Thermodynamics
Review and Relations

Review

- Gas filled piston

Motivation

Thermodynamics is a complete science. It was originally developed our of experimental observations in an effort to improve the efficiency of steam engine. Only macroscopic continues states of matter are considered. Thermodynamics enables quantities defined from energy and geometry to be simply related. An understanding of thermodynamics is essential since it easily to statistical mechanics.

Definitions and Convention

Signs The sign of energy, work and heat imparted on or extracted from the system simply depends on convention. Since, Engineers, Chemist and Physicist often use different conventions therefore a fundamental understanding is essential. Consider a bounded system.

- **Fetter's** convention defines all energy added to the system (E) in the form of heat (Q) added or work done (W) on the system to be positive.

- **Reif** defines the work (W) done *by* the system a positive quantity. However he does define a script (W) that positive for work done on the system.

Integrals are always evaluated

$$\int_{\text{initial state}}^{\text{final state}}$$

An **exact differential** or perfect differential is path independent and denoted by d

An **inexact differential** or imperfect differential is dependent on the path of integration and is denoted by đ

Macroscopic State or Macrostate

An **Isolated System** is unable to exchange energy in the form of heat or work with any other system.

Irreversible If the final situation is such that the imposition or removal of constrains of this isolated system cannot restore the initial situation, then the process is irreversible. [1]

Reversible If imposing or removing some constraints on the system enables it to restore it to it initial situation, the the process is reversible. [2]

If you make a movie of the system and you run it in reverse and it looks possible then the system is reversible.

Laws of Thermodynamics

A macroscopic treatment is assumed for all for laws.

Zeroth Law

If two systems are in thermal equilibrium with a third system they must be in thermal equilibrium with each other. [3]

As the name points out the law was an after thought, formulated in the 1930's. It confirms that temperature is a valid quantity for comparing systems.

First Law

The internal energy of an isolated system is constant. If the system interacts energy must be conserved by considering heat flow and work done. Using the sign conventions from class:

$$dE = \text{đ}Q + \text{đ}W$$

$E \rightarrow$ is the internal energy of the system
$Q \rightarrow$ is the heat absorbed by the system
$W \rightarrow$ is work done on the system

This convention used by Fetter is simple because imparting energy to the system will always be positive.

We see that the difference between initial and final energy states are independent of path. Think about for different ways to manipulate a gas piston system.

Process	Restriction	Result
Adiabatic	$W = 0$	$\Delta E = W$
Constant Vol	W=0	$\Delta E = Q$
Closed Cycle	$\Delta E = 0$	$Q = -W$
Free Expansion	$Q = W = 0$	$\Delta E = 0$

Fetter's conventions are followed

Second Law

Entropy is a state function of an isolated system that will tend to increase as the system changes microstates. If the system is not isolated the differential for energy can be defined as

$$\text{đ}S = \frac{\text{đ}Q}{T}$$

The second law is closely related to the reversibility of a system. If the entropy of the entire isolated system increases it is irreversible.

Feynman has some good thoughts to include here.

Third Law

The entropy of a system has the limiting property that as

$$T \rightarrow 0$$

$$S \rightarrow S_o$$

where S_o is a constant independent of all parameters of the particular system.

Thermodynamics Potentials

Starting with the fundamental thermodynamic relation four relations are developed for specific independent variables.

$$\text{đ}Q = TdS = dE + pdV$$

Internal Energy E(S,V)

Following from above

$$dE = EdS - pdV$$

Now since $E = E(S, V)$ we can make a *purely mathematical* assertion with the product rule:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

We can now clearly see that

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad \left(\frac{\partial E}{\partial V}\right)_S = -p$$

Taking the second derivative will lead to Maxwell's relations

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S$$

Thus giving use our first Maxwell Relation

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

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[1] Reif, p91
[2] Reif, p91
[3] Reif, p122

Author: W. Schlotter
wschlott@stanford.edu

Enthalpy H(S,p)

Enthalpy defined

$$H \equiv E + pV$$

We can thus look at the differential for $H(S,p)$

$$dH = TdS + Vdp$$

thus giving

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

and so we can arrive at another Maxwell Relation

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Helmholtz free energy F(T,V)

According to Fetter it's called a free energy because it represents the work that can be extracted in an isothermal process.

The Helmholtz free energy defined

$$F \equiv E - TS$$

Again we look at the differential form $F(T,V)$

$$dF = -SdT + -pdV$$

thus giving

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

and our Maxwell relation is

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

We might also want to consider the number of particles in the system as an independent variable. Now

$$dF = -SdT + -pdV + \sum_i \mu_i dN_i$$

Gibbs free energy G(T,p)

The Gibbs free energy defined

$$G \equiv E - TS + pV$$

Again we look at the differential form $G(T,p)$

$$dG = -SdT + Vdp$$

thus giving

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

and our Maxwell relation is

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

Summary of Thermodynamics Quantities

Heat Capacity

$$C_V = \left(\frac{\text{đ}Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Here the heat capacity is given for constant volume but switching V with p will give you heat capacity for constant pressure. The lower case c_v is the specific heat capacity which normalizes the heat capacity to molar mass or mass density

Volume Coefficient of expansion

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

Isothermal compressibility

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

Adiabatic Process Constant γ

$$\gamma \equiv \frac{c_p}{c_v}$$

For Adiabatic processes pV^γ is a constant

Chemical Potential We might also want to consider the number of particles in the system as an independent variable. Now

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

and so we can find the chemical potential for a given species i from

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

Classical Ideal Gas

Number of particles N is a pure number of order 10^{23} with $N = N_o n_m$

Number of Moles n_m or ν.

Avogadro's Number $N_o = 6.02\times 10^{23}$ entities per mole

Bolivians Constant $k_B = 1.38 \times 10^{-23} J/Kor 8.82^{-5} eV/K$and $k_B = \frac{R}{N_o}$

Universal Gas Constant $R = 8.31 J/mol \cdot K$ and $R = c_p - c_V$

A view versions of the ideal gas law

$$pV = n_m RT$$
$$pV = N k_B T$$

Derivative Crusher Algorithm

First bring y to the numerator

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

Next bring z to the numerator

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

Now we can introduce a new variable (eg w) usually from the Maxwell relations

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

Now we can use these relations to find thermodynamic constants

References and Further Reading

Reif, *Fundamentals of Statistical and Thermal Physics*,McGraw-Hill, Boston, (1965)

Related topics

Statistical Mechanics