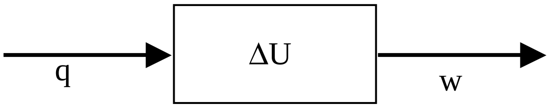
August 27, 2001

Reading: Chapter Two
Homework: 2.1,2.3,2.5,2.7

First law of thermodynamics: A statement of energy conservation.



Change in internal energy = heat input – work done

$$\Delta U = q - w$$

$$dU = \delta q - \delta w$$

Sign conventions:

- $q > 0$: heat input into the system from the surroundings.
- $w > 0$: work done by the system on the surroundings.
- $\Delta U > 0$: when the internal energy of the system increase.

dU is an exact differential, path independent; δq (δw) is a Pfaffian differential, path dependent.

U = K.E (kinetic energy) + P.E (potential energy). Microscopically, K.E is related to the motion of particles (proportional to the sum of square of particle velocities) and P.E is related to the interaction between particles (a function of particle positions and inter-particle potentials). Macroscopically, K.E. is related to temperature and P.E. is related to pressure and Volume.

For an one-component system:

State variables: P,V,T,U
State functions: P,V,T,U
Process functions: q, w

$V=V(P,T)$; $P=P(V,T)$; $T=T(P,V)$
$U=U(P,T) = U(P,T) = U(P,V)$
Treating U as a state variable: $V=V(U,P)$ or $V=V(U,T)$, etc.

Idea gas:

A hypothetical gas that obeys Boyles's and Charles' laws exactly at all temperatures and pressures is called *ideal gas*.

Boyle's law: $P_0 V(T, P_0) = PV(T, P)$;

Charles' law: $\frac{V(P_0,T_0)}{T_0}=\frac{V(P_0,T)}{T}$;

Idea gas law: $\frac{PV}{T}=\frac{P_0V_0}{T_0}=const.$

Where P_0 = standard pressure (1 atm)
T_0 = standard temperature (absolute scale with 0^oC=-273.15 K)
$V_0 = V(P_0,T_0)$ = 22.414 liters

Then, PV = RT,

$$R=\frac{P_0V_0}{T_0}=0.082057 \text{ liter atm/degreee mole} = 8.3144 \text{ joules/degree mole.}$$

Consider internal energy, U=U(V,T), so

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

For an idea gas, there is no interaction between particles. Consequently, $\left(\frac{\partial U}{\partial V}\right)_T=0$. U will be only a function of temperature T, U=U(V,T)=U(T), i.e., all the internal energy is kinetic. (In contrast, for a solid material, $\left(\frac{\partial U}{\partial V}\right)_T\neq 0$ because there are always strong interactions between particles or they won't form condensed phase.)

For a monatomic idea gas,

$$U=N\cdot(\frac{3}{2}k_BT)=\frac{3}{2}RT\,.$$

Usually, gases at very low pressures can be modeled as an idea gas because the interactions between particles are very weak.

Types of Process:

Isothermal (constant temperature):	T = constant
Isobaric(constant pressure):	P = constant
Isometric(constant volume):	V = constant

Adiabatic: q = 0

Definition of Heat Capacity:

$$C = \frac{q}{\Delta T} = \frac{\delta q}{dT}$$

$C_V = \left(\frac{\delta q}{dT}\right)_V$ --- the heat capacity at constant volume

$C_P = \left(\frac{\delta q}{dT}\right)_P$ --- the heat capacity at constant pressure

Isometric (Constant Volume) Process:

$$w = \int PdV = 0$$

$\Delta U = q_V$ or $dU = \delta q_V$

$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

For a monatomic idea gas, $C_V = \frac{3}{2}R$.

Isobaric (Constant Pressure) Process and Enthalpy H:

In an isobaric process in which pressure is kept constant, the work done by the system to take the system from state 1 to state 2 is

$$w = \int_1^2 PdV = P\int_1^2 dV = P(V_2 - V_1).$$

From the First Law

$$U_2 - U_1 = q_p - P(V_2 - V_1),$$

where subscript p denotes constant pressure. Rearrange

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p.$$

Introduce a state function, *enthalpy*, H, for the constant pressure process:

$$H = U + PV,$$

Then for an isobaric process,

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

Thus the enthalpy change during an isobaric process equals to the heat adsorbed or released from the system.

$$C_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$$

For a monatomic idea gas,

$$PV = RT$$
$$PdV = RdT$$
$$\delta q_p = dH = dU + PdV = C_V dT + RdT = (C_V + R)dT$$
$$C_P = \left(\frac{\delta q}{dT}\right)_P = C_V + R = \frac{5}{2}R$$