

Part II: First Law of Thermodynamics

Lecture 6:

- Some Consequences of the First Law
 - Heat Capacity
 - Specific heat Capacity
 - Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids
- Some Applications of the First Law

Some Consequences of the First Law

2-5 Heat Capacity

We have already defined heat capacity as the amount of heat required to raise the temperature of a mass of a system by 1°C. It is denoted by C .

$$Q = C \Delta T \quad 2-37$$

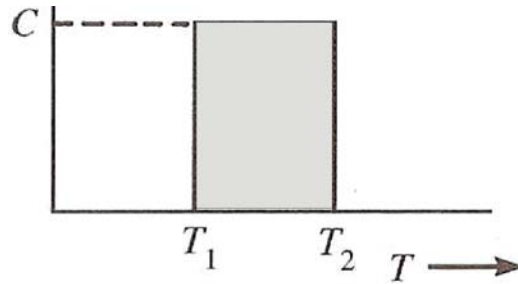
Where Q is in kJ, C in kJ/kg.°C.

Equation 2-37 is a general definition of heat capacity and it implies that the heat capacity of a system depends not only on the heat-absorbing ability but also, in a simple way, on the amount of substance present.

- When defining heat capacity in terms of material in the system, we have:
 - *Specific heat capacity*. Heat absorbed by 1 kg of material that undergoes a rise in temperature of 1°C.
 - *Molar heat capacity*. Heat absorbed by 1 kg mol of material that undergoes a rise in temperature of 1°C.
- When the heat capacity is essentially constant between the two temperatures T_1 and T_2 ,

$$Q = C \Delta T = C (T_2 - T_1) \quad 2-37a$$

See figure (it is numerically equal to the area under the curve).



If C varies significantly with temperature, then:

$$Q = \int_{T_1}^{T_2} C(T) dT \quad 2-38$$

and again, it is numerically equal to the area under the curve.

- We can express C by an empirical power series such as $C = a + bT + cT^2$
Then,

$$Q = \int_{T_1}^{T_2} (a + bT + cT^2) dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + c\left(\frac{1}{3}T_2^3 - \frac{1}{3}T_1^3\right)$$

Note: If the heat capacity cannot be expressed analytically as a function of temperature and experimental data is available, Q can be evaluated from the C vs. T graph. If a suitable function is available, the integration can be performed numerically by the use of integration rules.

2-6 Specific Heat Capacity

We already know that the quantity of heat exchange with a system depends on the path, thus, for different paths, C will be different.

- At **constant volume**, over a temperature range in which the heat capacity is constant, Equation 2-37 becomes

$$Q_V = C_V \Delta T \quad 2-39$$

And because the volume is constant, $Q_V = \Delta U$, thus

$$\Delta U = C_V \Delta T \quad 2-40$$

If C_V is the molar heat capacity, then for n moles,

$$\Delta U = n C_V \Delta T \quad 2-41$$

If, over the temperature range concerned, C_V is not constant

$$\Delta U = Q_V = \int_1^2 C_V(T) dT \quad 2-42$$

(ii) At **constant pressure**, we have similarly

$$Q_P = C_P \Delta T \quad 2-43$$

If in Eq 2-36 there are no other types of work involved except boundary work, then $Q_P = \Delta H$, and thus, for a constant C_P

$$\Delta H = C_P \Delta T \quad 2-44$$

and for n moles

$$\Delta H = n C_P \Delta T \quad 2-45$$

and if C_P varies, then

$$\Delta H = Q_p = \int_1^2 C_p(T) dT \quad 2-46$$

(iii) Relationship between **constant pressure** C_P and **constant volume** C_V .
For the molar heats, we have

$$C_P = C_V + R. \quad 2-47$$

The ratio of the 'heat capacities' is given by

$$\gamma = C_P / C_V \quad 2-48$$

For monatomic gases $\gamma = 1.67$.

Eq. 2-47 holds approximately for di- and polyatomic gasses

Heat capacity ratio of some important gases at 0.1 MPa pressure

Gas	Specific heat (kJ kg ⁻¹ K ⁻¹)		Molar heat capacity (Jmol ⁻¹ K ⁻¹)		$C_p - C_v$ (Jmol ⁻¹ K ⁻¹)	γ
	C_v	C_p	C_v	C_p		
Monatomic						
He	3.138	4.812	12.468	20.794	8.326	1.67
Ne	0.619	1.029	12.468	20.794	8.326	1.67
A						1.67
Hg						1.67
Na						1.67
Diatomic						
H ₂		0.014				1.40
N ₂	0.740	1.038	20.753	29.079	8.326	1.40
Air	0.718	1.005	20.8	29.114	8.314	1.4
O ₂	0.648	0.912	21.046	29.413	8.368	1.40
Triatomic						
CO ₂	0.640	0.833	28.451	36.945	8.494	1.30
H ₂ O	1.464	2.017	25.941	34.309	8.368	1.32
Polyatomic						
C ₂ H ₆	1.435	1.724	43.095	51.672	8.577	1.20

Example 2-11

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (a) the functional form of the specific heat and (b) the average specific heat value.

Solution

At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values ($T_{cr} = -147^\circ\text{C}$, $P_{cr} = 3390$ kPa for nitrogen, the main constituent of air). The internal energy change Δu of ideal gases depends on the initial and final temperatures only, and not on the type of process.

Thus, the solution given below is valid for any kind of process.

(a) The change in internal energy of air, using the functional form of the specific heat, is determined as follows. The $C_{P\ mol}(T)$ of air is given in the form of a third-degree polynomial expressed as

$$C_{P\ mol}(T) = a + bT + cT^2 + dT^3$$

where $a = 28.11$, $b = 0.1967 \times 10^{-2}$, $c = 0.4802 \times 10^{-5}$, and $d = -1.966 \times 10^{-9}$. Next we have

$$C_{V\ mol}(T) = C_{P\ mol} - R_{mol} = (a - R_{mol}) + bT + cT^2 + dT^3$$

Replacing it in Eq. 2-42 and performing the integral, we get

$$\Delta U = 6447.15 \text{ kJ / kmol}$$

The molar mass of air is 28.97 kg /kmol, thus, the change in internal energy per unit mass is:

$$\Delta u = \Delta U / M = 225.55 \text{ kJ / kg}$$

(b) The average value of the constant-volume specific heat $C_{v,av}$ is determined from the values at 300 and 600 K. At the average temperature 450 K tables give the value to be

$$C_{v,av} = C_{V@450K} = 0.733 \text{ kJ/(kg . K)}$$

Thus $\Delta u = C_{v,av} (T_2 - T_1) = 219.9 \text{ kJ / kg}$

This answer differs from the above result by only 1.2 percent. This close agreement is not surprising since the assumption that C_v varies linearly with temperature is a reasonable one at temperature intervals of only a few hundred degrees. If we had used the C_v value at $T_1 = 300$ K instead of at T_{av} , the result would be 215.4 kJ/kg, which is in error by about 3 percent. Errors of this magnitude are acceptable for most engineering purposes.

Example 2-12

A piston-cylinder device initially contains 0.5 m^3 of nitrogen gas at 400 kPa and 27°C . An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of 2800 J occurs during the process. Determine the final temperature of the nitrogen.

Solution

This time, we take the nitrogen in the piston-cylinder device as our system. At the specified conditions, the nitrogen gas can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values ($T_{cr} = -147^\circ\text{C}$, $P_{cr} = 3390 \text{ kPa}$).

First, let us determine the electrical work done on the nitrogen:

$$W_e = V I \Delta t = 72 \text{ kJ}$$

The mass of nitrogen is determined from the ideal-gas relation

$$m = PV / RT = 2.25 \text{ kg}$$

The conservation of energy gives:

$$Q + W_e + W_b = \Delta U$$

For a constant pressure process of a closed system,

$$Q + W_e = \Delta H = mC_p (T_2 - T_1)$$

Using the value of $C_p = 1.039 \text{ kJ/kg}$ from the table, we get $T_2 = 56.6^\circ\text{C}$

2-7 Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids

The difference between C_p and C_v for liquids and solids is rather small, and, except for where high accuracy is required, it is sufficient to take $C_p = C_v$. The reason for this is that the thermal expansion coefficients of liquids and solids are very small, so that the volume change on increasing the temperature by 1°C is very small; correspondingly the work produced by the expansion is small and little energy is required for the small increase in the spacing of the molecules.

A substance whose specific volume (or density) is constant is called an incompressible

substance. The specific volumes of solids and liquids essentially remain constant during a process. Therefore, liquids and solids can be approximated as **incompressible substances** without sacrificing much in accuracy. The constant-volume assumption should be taken to imply that the energy associated with the volume change, such as the boundary work, is negligible compared with other forms of energy. Otherwise, this assumption would be ridiculous for studying the thermal stresses in solids (caused by volume change with temperature) or analyzing liquid-in-glass thermometers. For solids and liquids,

$$C_p = C_v = C \quad 2-49$$

Example: C_p for asphalt is 0.920 kJ / kg . °C

Like those of ideal gases, the specific heats of incompressible substances depend on temperature only.

$$dU = C_v dT = C(T) dT \quad 2-50$$

The change in the internal energy between two states is

$$\Delta U = U_2 - U_1 = \int_1^2 C(T) dT \quad 2-51$$

For small temperature intervals, we can use an average value for C

$$\Delta U \approx C_{av}(T_2 - T_1) \quad 2-52$$

For the enthalpy, by using its definition, we get

$$\Delta H = \Delta U + V\Delta P \quad (\text{kJ}) \quad 2-53$$

The second term in the above equation is often small compared with the first term and can be neglected without significant loss of accuracy.

2-8 Heat Conduction

We have seen that the for a temperature gradient dT / dx the heat flows as

$$\dot{Q}_{cond} = -kA \frac{dT}{dx} \quad (2-8)$$

where k is the thermal conductivity of the material (in $\text{W/m}^0\text{C}$).

A substance with a large thermal conductivity is known as a *thermal conductor*, and one with a small value of k as a *thermal insulator*. The numerical value of k depends on a number of factors, one of which is the temperature. If the temperature difference between parts of a substance is small, k can be considered to be almost constant throughout the substance.

Examples of practical situations. In all cases, we shall assume that k is constant throughout the conducting substance.

- (a) *Linear flow of heat perpendicular to the faces of a slab.* If the temperature difference $T_1 - T_2$ and the thickness d are small, then

$$\dot{Q} = kA \frac{T_1 - T_2}{d}$$

- (b) *Radial flow of heat between two coaxial cylinders.* If the conducting material lies between an inner cylinder of radius r_1 kept at temperature T_1 and an outer cylinder of radius r_2 , and temperature T_2 both of length l , then there will be a steady radial flow of heat at the constant rate.

The area through which heat flows depends on the distance from the cylinders. For a distance r from the axis of the cylinders, the area is $A = 2\pi rl$ and for a thickness dr , the temperature gradient is dT/dr . Thus,

$$\dot{Q} = -k2\pi rl \frac{dT}{dr}$$

$$dT = -\frac{\dot{Q}}{2\pi lk} \frac{dr}{r}$$

and after integration:

$$T_1 - T_2 = \frac{\dot{Q}}{2\pi lk} \ln\left(\frac{r_2}{r_1}\right)$$

(c) *Radial flow of heat between two concentric spheres.* If the conducting material lies between an inner sphere of radius r_1 held at constant temperature T_1 and an outer sphere of radius r_2 held at constant temperature T_2 there will be a steady radial flow of heat at a constant rate. In this case by following a procedure similar to the concentric cylinders we get:

$$T_1 - T_2 = \frac{\dot{Q}}{4\pi k} \ln\left(\frac{r_2}{r_1}\right)$$

2-9 Reversible and irreversible processes

Reversible isothermal process

An ideal gas is placed in a cylinder with a piston, and expands very slowly and keeps the temperature constant all the time by either withdrawing heat from, or supplying heat to the system. Let P_1, V_1, T_1 be the initial state and P_2, V_2, T_2 be the final state.

For a perfect gas, $\Delta U = C_V \Delta T = 0$, and from the first law we have $Q + W = 0$

The work done by the gas for a small increase in volume dV is $dW = -P dV$
The total work between the two states is

$$W = -Q = -\int_1^2 P dV \tag{2-54}$$

which for ideal gases can be written as

$$W = -Q = -nRT \int_1^2 \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Since at constant temperature $P_1 V_1 = P_2 V_2$

$$W = -Q = -nRT \int_1^2 \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{P_1}{P_2}\right)$$

This equation can be also written as

$$P_2 = P_1 \exp\left(\frac{W}{nRT}\right) \quad 2-55$$

Irreversible isothermal process

The numerical value of the work done on the surroundings, whether positive or negative, is always a maximum in reversible process. This is, in fact, true for any kind of work and for any path. Since only irreversible processes are observable (the reversible processes are the hypothetical processes) we conclude that all observable processes produce less work than the maximum work, and result in dissipation of work as heat.

Adiabatic irreversible process (Q = 0)

In this case

$$\Delta U = W \quad 2-56$$

The change ΔU can be calculated by considering that each individual small adiabatic change $(\Delta U)_A$ is the sum of an isocoric $(\Delta U)_V$ and an isothermal process $(\Delta U)_T$, thus

$$(\Delta U)_A = (\Delta U)_V + (\Delta U)_T$$

For an isothermal process $(\Delta U)_T = 0$

$$[\Delta U]_V = n \int_1^2 C_V [T] dT \quad 2-57$$

thus

$$[\Delta U]_A = n \int_1^2 C_V dT$$

so the general equation for the adiabatic change gives

$$\Delta U = n \int_1^2 C_V dT = - \int_1^2 P dV = W \quad 2-58$$

Example 2-13

5 mol of an ideal monatomic gas, with the specific heat at constant volume being $20.92 \text{ J mol}^{-1} \text{ K}^{-1}$, expands irreversibly but adiabatically from an initial pressure of 2.02 MPa against a constant external pressure of 0.101 MPa until the temperature drops from the initial value of 27°C to a final value of 7°C . How much work has been done in the process? What is the final volume?

Solution

Eq. 2-58 gives $\Delta U = n C_V (T_2 - T_1) = -2.09 \text{ kJ}$ which is equal to the work done W . The final volume can be found as follows:

$$W = -P_{ext} (V_2 - V_1) = -2.09 \text{ kJ}$$

so

$$(V_2 - V_1) = 0.02 \text{ m}^3$$

$P_1 V_1 = nRT_1$, that give for $V_1 = 0.006 \text{ m}^3$, so $V_2 = 0.026 \text{ m}^3$

Adiabatic reversible process ($Q = 0$)

For ideal gases, the adiabatic processes are described by (see eq. 1-60)

$$PV^\gamma = \text{a constant} \quad 2-59$$

$$TV^{\gamma-1} = \text{a constant} \quad 2-60$$

where $\gamma = C_P / C_V$, and $\gamma - 1 = R / C_V$.

For van der Waals gases, the above equation becomes:

$$T (V - b)^{\gamma-1} = \text{a constant} \quad 2-61$$

For ideal gases, by replacing V with nRT/P in Eq.2-59 we get

$$T^\gamma P^{1-\gamma} = \text{const} \quad 2-62$$

or

$$T P^{1/\gamma - 1} = \text{a constant} \quad 2-63$$

For real gases, some of the adiabatic expansion forms are:

$$T[V - b]^{\gamma-1} = \text{const.}$$

$$T \left(P + \frac{a}{V^2} \right)^{1/\gamma-1} = \text{const.} \quad 2-64$$

$$\left(P + \frac{a}{V^2} \right) [V - b]^\gamma = \text{const}$$

The work done in a adiabatic expansion can be calculated from

$$W = - \int_1^2 P dV \quad 2-65$$

where P is (const. $\times V^\gamma$) which gives

$$W = - \frac{1}{1-\gamma} \left[C V^{1-\gamma} \right]_{V_1}^{V_2} \quad 2-66$$

where C is a constant. This becomes

$$W = - \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1] \quad 2-67$$

In adiabatic processes, from $\Delta U = Q + W$, $Q = 0$, we get $W = \Delta U$

But $\Delta U = C_V \Delta T$, thus,

$$W = - C_V \Delta T \quad 2-68$$

And for a real gas

$$W = - C_V \Delta T + a \Delta (1/V) \quad 2-69$$

Enthalpy ($H = U + PV$)

For an isobaric process the first law can be written as

$$\Delta U = Q + W = Q_P - P (V_2 - V_1)$$

rearranging, we get

$$\Delta H = Q_P \quad 2-70$$

Thus,

- *The heat absorbed in any reversible isobaric process is equal to the difference between the enthalpies of the system in the end states of the process.*
- *Enthalpy, like energy U or temperature T , is a function of state of the system alone and is independent of the path through which that state is reached.*

Because $Q_P = C_P \Delta T = \Delta H$

We get

$$C_P = (\partial H / \partial T)_P \quad 2-71$$

Consider a stationary closed system undergoing a constant-volume process ($W_b = 0$). The first-law relation for this process can be expressed in the differential form as

$$\delta Q - \delta W_{other} = dU$$

The left-hand side of this equation represents the amount of energy transferred to the system in the form of heat and/or work. From the definition of C_V , this energy must be

equal to $C_V dT$, where dT is the differential change in temperature. Thus,

$$C_V dT = dU \text{ at constant volume}$$

In other words,

$$C_V = (\partial U / \partial T)_V \quad 2-72$$

For ideal gases, the work done in an isothermal process is given by (see Part I)

$$W = -\int_1^2 P dV \quad (2-65)$$

$$W = -\int_i^f P_{ext} dV = -nRT \int_i^f \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

For real gases, in order to calculate the work in an **isothermal process**, from the van der Waals equation for $n = 1$

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

we take the pressure out and get

$$W = -\left[RT \ln \left(\frac{V_2 - b}{V_1 - b} \right) + \frac{a}{V_2} - \frac{a}{V_1} \right] \quad 2-73$$

Van der Waals equation gives

$$PV = \frac{RTV}{V - b} - \frac{a}{V}$$

It can be shown that for real gases there is a small change in the internal energy with the change in the volume at constant temperature:

$$(\partial U / \partial V)_T = a / V^2$$

Thus, for an isothermal process,

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

which leads to

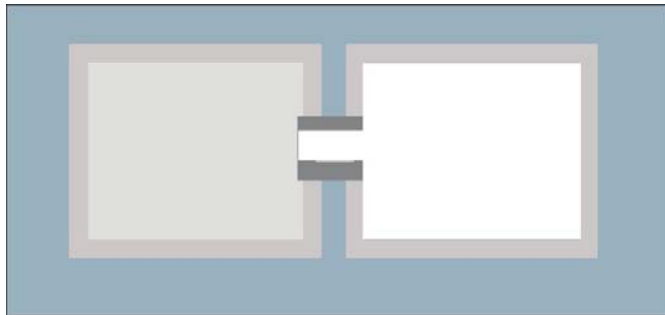
$$\Delta H = bRT \left(\frac{1}{V_2 - b} - \frac{1}{V_1 - b} \right) - \frac{2a}{V_2} + \frac{2a}{V_1} \quad 2-74$$

Joule and Joule – Thomson experiment

It is interesting to see how the energy of a gas depends on its volume, or how the enthalpy of a gas depends on pressure. For this purpose, Joule and Gay-Lussac carried out a series of experiments and later Joule and Thomson carried out another set of experiments. These two experiments are now known as the Joule experiment and the Joule-Thomson experiment.

Joule experiment

- Two containers, one containing a gas at a given pressure and temperature and the other evacuated, joined by a tube provided with a stopcock are immersed in a calorimeter bath



- The stopcock is opened, the gas is allowed to expand freely from one container into the other and then the net temperature change attending the process is measured after reaching thermal equilibrium.
- It is observed that, when ordinary gases at moderate pressures are subjected to the Joule experiment, the net temperature change is very small so that we can assume that the temperature change is actually zero.
- There is no work done by the system against an external pressure, thus $W = 0$
- There no heat exchanged with the environment, thus $Q = 0$

- In conclusion,

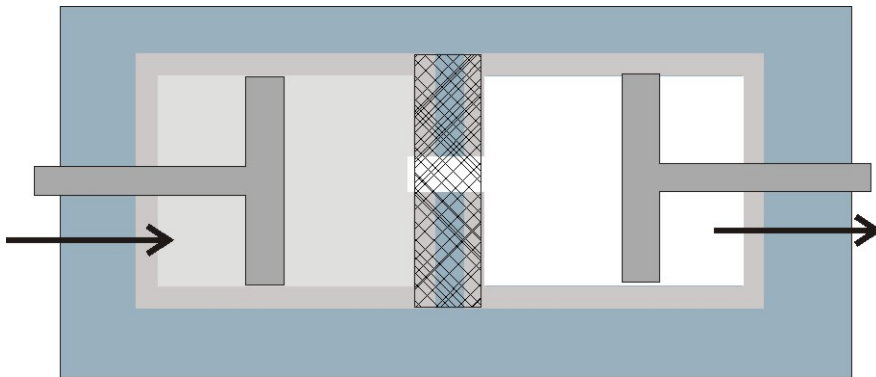
$$\Delta U = Q + W = 0$$

and the energy of an ideal gas is a function of temperature only and it does not depend on its volume. It follows that C_V depends on T only.

$$dU = C_V(T) dT$$

Joule – Thomson experiment

Joule and Thomson devised another experiment in such a way that the temperature change due to expansion of a gas would much more accurately be measured.



Note: The results of this experiment provide information about intermolecular forces. This information can be used to in the liquefaction of gases such as hydrogen and helium.

A cylindrical tube, insulated to prevent any transfer of heat to the surroundings, is fitted with two pistons and a porous plug which is capable of allowing gas to flow slowly through it. The left tube is initially filled with a certain amount of a gas at temperature T_1 , volume V_1 and pressure P_1 ; the right tube is empty. The gas is then allowed to flow slowly through the plug in such a way that its pressure in left tube is kept constant at P_1 by the movement of the piston towards the plug. At the same time the right piston is adjusted in such a way that the low pressure $P_2 (< P_1)$ is kept constant. The final volume in right tube after all the gas has streamed through the porous plug, is V_2 and its temperature T_2 . The significant datum obtained in this experiment is the change in temperature due to flow of the gas through the porous plug. This can be obtained by measuring temperatures T_1 and T_2 .

In this experiment:

- $Q = 0$
- The change in the internal energy of the system is due to the work done

$$W = P_1 V_1 - P_2 V_2$$

But

$$\Delta U = U_2 - U_1 = P_1 V_1 - P_2 V_2$$

By rearranging we get

$$\Delta H = 0$$

This shows that the Joule-Thomson experiment is carried out under constant-enthalpy conditions.

Note:

- When the gas involved is perfect, H is a function of T only, and therefore $\Delta H = 0$ implies that $\Delta T = 0$, thus no temperature change for a perfect gas.
- For a real gas it generally depends on whether T_2 is greater or smaller than T_1 . At the critical temperature (called the *Joule-Thomson inversion temperature*). Above this temperature there will be heating; below this temperature there will be cooling upon Joule-Thomson expansion.

The *Joule-Thomson coefficient* (μ) is defined as the change in temperature per unit change in pressure when the enthalpy is constant. In terms of partial derivatives

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H. \quad 2-75$$

The sign of the coefficient indicates if the gas cools or warms up upon expansion.

- if the gas cools in the process of streaming through the plug, $\mu > 0$. Conversely, when $\mu < 0$ there is an increase in temperature.

If we consider H as a function of temperature and pressure, the total differential of H is given by

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

It can be shown that if C_p remains constant over a small temperature range, then (see derivation in the text page 100)

$$\Delta T = \frac{T(\partial V/\partial T)_P - V}{C_p} \Delta P. \quad 2-76$$

This is the equation for the differential Joule-Thomson effect, ΔT being the increase in temperature for a change ΔP in pressure in the proximity of the temperature T . In their experiment, Joule and Thomson found that the decrease in temperature was proportional to the difference in pressure on the two sides of the porous plug.

For a van der Waals gas, U is not a function of temperature only, whereas for an ideal gas, U is a function only of temperature. It can be shown (see text page 102) that

$$U = U_0 + C_V T - a/V \quad 2-77$$

where U_0 is a constant of integration.

Similarly, the enthalpy for van der Waals gases is expressed as

$$H = U_0 + (C_V + R)T + P \left(b - \frac{2a}{RT} \right). \quad 2-78$$

For a small pressure change, the expansion should still be at constant enthalpy, thus

$$H(P + dP, T + dT) = H(P, T). \quad 2-79$$

The left-hand side of Eq. 2-79 can be expanded by Taylor expansion as

$$H(P + dP, T + dT) \simeq H(P, T) + \left(\frac{\partial H}{\partial P} \right)_T \partial P + \left(\frac{\partial H}{\partial T} \right)_P \partial T.$$

Combining this with 2-79 gives

$$\left(\frac{\partial H}{\partial P} \right)_T \partial P + \left(\frac{\partial H}{\partial T} \right)_P \partial T \simeq 0$$

or

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

where it was assumed that $\partial P/P$ and same for T are much smaller than 1.

By differentiating both sides of eq 2-78 with respect to P , we get

$$\left(\frac{\partial H}{\partial P} \right)_T = b - \frac{2a}{RT}$$

which leads to

$$\frac{\partial T}{\partial P} = - \frac{b - 2a / RT}{C_p}$$

So, for a Joules-Thomson expansion of a van der Waals gas,

$$b - \frac{2a}{RT} = \left(\frac{\partial H}{\partial P} \right)_T = -C_p \left(\frac{\partial T}{\partial P} \right)_H$$

At the inversion temperature T_i $\mu = \partial T / \partial P = 0$, so we can find

$$T_i = 2a / Rb \tag{2-80}$$

- At this temperature the Joule-Thomson effect is zero; no change in temperature occurs on expansion. Below T_i there is cooling and above it heating for Joule-Thomson expansion
- Evidently the Joule-Thomson effect depends on both a and b , even though it may depend only on a as it is the cohesion force a/V^2 against which work is to be done.
- By differentiating Eq. 2-78 with respect to T , and replacing $(\partial H / \partial T)$ by C_p , we get

$$C_p - C_v = R + 2aP / RT^2 \tag{2-81}$$

This shows that in the case of a van der Waals gas the difference between C_p and C_v is greater than that in the case of an ideal gas.

Some Applications of the First Law

The first law of thermodynamics is

$$dU = dQ + dW \quad 2-82$$

The energy equation of a system is the relation between the internal energy U and the state variables of the system: pressure, volume and temperature.

$$U = f(T, V) \text{ and } dW = -P dV$$

The quantity of heat dQ becomes

$$dQ = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV. \quad 2-83$$

This equation is a general equation and can be applied to any substance and to any reversible process.

$$\text{A. } V = \text{constant} \quad (dQ)_V = C_V(dT)_V$$

And from Eq, 2-83 we obtain the eq. for C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

$$\text{B. } P = \text{constant} \quad (dQ)_P = C_P(dT)_P.$$

And Eq. 2-83 becomes

$$C_P(dT)_P = C_V(dT)_P + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] (dV)_P. \quad 2-84$$

or

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P. \quad 2-85$$

C. $T = \text{constant}$

Eq. 2-83 becomes

$$[dQ]_T = P[dV]_T + \left(\frac{dU}{dV} \right)_T [dV]_T \quad 2-86$$

D. $Q = 0$

Eq. 2-83 becomes

$$C_V dT = - \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV. \quad 2-87$$

or

$$C_V \frac{\partial T}{\partial V} = - \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right]. \quad 2-88$$

$U = f(T, P)$

Differentiating dV

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP.$$

and similarly dU , the first law can be written as

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP.$$

2-89

$P = \text{constant}$ $(dQ)_P = C_P(dT)_P.$

$$C_P = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right]$$

2-90

and Eq. 2-89 becomes

$$dQ = C_P dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + \left(\frac{\partial V}{\partial P} \right)_T \right] dP$$

2-91

$V = \text{constant}$ $(dQ)_V = C_V(dT)_V$

$$C_V(dT)_V = C_P(dT)_V + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] (dP)_V$$

2-92

or

$$C_V = C_P + \left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{dP}{dT} \right)_V.$$

2-93

Similar equations can be obtained for $U = f(P, V)$

Internal Energy of Gases

It will be shown later that for any substance

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

2-94

we can compute $(dU / dV)_T$

For one mole of ideal gas, from $PV = RT$ we get $(dP / dT)_V = R / V$, thus

$$(dU / dV)_T = -P + TR / V = P - P = 0$$

This shows that at constant temperature the internal energy of an ideal gas is independent of volume or density.

By differentiating with respect to P , we also get;

$$(dU / dP)_T = 0.$$

In conclusion, the internal energy of an ideal gas depends on temperature only. Thus

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V.$$

becomes

$$C_V = \frac{dU}{dT} \quad 2-95$$

and in general

$$U = U_0 + \int_{T_0}^T C_V dT \quad 2-96$$

where U_0 is a constant.

For a mole of van der Waals gas

$$P = \frac{RT}{V - b} - \frac{a}{V^2}.$$

By differentiating with respect to T at constant volume

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

and substituting in Eq.2-94, we get

$$\left(\frac{dU}{dV}\right)_T = \frac{a}{V^2}$$

We have

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

becomes

$$dU = C_V dT + (a / V^2) dV$$

Thus

$$U = U_0 + \int_{T_0}^T C_V dT + \left[\frac{a}{V_0} - \frac{a}{V}\right] \quad 2-97$$

This shows that *the internal energy of a van der Waals gas depends on its volume and temperature*. Since the van der Waals constant *b* is a measure of molecular diameter only, it does not affect the energy, and hence it does not appear in the energy equation.