) to provide the electrical energy for Dr. Peppley's house?

Temperature!

Almost always will be Celsius or Kelvin scale!



Be very careful to use Kelvin when necessary!

WORK (W):

Work is energy leaving or entering a system.

Work can take many forms, but classically work is defined as moving an object against a resisting force.

$$\delta W = F \cdot d\ell$$

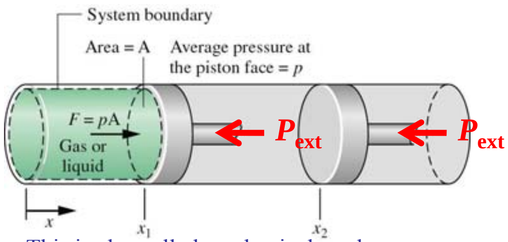
F = applied force (N)

$d\ell$ = differential displacement (m)

- Work is a form of energy in transit (i.e., energy being transferred across the boundary between a thermodynamic system and its surroundings).
- It can only exist or be identified at that boundary. (As it enters the system it will become internal energy for example.)
- Has units of Newton × metre = Joule
- By convention, transfer of work into the system from the surroundings is positive and transfer out of the system to the surroundings is negative.
- When the system does work the sign is negative relative to the system.

Expansion or Compression Work

Consider a closed system consisting of a fluid contained in a piston-cylinder as the fluid expands from position x_1 to x_2 .



$$W = -\int_{V_1}^{V_2} P_{ext} dV^t$$

- This is also called mechanical work.
- During the process the gas exerts a force normal to the surface of the piston = pressure × area (P×A) against an ext. pressure or resistance.
- The incremental work **done** is $dW = P \cdot A \cdot dx$
- But "*A dx*" is the volume of a differential length of the cylinder "*dV*"
- When the system **does** work the sign is negative relative to the system and therefore $dW = -PdV$
- Note that the text uses V^t for total volume and V for molar volume. (e.g., L/mol)

Types of Energy that a System can Possess

The energy a system possesses determines its capacity to do work.

Kinetic (**E_K**) :

$$E_k = \tfrac{1}{2} mu^2 : \text{units Joule} = \text{J} = [\text{kg}][\text{m/s}]^2$$

$$\dot{E}_k = \tfrac{1}{2} \dot{m}u^2 \;: \text{units Watt} = \text{W} = \text{J/s} = [\text{kg/s}][\text{m/s}]^2$$

Note the dot above means rate

Potential (**E_P**) :

$$E_p = mgz \;\Rightarrow \text{J} = [\text{kg}][\text{m/s}^2][\text{m}]$$

$$\dot{E}_p = \dot{m}gz \;\Rightarrow \text{W} = \text{J/s} = [\text{kg/s}][\text{m/s}^2][\text{m}]$$

Note: These equations represent power which is the rate of energy production

Internal (**U**) : All energy possessed by a system other than kinetic or potential. Typically molecular level energy of vibration, rotation and translation, as well as interactions between molecules.

E_i = energy kinetic or potential, m = mass, u = velocity,

$\dot{E}_i$ = energy entering the system per unit time,

$\dot{m}$ = mass entering the system per unit time

Heat – Thermal energy in transit

Consider what happens when a hot brick is placed in contact with a cold brick.

Thermodynamic definition of heat, Q : Heat is thermal energy entering or leaving a system.

Heat is transferred across the boundary of a system at a given temperature to another system (or surroundings) at a lower temperature.

Heat moves as a consequence of temperature difference from the hot body to the cold body.

Heat transferred to the system is positive

Heat – Thermal energy in transit

Heat moves as a consequence of temperature difference from the hot body to the cold body.

Heat transferred to the system is positive

Zeroth Law of Thermodynamics:

If System A is in thermal equilibrium with System B and System B is in thermal equil'm with System C then System A and C must also be in thermal equilibrium.

Means the same thing as saying that the hot body and cold body will come to the same temperature eventually

Heat transfer modes :

Conduction : *The transfer of energy through contact from more energetic particles to less energetic particles through a material.*

Convection : *The transfer of energy through the movement of fluid (gas or liquid) to a solid surface.*

Radiation : *Energy transferred by the emission of photons as a consequence of changes in the electronic configuration of atoms or molecules.*

First Law of Thermodynamics

"Although energy assumes many forms, the total quantity of energy is constant and when energy disappears in one form, it appears simultaneously in other forms."

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

Consider a fixed position, closed system, at rest : For a given process Q joules of thermal energy enter the system and W joules of work are done on the system.

$$\Delta U = Q + W \quad \text{finite changes}$$

$$dU = \delta Q + \delta W \quad \text{differential changes}$$

Important! Note the plus (+) sign on work (W) will be used in this course in the First Law

First Law of Thermodynamics

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

Consider a fixed position, closed system, at rest :

- Closed system means that there is no transfer of matter across the boundary which also means there is no transfer of internal energy (U) across the boundary
- Consider the surroundings. The only means of energy exchange is by heat (Q) or work (W). This means that $\Delta E_{surr} = (-Q) + (-W)$ or in differential terms $dE_{surr} = -dQ - dW$
- Now consider the system ΔE_{sys} . Changes are only U, E_k , E_p
- $\Delta E_{sys} = \Delta U + \Delta E_k + \Delta E_p$ but since the system is not moving $\Delta E_k = \Delta E_p = 0$
- So $\Delta E_{sys} = \Delta U$ but we also no that $\Delta E_{sys} = -\Delta E_{surr}$
- This means:

$$\Delta U = Q + W \qquad dU = \delta Q + \delta W$$

Finite Changes — Differential Changes

Thermodynamic Systems

The first step in all problems in thermodynamics is to define a system, either a body, a device or a defined region of space.

The system is simply whatever we want to study. We typically think of it as being inside an envelope that represents the boundaries.

Surroundings:

The surroundings are anything outside the defined system. Sometimes we specify these regions as reservoirs of heat at given temperature for example.

<u>Types of Systems:</u>

Isolated: No transfer of energy or matter across the boundary. No heat or work leaves or enters the system.

Closed: No transfer of matter across the boundary. But heat or work can leave or enter the system.

Open: Exchange of matter and energy with surroundings. This is the type of system on which we must do mass and energy balances for streams entering and leaving the system.

The Equilibrium State

Classical thermodynamics deals primarily with changes from one equilibrium state to the other. The general characteristics of the **<u>equilibrium state</u>** :

- No unbalanced mechanical forces
- No material changes or concentration changes
- No thermal changes
- All net flows of mass, transfer of heat, and transfer of work between the system and surroundings are zero.
- There are no net driving forces acting to change the system.

Another system condition is **<u>steady state.</u>** The characteristics of **steady-state** are :

- Applies to flow processes
- No accumulation (of material or energy) within the system with time
- No change in mass and no change in fluid properties within the system
- Commonly involves fluid flow across a system boundary
- Note: The flow in and flow out can be changing as long as they remain balanced.

Thermodynamic Fundamentals

Thermodynamics is concerned with the macroscopic properties of a ***system,*** and how they can be related to the energy of the system.

A *property* is a macroscopic characteristic of a system to which a number can be given.

Intensive Properties:

Independent of the quantity of material making up the system. (e.g., density, temperature, specific heat, molar heat capacity, pressure of gas)

Extensive Properties:

Dependent of the quantity of material making up the system. (e.g., mass, volume, internal energy, enthalpy, etc.) [Note by dividing by unit quantity we can make these preperties intensive.]

State Properties :

Matter exists in different forms or phases.

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State Properties :

State is the condition of the system as described by its properties.

State Properties are independent of the path taken to reach a specific equilibrium state.

Each given state each State Property has a definite value that can be assigned without knowledge of how the system arrived at that state.

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Thermodynamic Fundamentals

State Properties :

State is the condition of the system as described by its properties.

State Properties are independent of the path taken to reach a specific equilibrium state.

Each given state each State Property has a definite value that can be assigned without knowledge of how the system arrived at that state.

Therefore the change in the value of a State Property is determined only by the start and end states and is independent of the particular way the change of state occurred.

The specification of 2 state variables uniquely determines the value of all other state variables of a single component, one phase system at equilibrium (for a specific system).

Matter exists in different forms or phases.

A phase is defined as a quantity of matter that is homogeneous throughout in chemical composition and physical structure.

The Phase Rule

For multphase systems at equilibrium the number of independent state variable that must be arbitrarily fixed to establish its intrinsic state is given by:

$$F = 2 - \pi + N$$

Where π is the number of phases, N is the number of chemical species (components) and F is the degrees of freedom of the system.

Sample Problem: Find the number of degrees of freedom:

(a) Liquid water in equilibrium with its vapour

(b) Liquid water in equilibrium with a mixture of water vapour and nitrogen

(c) A liquid solution of alcohol in water with its vapour.

The Phase Rule

$$F = 2 - \pi + N$$

Sample Problem: Find the number of degrees of freedom:

a)Liquid water in equilibrium with its vapour

2 phases, 1 component: $\pi = 2$, $N = 1$ $F = 2 - 2 + 1 = 1$

Only one state variable needs to be defined to establish the equilibrium state of the system. (e.g., density, temperature, molar heat capacity, pressure, specific volume)

b)Liquid water in equilibrium with a mixture of water vapour and nitrogen

2 phases, 2 components: $\pi = 2$, $N = 2$ $F = 2 - 2 + 2 = 2$

Two state variables need to be defined to establish the equilibrium state of the system. (e.g., any single phase properties plus composition of phases because there is more than one component.

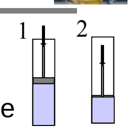
c)A liquid solution of alcohol in water with its vapour.

2 phases, 2 components : $\pi = 2$, $N = 2$ $F = 2 - 2 + 2 = 2$

Same as b) except that in b) we could assume that nitrogen is not soluble in water and that the liquid phase is pure water.

Processes And Cycles

A process is a transformation from one state to another.



A cycle is a sequence of processes that begins and ends at the same state.

Initial and final state both at equilibrium.

Adiabatic

System does not exchange heat with the surroundings. Perfectly insulated.

Isothermal

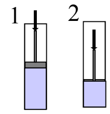
Temperature of the system does not change. (i.e., $dT = 0$). Note that heat can be exchanged with the surroundings but no change in internal energy or enthalpy for ideal gas. ($dU = 0$ and $dH = 0$)

Isobaric

Pressure of the system does not change. (i.e., $dP = 0$). Typical of process occurring at atmospheric pressure. Important for concept of enthalpy.

Reversible

Processes And Cycles



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Isobaric

Pressure of the system does not change. (i.e., dP = 0). Typical of process occurring at atmospheric pressure. Important part of concept of enthalpy.

Reversible System is always in an "almost equilibrium" state throughout process

All the intermediate points throughout the process are considered equilibrium states so that equations of state can be used for integrals (e.g., $PV^t = nRT$)

Can be approximated by making a very large number of very small steps.

The system is at equilibrium at the ***start*** and ***end*** of the process as well as throughout the process

Reversibility represents an "ideality" in mechanical sense since there can be absolutely no losses due to friction.

For an irreversible process it is important to remember that the system is at equilibrium at the start and finish of the process

Can be approximated by making a very large number of very small steps.

The system is at equilibrium at the ***start*** and ***end*** of the process as well as throughout the process

Reversibility represents an "ideality" in mechanical situation since there can be absolutely no losses due to friction.

For an irreversible process it is important to remember that the system is at equilibrium at the start and finish of the process

Energy Analysis of Cyclic Processes

Many applications (e.g. power generation, refrigeration) require cyclic processes.)

The energy balance for a cyclic process is :

$$dE_{cycle} = \delta Q_{cycle} + \delta W_{cycle}$$

Integrating around the cycle gives $\Delta E_{cycle} = Q_{cycle} + W_{cycle}$

Where Q and W represent the **net** amounts of energy transfer by heat and work to the system for the cycle. (Note that for an engine W < 0 because it *does* work)

Very Important!! Since the system returns to its initial state at the end of the cycle there is

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Very Important!! Since the system returns to its initial state at the end of the cycle there is ***no net change in the system's energy*** ($\Delta E_{cycle} = 0$) because it is a state variable.

This means that for the overall cycle $Q_{cycle} = - W_{cycle}$

In words: "For a true cyclic process the "**net**" work given off by the system is equal to the "**net**" heat added to the system."

We can also write this mathematically in differential form:

$$\oint \delta Q_{cycle} = -\oint \delta W_{cycle} \quad \text{where} \oint \text{ means to integrate around a cycle}$$

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Enthalpy

In the analysis of certain processes, certain combinations of thermodynamic properties are encountered. One such is **enthalpy**.

Consider the **reversible** expansion of a gas at **constant pressure** in a piston-cylinder assembly :

From the First Law we get $dU = dQ + dW$

Rearranging we get $dQ = dU - dW = dU + PdV$

Integrating at constant pressure from state 1 to state 2

Enthalpy

In the analysis of certain processes, certain combinations of thermodynamic properties are encountered. One such is **enthalpy**.

Consider the reversible expansion of a gas at constant pressure in a piston-cylinder assembly :

From the First Law we get $dU = dQ + dW$

Rearranging we get $dQ = dU - dW = dU + PdV$

Integrating at constant pressure from state 1 to state 2

$$\int_1^2 dQ = \int_1^2 dU + P\int_1^2 dV$$

$$= (U_2 - U_1) + P(V_2 - V_1)$$

The triple equal sign means this is a definition

Next we collect the terms for each state and Define a new state property

$$\int_1^2 dQ = (U_2 + PV_2) - (U_1 + PV_1)$$

$$= H_2 - H_1 = \Delta H$$

$$H \equiv U + PV$$

enthalpy is a useful defined property because it occurs often

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enthalpy is a useful defined property because it occurs often

Since many processes occur at atmospheric pressure.

The heat transfer that occurs in a reversible constant pressure process for a closed system is equal to the change in enthalpy.

... But enthalpy changes can occur in many different processes

Enthalpy has units of [energy per unit mass] or [energy per mole]

Heat capacity, C (or c)

Materials have an ability to absorb or liberate a specific quantity of heat for a given temperature change. This is called heat capacity.

$$C \equiv \frac{1}{n}\frac{dQ}{dT}\left[\frac{J}{mol\,K}\right] \qquad c \equiv \frac{1}{m}\frac{dQ}{dT}\left[\frac{J}{g\,K}\right]$$

(Molar) (Specific)

The smaller the change in T is for a given amount of heat added to the material the larger the heat capacity

As defined above, C is not a state function because it depends on how it is measured (e.g., system could be heated while keeping volume constant or system could be heated while keeping pressure constant.)

Constant Volume Case: Consider a closed system undergoing a reversible constant volume process where work is only mechanical (no chemical change, electrical work, etc.)

From the First Law we know $dU = dQ + dW$

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Mechanical work is: $dW = - PdV$ and substituting

$$dU = dQ - PdV$$

but $dV = 0$ for constant volume therefore: $\mathbf{dU = dQ}$

0

The triple equal sign means this is a definition

for a constant volume process : $$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{n}\left(\frac{dQ}{dT}\right)_V$$

Note: In text (SVA) both U and V are defined as molar quantities (see pages 23 and 24 of text)

Heat capacity, C

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dU = dQ - PdV (0)

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Constant Pressure Case: Consider a closed system undergoing a reversible constant pressure process where work is only mechanical (no chemical change, electrical work, etc.)

By same steps as const. V we get to: dU = dQ – PdV

dV is ***not*** 0 so we need an expression fo dV?

Recall that: **H = U + PV**

Taking the differential: **dH = dU + d(PV) = dU + (PdV + VdP)**

Heat capacity, C

Constant Pressure Case: Consider a closed system undergoing a reversible constant pressure process where work is only mechanical (no chemical change, electrical work, etc.)

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We need an expression fo dV?

Recall that: **H = U + PV**

Taking the differential: **dH = dU + d(PV) = dU + (PdV + VdP)** (0)

But for a constant pressure process dP = 0

We can rearrange this equation now to give: **PdV = dH – dU**

This can be substituted back into the First Law to give: **dU = dQ – dH + dU**

Simplifying this yields (for a constant pressure process): **dH = dQ**

for a constant pressure process : $$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{n}\left(\frac{dQ}{dT}\right)_P$$

Course Logistics Reminders and Updates

- Tutorial 1 Group A 2:30 PM Fri Jan 13 Dupuis 217, Group B Mon Jan 16 Ellis 324
- Sample problems from this week's suggested problems. Given by TA.
- I will post the solution to the recommended textbook problems over the weekend and some recommendations for problems next week.
- Check the website often for updates.
- Week 1 (Jan 9 - 13) Suggested Study Problems (Smith, Van Ness and Abbott, Seventh Edition):
- Chapter 1 Problems 5, 10, 14 and 18.
- Chapter 2 Problems 4,7,12,17,23,28,36,37