

Supplementary Notes for Chapters 1-3 Context and Approach 1 <sup>st</sup> Law: Concepts and Applications
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These notes are intended to summarize and complement the material presented in our textbook the 3<sup>rd</sup> edition of *Thermodynamics and Its Applications* and discussed in our graduate thermodynamics class (10.40). For the most part, we use the same notation and make references to illustrations and equations contained in the text. Hopefully you will find these notes helpful for self study and review. We strongly urge you to consider the example problems and other problems that appear at the end of each chapter from Chapter 3 onwards. We begin by summarizing the learning objectives for Chapter 1-3.

### **Learning Objectives\***

#### **Chapter 1**

After finishing this chapter you should be able to:

- Describe the three general types of problems that are encountered in thermodynamics
- List the basic problem solving steps and identify the types of information required to solve thermodynamics problems
- Understand the difference between the postulatory and historical approach to teaching/learning thermodynamics

#### **Chapter 2**

After finishing this chapter you should be able to:

- Clearly and without jargon define: system, boundary, environment, primitive properties, derived properties, thermometric temperature, event interaction, adiabatic, diathermal, phase, restraint, thermodynamic processes, path and state
- Explain the difference between an open, closed and isolated system
- Give an example of an adiabatic wall and explain why it is useful
- Describe and give examples of a simple and a composite system
- Understand what is meant by a stable equilibrium state and how it may be characterized
- Explain the difference between intensive and extensive properties
- Describe situations where thermodynamic properties are not independently variable
- Use the nomenclature and unit systems employed in engineering thermodynamics

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\*contributed in part by Professor Brad Eldredge, University of Idaho

## Chapter 3

After finishing this chapter you should be able to:

- Clearly define and give examples of work, adiabatic work interactions, heat interactions, ideal gas, energy, internal energy, enthalpy and heat capacity
- Be able to calculate  $PdV$  work interactions for quasi-static, closed system expansions and compressions
- Understand the connection between Joule's experiments and adiabatic work interaction
- Write the complete general form of the 1<sup>st</sup> Law and show how to simplify it for simple open and closed systems and for steady state and transient situations
- Using the 1<sup>st</sup> Law, calculate the change in energy for a closed systems going from State 1 to State 2 and determine the heat and/or work required to effect this change
- Using the 1<sup>st</sup> Law, calculate the change in energy for open system undergoing a change from State 1 to State 2 and determine the heat, work and/or mass flows required to make this change

### Postulatory versus Historical Approach

*Postulatory* – axioms that cannot be proved from first principles are stated – they represent the minimum set of rules, consistent with the experimental body of knowledge, that determine how systems behave in terms of the interchange of energy (heat, work, ... ) and mass.

*Historical* – chronological development of concepts (and misconceptions) based on an evolving set of experimental knowledge.

Postulates tend to be abstract – but with continued exposure they become the logical set of rules needed to formulate the thermodynamic laws and relationships that govern the behavior of systems that transfer energy by heat and work interactions and by mass transfer. In addition, the postulates provide a means of specifying the distribution of components in phase and chemical equilibrium as well as the stability of specific phases.

Within the context of the historical development, our predecessors faced problems and situations that they couldn't explain with existing principles in physics and mathematics. Consequently, they proceeded to create new theories and "laws" verifying their hypotheses with experiments. The amalgamation of their work is captured in the four main postulates of our text.

In table I and the two figures that follow, major contributors to classical chemical and statistical thermodynamics are briefly described in a historical context.

## Major Early Contributors to Classical Chemical and Statistical Thermodynamics

Scientist	Years	Contributions
Black	1760-1766	Calorimetry
Count Rumford (B. Thompson)	1798	Mechanical equivalent of heat
Carnot	1824	Heat engines and conversion of heat into work
Mayer	1842	Interconversion of heat and work
Joule	1843-1852	Interconversion of heat and work
W. Thomson (Kelvin)	1848-189	Absolute temperature scale
Clausius	1850	2 <sup>nd</sup> law concepts
W. Thomson (Kelvin)	1851	2 <sup>nd</sup> law, dissipation of energy
Clausius	1854-1865	Concept of entropy
Maxwell	1870-1879	Heat, statistical basis for 2 <sup>nd</sup> law, clarification of many key issues
Boltzmann	1871	Thermodynamic properties from distribution functions
Gibbs	1873	Chemical thermodynamics
Gibbs	1876-1878	Chemical potential; phase rule; fundamental equation
Gibbs	1902	Defined classical statistical thermodynamics; created ensembles
Helmholtz	1882	Theory of equilibrium; free and bound energy ( $A$ defined)
van't Hoff	1884-1887	Chemical thermodynamics; theory of equilibrium constant; solutions
Duhem	1890	Mixtures
Caratheodory	1909	Adiabatic work and 1 <sup>st</sup> law
Nernst	1906	Heat theorem (3 <sup>rd</sup> law)
Simon	1927	Improved version of 3 <sup>rd</sup> law

Adapted from Laidler, K.J. (1993). *The World of Physical Chemistry*, Oxford.

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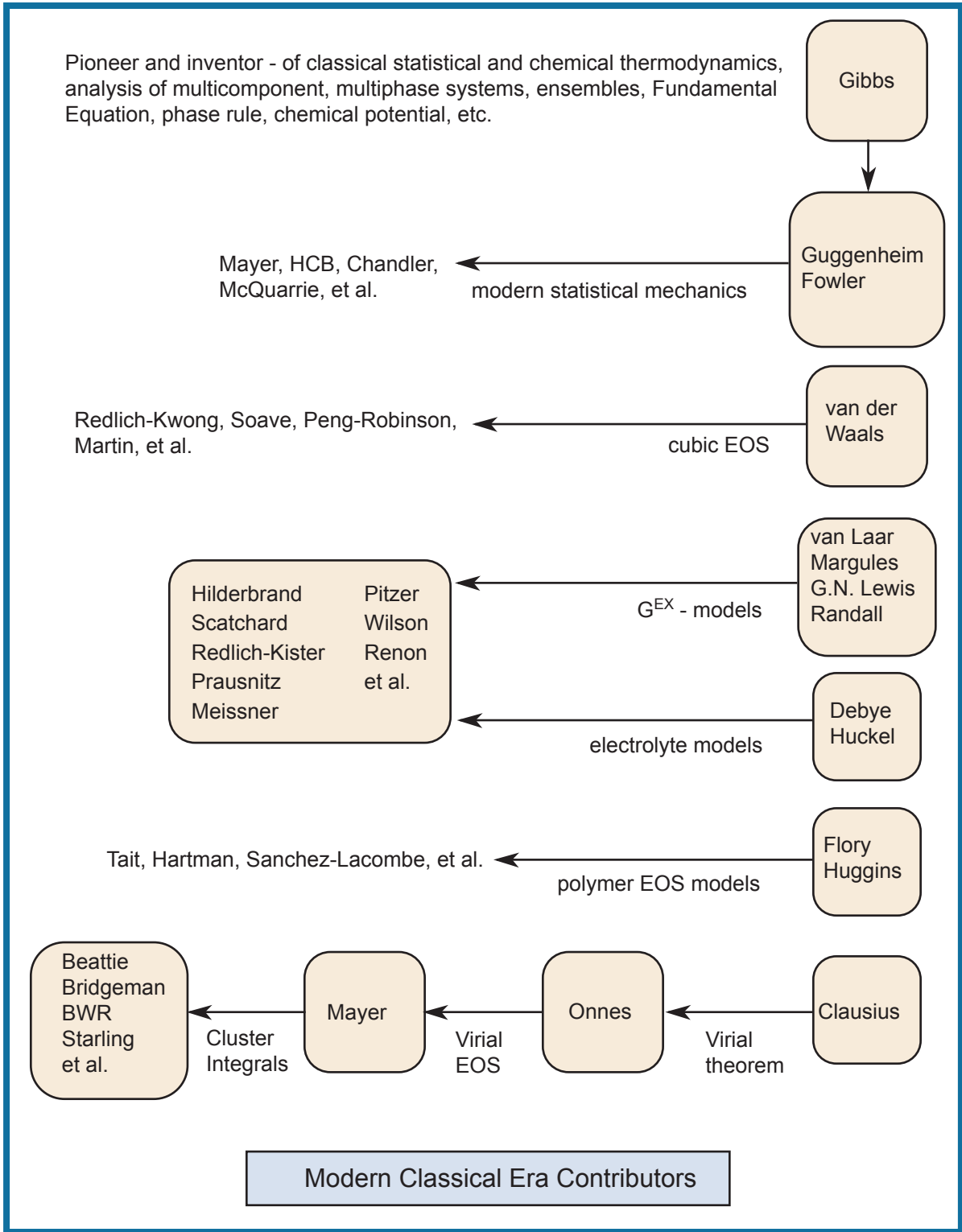


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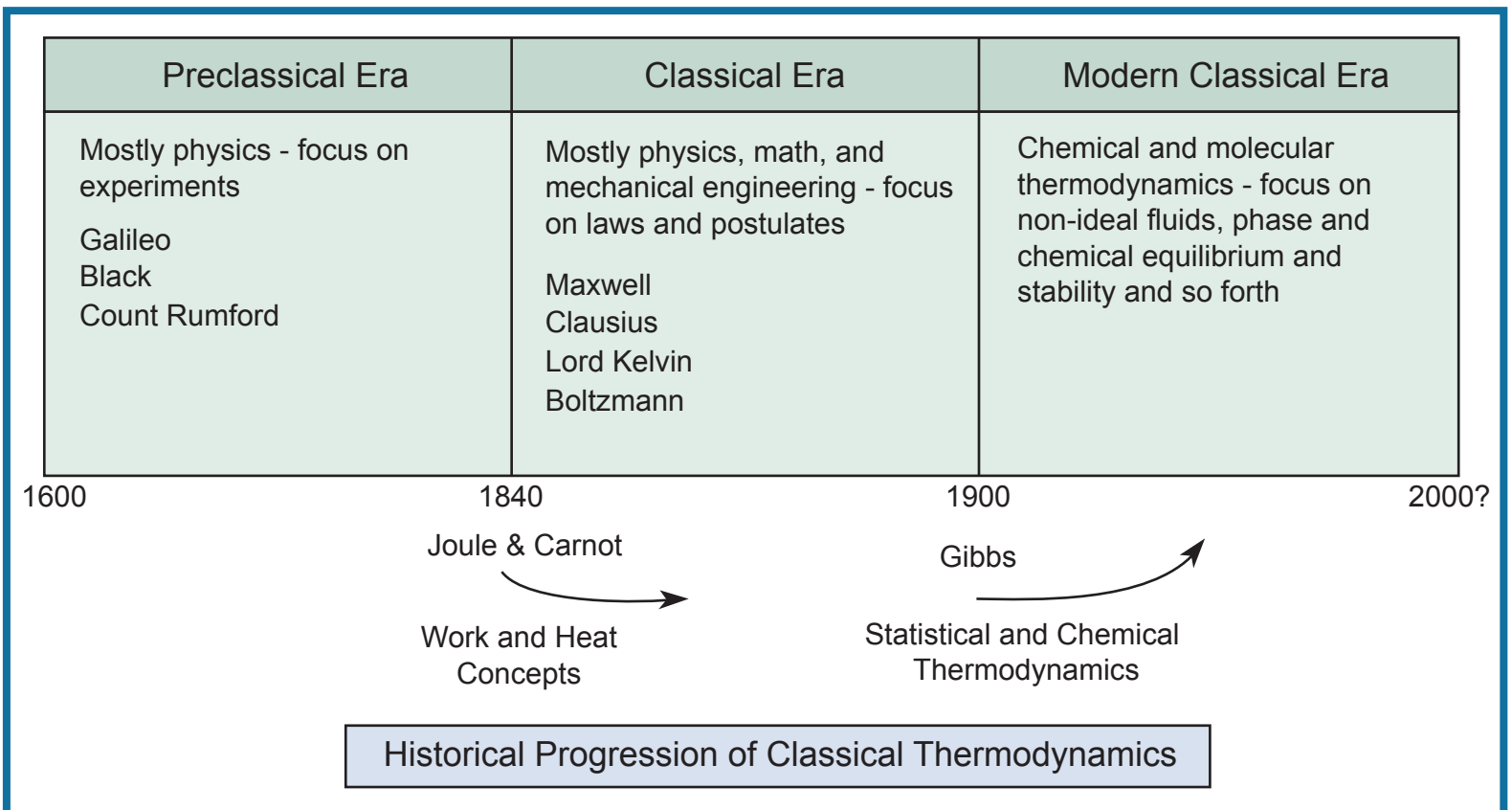
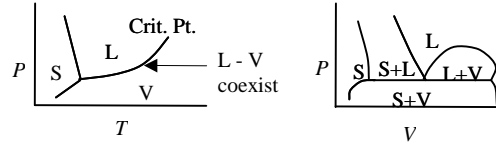


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## Discussion of Postulates (listed in Appendix A)

1. For closed simple systems with given internal restraints, there exist stable equilibrium states that can be characterized completely by two independently variable properties in addition to the masses of the particular chemical species initially charged.

- "closed, simple systems"
- "independently variable properties"
- masses of each component known
- consistent with the Gibbs phase rule
- restatement of Duhem's theorem



$$F = n + 2 - \pi = 3 - \pi \text{ for pure } n=1 \text{ system}$$

2. In processes for which there is no net effect on the environment, all systems (simple and composite) with given internal restraints will change in such a way that they approach one and only one stable equilibrium state for each simple subsystem. In the limiting condition, the entire system is said to be at equilibrium.

- applies to all *isolated* systems
- describes the natural tendency of processes to approach equilibrium at a minimal energy and maximal entropy state
- linking postulates I and II provides a means for mathematically describing the criteria of phase and chemical equilibria

3. For any states (1) and (2), in which a closed system is at equilibrium, the change of state represented by (1) to (2) and/or the reverse change (2) to (1) can occur by at least one adiabatic process and the adiabatic work interaction between this system and its surroundings is determined uniquely by specifying the end states (1) and (2).

- adiabatic work interactions of any type in closed systems are state functions.
- adiabatic form of the 1st law :  $d\bar{E} = \delta W_{adiabatic} = \delta Q + \delta W$   
where  $\delta W$  and  $\delta Q$  are the actual heat and work interactions that occur for non-adiabatic processes between the same end states (1) and (2).

4. If the sets of systems A,B, and A,C each have no heat interaction when connected across nonadiabatic walls, there will be no heat interaction if systems B and C are also connected.

- "Zeroth law of thermodynamics"
- concept of thermal equilibrium and the absence of a heat interaction
- temperature differences are needed for heat transfer to occur

## Work Interactions

In general, all work interactions are path dependent and are defined to occur at the boundary of a system. The symbol  $\delta$  is used here to designate a path dependent property. Work in general can be represented by the dot product of a boundary force  $\mathbf{F}_s$  and an extensive displacement  $\underline{x}$  which can be expressed differentially using  $d\underline{x}$ . Thus,

$$\delta W = \mathbf{F}_s \cdot d\underline{x} = \mathbf{F}_{\sigma \text{ boundary}} d\underline{x}$$

*Sign convention for work:*

$W$  or  $\delta W > 0$  if the surroundings does work on the system. In this manner it is possible to maintain a consistent convention that work transferred into a system will increase its energy content and work transferred out to the surroundings will decrease its energy content

*Specific type of work interaction*       $\delta W = \mathbf{F}_s \cdot d\underline{x}$

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pressure-volume —  $-PdV$  (expansion or compression of system volume)

surface deformation —  $\sigma d\underline{a}$  ( $\sigma$  = surface tension,  $\underline{a}$  = surface area)

electric charge transfer —  $\exists dq$  ( $\exists$  (or  $\epsilon$ ) = electromotive force or potential,  $q$  = charge)

electrical polarization —  $\mathbf{E} d\underline{\mathbf{D}}$  ( $\mathbf{E}$  = electric field strength,  $\underline{\mathbf{D}}$  = electric displacement)

magnetic polarization —  $\mathbf{M} d\underline{\mathbf{B}}$  ( $\mathbf{M}$  = magnetization,  $\underline{\mathbf{B}}$  = magnetic induction)

frictional —  $F_f dx$

stress-strain —  $V_o(F_x/\underline{a})d\underline{\Omega}$  ( $F_x/\underline{a}$  = stress,  $d\underline{\Omega}$  = linear strain =  $dx/x_o$ ) and  $V_o d\underline{\Omega}/\underline{a} = dx$

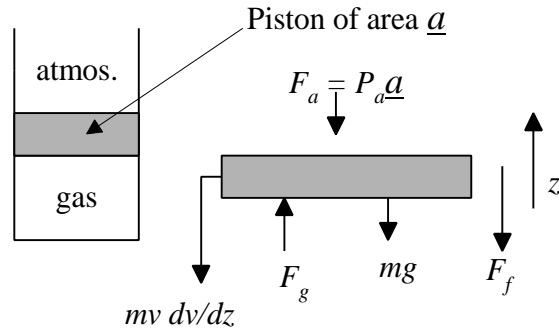
general shaft work —  $\delta W_s$

*Pressure-volume work:*

Consider a piston cylinder geometry with quasi-static conditions, thus the path can be described differentially. Define the gas inside the cylinder below the piston as the system, in this case the work effect at the piston-gas boundary is,

$$\delta W_{\text{system}} = \delta W_g = -P_{\text{gas}} dV_{\text{gas}} = F_g dx = -P_g \underline{a} dx$$

We can also describe  $\delta W_g$  using external effects by employing a force balance to connect  $F_g$  to effects in the surroundings:



$$F_g = P_a \underline{a} + mg + mv \frac{dv}{dz} + F_f$$

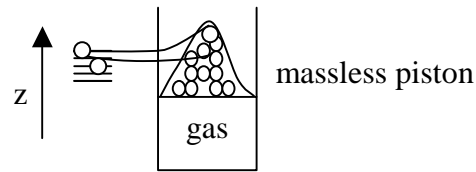
$$\delta W_{gas} = F_g \cdot d\underline{x} = P_a \underline{a} dz + mg dz + mv dv + F_f dz$$

where  $dW_{atmos.} = P_a \underline{a} dz$  ;  $\delta W_{piston} = mg dz + mv dv$  and  $dW_{wall} = F_f dz$ , i.e. frictional dissipation at the wall. Integrating,

$$W_{gas} = (P_a \underline{a} + mg)(z_2 - z_1) + \frac{m}{2}(v_2^2 - v_1^2) + \int F_f dz$$

Note that  $F_f dz$  may be small and can safely be neglected in many cases.

Alternative conceptualization--a piston-cylinder arrangement with the gas contained selected as the system. Small weights are removed and placed in storage in a gravitational field in such a manner that the  $P$ - $V$  history of the gas expansion is reproduced exactly.



This effectively is a quasi-static process where the net work is equal to the  $\Delta PE$  contained in the stored weights. Thus we can always equate the work done by a system to the rise or fall of weights (differentially) in the surroundings

In other words, 
$$\sum dW_{surroundings} + \sum dW_{system} = 0$$

as a direct result of the dynamic force balance that maintains 
$$\sum F_{system} + \sum F_{surroundings} = 0$$



## Adiabatic Work Interactions and Postulate III

Having developed the definitions of various types of work interactions, we can now examine the consequences of Postulate III in detail. First, we need to establish a convention for the sign of a work interaction. In 10.40 we assume that work is positive if the surroundings do work on the system to increase its energy content.

$$\delta W > 0 \text{ and with Postulate III } d\underline{E} = + \delta W_{adiabatic} \text{ and } \Delta\underline{E} = + W_{adiabatic}$$

Now what exactly is an adiabatic work interaction? Here we must rely on some rather specific definitions.

We recommend that you carefully read section 3.2 to firm up your understanding of adiabatic work interactions. Then proceed to examine the third postulate in the context of a change in state from (1) to (2) (or from (2) to (1)) for a closed system given by a change in the total system energy ( $\underline{E}$ ) and represented by an adiabatic process occurring at least in one direction from (1) to (2) or from (2) to (1).

## Historical Perspective -- Joule's Experiments

The 1st Law of thermodynamics resulted in part from a series of experiments carried out by Joule between 1843 and 1848. His experiments dealt with adiabatic work interactions and showed an almost exact proportionality between the amount of work expended on a system and the rise in temperature observed in a fixed mass of liquid water. Joule used a paddle wheel (shaft work) in one experiment, the compression of a gas ( $PdV$  work) in another, an electric current (electrical work) in a third test, and frictional work ( $F_f dx$ ) in a fourth set of experiments. He viewed that the change of state of the water resulted from a conversion of work into "heat" and demonstrated that a constant conversion factor existed regardless of the type of work expended, namely that  $4.184 \text{ J} = 1 \text{ calorie}$ . Since heat is only transferred across a system boundary, it is incorrect to regard the temperature increase of the water as induced by a heat interaction. Strictly speaking, it corresponds to a change in internal energy for an adiabatic system.

## Heat Interactions

Heat in a classical sense in thermodynamics is "devoid of any microscopic (physical or molecular) significance" and is defined in terms of the difference between the adiabatic work interaction and the actual work interaction that occurs as the system changes from state 1 to state 2.

$$Q = W_{adiabatic} - W = \underline{E}_2 - \underline{E}_1 - W \quad \text{or} \quad \delta Q = d\underline{E} - \delta W$$

where the energy difference  $\underline{E}_2 - \underline{E}_1 = \Delta\underline{E}$  is a state function which can be computed from an adiabatic work interaction. Like  $\delta W$ ,  $\delta Q$  is a path-dependent function that occurs only at the boundary of a system.

## Path versus State Functions

In the above treatment two different differential operators  $d$  and  $\delta$  have been used to indicate exact and path-dependent functional behavior, respectively.  $\delta$  refers to the path dependent transfer of a differential amount of work or heat (and mass as well).  $d$  refers to a differential change in a state function such as  $\underline{E}$  or  $\underline{U}$ . When these functional differentials are integrated important differences appear. For example,

$$\int \delta W = W \text{ and } \int \delta Q = Q \text{ (total amount of work or heat as a path dependent line integral)}$$

$$\int d\underline{E} = \Delta E = \underline{E}_2 - \underline{E}_1 \text{ (total change of the system energy } \underline{E} \text{ from state 1 to state 2 as indicated by the difference operator } \Delta)$$

$$\oint d\underline{E} = 0 \text{ (total change of } \underline{E} \text{ around a closed cycle is zero)}$$

$$\oint \mathbf{d}W \neq 0 \text{ or } \oint \mathbf{d}Q \neq 0 \text{ (in general, these line integrals are not necessarily zero)}$$

## First Law for Thermodynamics for Simple, Open Systems

entering streams — in  
 leaving streams — out  
 state 1 — initial condition  
 state 2 — final condition

Although the system A bounded by the  $\sigma$ -surface is open, the composite system A +  $\delta n_{in}$  is closed. If  $\underline{E}$  is the total energy of system A, then by applying the 1st law to the closed composite system:

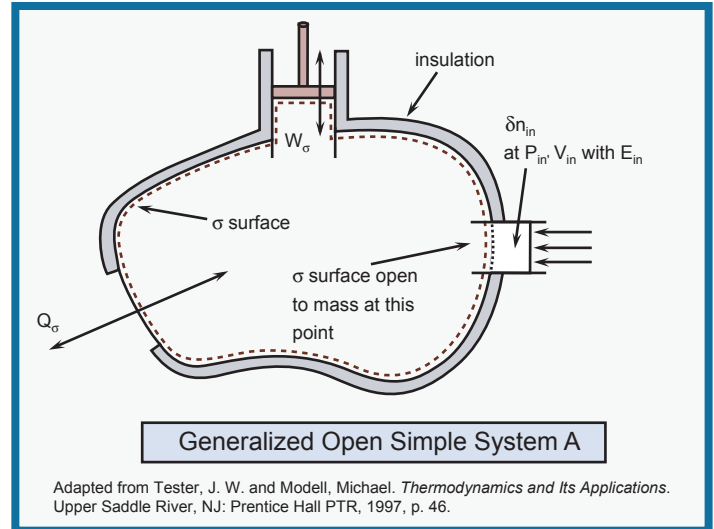


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$$\underline{E}_2 - (\underline{E}_1 + E_{in} \delta n_{in}) = \delta Q + \delta W + P_{in} V_{in} \delta n_{in}$$

If the composite system is simple then  $\underline{E} = \underline{U}$  in system A and  $E_{in} = U_{in}$  for the incoming stream then we can define a new property the enthalpy  $H$  of the incoming stream as

$$H_{in} \equiv (U + PV)_{in}$$

Therefore, the open system form of the 1st law can be written in differential form for this particular simple system A as:

$$d\underline{U} = \delta Q_{\sigma} + \delta W_{\sigma} + H_{in} \delta n_{in}$$

Generalizing for multiple entering and exiting streams:

$$d\underline{U} = \delta Q_{\sigma} + \delta W_{\sigma} + \sum_{in} H_{in} \delta n_{in} - \sum_{out} H_{out} \delta n_{out} \quad (3-60)$$

Note that we have retained the path dependent differential operator  $\delta$  for  $n_{in}$  and  $n_{out}$  because, strictly speaking, only  $dN$  of the system is a state variable with:

$$dN = \delta n_{in} - \delta n_{out} \quad (3-58)$$

or for the case of multiple streams

$$dN = \sum_{in} \delta n_{in} - \sum_{out} \delta n_{out}$$

## First Law for Open, Non-simple Systems with PE + KE Effects

*Decomposition of  $\underline{E}$  into three main components*

1. KE due to inertial effects (velocity/acceleration of center of mass)
2. PE due to location in gravitational field of the earth
3. Internal ( $\underline{U}$ ) – everything else associated with microscopic energy storage on a molecular level. This uncoupling requires that we use constitutive equations for kinetic and potential energy which are easily obtained from our experience in physics and mechanics, namely:

$$\underline{E} = \underline{E}_{KE} + \underline{E}_{PE} + \underline{U} \quad (3-61)$$

$$d\underline{E} = d\underline{E}_{KE} + d\underline{E}_{PE} + d\underline{U} \quad (3-62)$$

where

$$\underline{E}_{KE} = \frac{m|\langle \mathbf{v} \rangle|^2}{2} = \frac{mv^2}{2} \quad \text{and} \quad \underline{E}_{PE} = mgz$$

here  $m$  is the mass of the system or subsystem of interest and  $|\langle \mathbf{v} \rangle|$  is the magnitude of the velocity vector  $\langle \mathbf{v} \rangle$ .

By following the decomposition of  $\underline{E}$  outlined above and the mathematical approach that led to Eq. (3-60), we obtain a general expression for the *First Law* for an open system with its center of mass located at a vertical distance  $\langle z \rangle$  from a reference plane at  $z = 0$  and traveling with velocity  $\langle \mathbf{v} \rangle$  as shown in Figure 3.11. Note that now we will employ a mass (rather than mole) basis for the intensive enthalpy terms in the summations of Eq. (3-60): that is  $H_{in}$  and  $H_{out}$  have SI units of J/kg. The incoming and outgoing streams also need their appropriate potential energy contributions (from  $gz_{in}\delta n_{in}/2$  and  $gz_{out}\delta n_{out}$ ) and kinetic energy contributions (from  $v_{in}^2\delta n_{in}/2$  and  $v_{out}^2\delta n_{out}/2$ ). For this case, the **general form of the First Law for open, non-simple systems** is written as:

$$d\underline{E} = \delta Q_{\sigma} + \delta W_{\sigma} + \sum_{in} \left[ H_{in} + gz_{in} + \frac{v_{in}^2}{2} \right] \delta n_{in} - \sum_{out} \left[ H_{out} + gz_{out} + \frac{v_{out}^2}{2} \right] \delta n_{out} \quad (3-63)$$

$$\text{with} \quad d\underline{E} = d \left[ \underline{U} + mg\langle z \rangle + \frac{m|\langle \mathbf{v} \rangle|^2}{2} \right]$$

For any transient process we can use Eq. (3-58) to obtain the rate of change of mass or moles ( $dN/dt$ ) for the system and differentiate Eq. (3-63) to obtain the rate of change of the system's total energy ( $d\underline{E}/dt$ ). Thus,

$$\frac{d\underline{E}}{dt} = \frac{dQ_s}{dt} + \frac{dW_s}{dt} + \sum_{in} \left[ H_{in} + gz_{in} + \frac{v_{in}^2}{2} \right] \frac{dn_{in}}{dt} - \sum_{out} \left[ H_{out} + gz_{out} + \frac{v_{out}^2}{2} \right] \frac{dn_{out}}{dt} \quad (3-64)$$

to avoid ambiguities, a mass basis should be selected if kinetic and potential energy effects are to be included. The sums run over all incoming and outgoing streams. For operation at steady state with single inlet and outlet streams, Eq. (3-64) is greatly simplified because both

$$\frac{dE}{dt} = 0 \quad \text{and} \quad \frac{dN}{dt} = 0$$

As for the system, the total energy  $E$  and mass/moles  $N$  are constant.

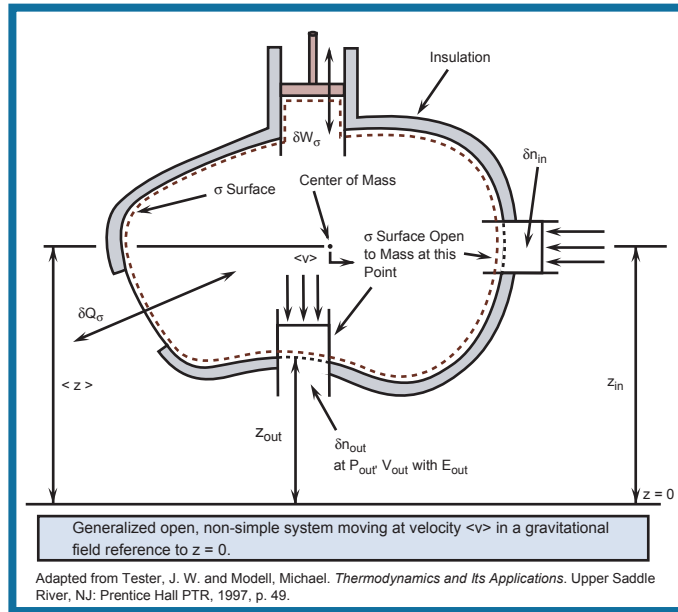


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which implies that  $\delta n_{in} = \delta n_{out}$  and

$$\frac{\delta n_{in}}{\delta t} = \frac{\delta n_{out}}{\delta t} \equiv \frac{\delta n}{\delta t} = \dot{n} \quad (3-66)$$

Therefore, Eq. (3-64) is modified for *steady state conditions* to:

$$\frac{\delta Q_{\sigma}}{\delta t} + \frac{\delta W_{\sigma}}{\delta t} = \dot{Q}_{\sigma} + \dot{W}_{\sigma} = (\Delta H_{ss} + \Delta PE_{ss} + \Delta KE_{ss}) \dot{n} \quad (3-67)$$

where

$$\Delta H_{ss} \equiv H_{out} - H_{in}; \quad \Delta PE_{ss} \equiv g(z_{out} - z_{in}); \quad \Delta KE_{ss} \equiv \frac{v_{out}^2 - v_{in}^2}{2}$$

represent the time-invariant changes between the outlet and inlet stream quantities.

In some practical situations, other forms of macroscopic energy storage besides kinetic or gravitational potential energy may be important. To account for these effects, which could include storage in rotational modes, electric or magnetic fields, and elastic deformation by stress-strain effects, it is relatively straightforward to modify Eqs. (3-63) and (3-64) (see Chapter 18). Further, you may encounter problems where incoming and outgoing stream fluxes are distributed on the  $\sigma$ -boundary that encloses the system. In addition, the heat flux may also be distributed on the  $\sigma$ -surface rather than occurring at discrete locations and there may be multiple work interactions. In these cases, an integral form of Eq. (3-64) should be used:

$$\boxed{\int_{\underline{V}} \frac{\partial(\mathbf{r}E)}{\partial t} d\underline{V} = - \int_{\underline{a}_s} \mathbf{q} \cdot \mathbf{n} d\underline{a}_s + \sum_i \dot{W}_{s,i} - \int_{\underline{a}_s} \rho \left( H + gz + \frac{v^2}{2} \right) \mathbf{v} \cdot \mathbf{n} d\underline{a}_s} \quad (3-68)$$

where  $\mathbf{q}$  and  $\mathbf{v}$  represent vectors for the heat flux and fluid velocity, and  $\mathbf{n}$  is the unit normal vector, perpendicular to the  $\sigma$ -surface pointing outward. Note that there are two types of integrals involved, one for the total energy over the volume  $\underline{V}$  of the system and another for the heat and mass flux contributions over the surface area of the  $\sigma$ -boundary  $\underline{a}_\sigma$ . Note that we have inserted an underbar with the term  $\underline{a}_\sigma$  to emphasize that as used here it is the total extensive area. The parameters  $\mathbf{q}$ ,  $\rho \left( H + gz + v^2 / 2 \right)$  and  $\mathbf{v}$  are spatially dependent.

**Energy and the 1<sup>st</sup> law Treatment  
Summary of mathematical forms**

System	Expression
1. closed, general	$d\bar{E} = \delta Q + \delta W$
2. closed, simple	$d\bar{E} = d\bar{U} = \delta Q + \delta W$
3. closed, simple, only $PdV$ work	$d\bar{U} = \delta Q - Pd\bar{V}$
4. open, simple	$d\bar{U} = \delta Q_\sigma + \delta W_\sigma + \sum_{in} H_{in} \delta n_{in} - \sum_{out} H_{out} \delta n_{out}$
5. open, non-simple PE+KE only (use mass basis)	$d\bar{E} = \delta Q_\sigma + \delta W_\sigma + \sum_{in} \left( H_{in} + gz_{in} + \frac{v_{in}^2}{2} \right) \delta m_{in} - \sum_{out} \left( H_{out} + gz_{out} + \frac{v_{out}^2}{2} \right) \delta m_{out}$ $d\bar{E} = d \left( \bar{U} + mg\langle z \rangle + \frac{m\langle v^2 \rangle}{2} \right)$
6. steady state, open, non-simple	$d\bar{E} = 0 \quad dm = 0 \quad \text{or} \quad dN = 0 \quad (\text{if no reactions})$ $\frac{d\bar{E}}{dt} = \frac{dm}{dt} = \frac{dN}{dt} = 0$ $\frac{\delta n_{in}}{\delta t} = \frac{\delta n_{out}}{\delta t} = \dot{n}$ <p>plus expression (5)</p> $\frac{d\bar{E}}{dt} = 0 \quad \frac{\delta Q_\sigma}{\delta t} + \frac{\delta W_\sigma}{\delta t} = (\Delta H_{ss} + \Delta PE_{ss} + \Delta KE_{ss}) \dot{n}$ $\Delta H_{ss} = H_{out} - H_{in} \quad \Delta PE_{ss} = g(z_{out} - z_{in}) \quad \Delta KE_{ss} = \frac{v_{out}^2 - v_{in}^2}{2}$
7. non-simple, open distributed interaction along $\sigma$ -surface	$\int_{\underline{V}} \left( \frac{\partial(\mathbf{r}E)}{\partial t} \right) d\underline{V} = - \int_{\underline{a}_s} \mathbf{q} \cdot \underline{\mathbf{n}} d\underline{a}_s + \sum \dot{W}_{s,i} - \int_{\underline{a}_s} \mathbf{r} \left( H + gz + \frac{v^2}{2} \right) \mathbf{v} \cdot \underline{\mathbf{n}} d\underline{a}_s$