

state, and thus the difference between the values of H in two states depends only on the states and is independent of the path taken by the system in moving between them. For a constant-pressure process, $\Delta H = \Delta U + P\Delta V = (q_p - P\Delta V) + P\Delta V = q_p$. The definition of the constant-pressure molar heat capacity as $c_p = (\delta q/dT)_p = (\partial H/\partial T)_p$ (which is an experimentally measurable quantity) facilitates determination of the change in H as the result of a constant-pressure process as $\Delta H = \int_1^2 c_p dT$.

(5.) For an ideal gas, the internal energy U is a function only of temperature, and $c_p - c_v = R$.

6. The process path of an ideal gas undergoing a reversible adiabatic change of state is described by $PV^\gamma = \text{constant}$, where $\gamma = c_p/c_v$. During an adiabatic expansion, as $q = 0$, the decrease in the internal energy of the system equals the work done by the system.

7. As the internal energy of an ideal gas is a function only of temperature, the internal energy of an ideal gas remains constant during an isothermal change of state. Thus the heat which enters or leaves the gas as a result of the isothermal process equals the work done by or on the gas, with both quantities being given by

$$w = q = RT \ln \left(\frac{V_2}{V_1} \right) = RT \ln \left(\frac{P_1}{P_2} \right)$$

8. Only the differences in the values of U and H between two states, i.e., the values of ΔU and ΔH , can be measured. The absolute values of U and H in any given state cannot be determined.

2.10 NUMERICAL EXAMPLES

Ten liters of an ideal gas at 25°C and 10 atmospheres pressure are expanded to a final pressure of 1 atmosphere. The molar heat capacity of the gas at constant volume, c_v , is $3/2 R$ and is independent of temperature. Calculate the work done, the heat absorbed, and the change in U and in H for the gas if the process is carried out (a) isothermally and reversibly, and (b) adiabatically and reversibly. Having determined the final state of the gas after the reversible adiabatic expansion, verify that the change in U for the process is independent of the path taken between the initial and final states by considering the process to be carried out as

- (i) An isothermal process followed by a constant-volume process
- (ii) A constant-volume process followed by an isothermal process
- (iii) An isothermal process followed by a constant-pressure process
- (iv) A constant-volume process followed by a constant-pressure process
- (v) A constant-pressure process followed by a constant-volume process

The size of the system must first be calculated. From consideration of the initial state of the system (the point a in Fig. 2.3)

(b) *The reversible adiabatic expansion.* If the adiabatic expansion is carried out reversibly, then during the process the state of the system is, at all times, given by $PV^\gamma = \text{constant}$, and the final state is the point c in the diagram. The volume V_c is obtained from $P_a V_a^\gamma = P_c V_c^\gamma$ as

$$V_c = (10 \times 10^{5/3})^{3/5} = 40 \text{ liters}$$

and

$$T_c = \frac{P_c V_c}{nR} = \frac{1 \times 40}{4.09 \times 0.0821} = 119^\circ \text{K}$$

The point c thus lies on the 119°K isotherm. As the process is adiabatic, $q = 0$ and hence

$$\begin{aligned} \Delta U_{(a \rightarrow c)} &= -w = \int_a^c n c_v dT = n c_v (T_c - T_a) \\ &= 4.09 \times 1.5 \times 8.3144 \times (119 - 298) \text{ joules} \\ &= -9.13 \text{ kilojoules} \end{aligned}$$

The work done by the system as a result of the process equals the decrease in the internal energy of the system = 9.13 kilojoules.

(i) *An isothermal process followed by a constant-volume process* (the path $a \rightarrow e \rightarrow c$; that is, an isothermal change from a to e , followed by a constant-volume change from e to c).

$\Delta U_{(a \rightarrow e)} = 0$ as this is an isothermal change of state

$\Delta U_{(e \rightarrow c)} = q_v$ ($\Delta V = 0$ and hence $w = 0$)

$= \int_e^c n c_v dT$ and as the state e lies on the 298°K isotherm then

$$\Delta U_{(e \rightarrow c)} = 4.09 \times 1.5 \times 8.3144 \times (119 - 298) \text{ joules} = -9.13 \text{ kilojoules}$$

Thus

$$\Delta U_{(a \rightarrow c)} = \Delta U_{(a \rightarrow e)} + \Delta U_{(e \rightarrow c)} = -9.13 \text{ kilojoules}$$

(ii) *A constant-volume process followed by an isothermal process* (the path $a \rightarrow d \rightarrow c$; that is, a constant-volume change from a to d , followed by an isothermal change from d to c).

$$\Delta U_{(a \rightarrow d)} = q_v \quad (\Delta V = 0 \text{ and hence } w = 0)$$

$$= \int_a^d n c_v dT \text{ and as the state } d \text{ lies on the } 119^\circ\text{K isotherm then}$$

$$\Delta U_{(a \rightarrow d)} = 4.09 \times 1.5 \times 8.3144 \times (119 - 298) \text{ joules} = -9.13 \text{ kilojoules}$$

$$\Delta U_{(d \rightarrow c)} = 0 \text{ as this is an isothermal process and hence}$$

$$\Delta U_{(a \rightarrow c)} = \Delta U_{(a \rightarrow d)} + \Delta U_{(d \rightarrow c)} = -9.13 \text{ kilojoules}$$

(iii) An isothermal process followed by a constant-pressure process (the path $a \rightarrow b \rightarrow c$; that is, an isothermal change from a to b , followed by a constant-pressure change from b to c).

$$\Delta U_{(a \rightarrow b)} = 0 \text{ as this process is isothermal}$$

$$\Delta U_{(b \rightarrow c)} = q_p - w \text{ and as } P_b = P_c \text{ then } w = P_b(V_c - V_b)$$

$$= \int_b^c n c_p dT - P_b(V_c - V_b)$$

As $c_v = 1.5 R$ and $c_p - c_v = R$, then $c_p = 2.5 R$; and as 1 liter-atmosphere equals 101.3 joules,

$$\begin{aligned} \Delta U_{(b \rightarrow c)} &= [4.09 \times 2.5 \times 8.3144 \times (119 - 298)] - [1 \times (40 - 100) \\ &\quad \times 101.3] \text{ joules} \\ &= -15.218 + 6.078 = -9.14 \text{ kilojoules} \end{aligned}$$

Thus

$$\Delta U_{(a \rightarrow c)} = \Delta U_{(a \rightarrow b)} + \Delta U_{(b \rightarrow c)} = -9.14 \text{ kilojoules}$$

(iv) A constant-volume process followed by a constant-pressure process (the path $a \rightarrow f \rightarrow c$; that is, a constant-volume change from a to f , followed by a constant-pressure change from f to c).

$$\Delta U_{(a \rightarrow f)} = q_v \quad (V_a = V_f \text{ and hence } w = 0)$$

$$= \int_a^f n c_v dT$$

From the ideal gas law

$$T_f = \frac{P_f V_f}{nR} = \frac{1 \times 10}{4.09 \times 0.0821} = 30^\circ\text{K}$$

i.e., the state f lies on the 30°K isotherm. Thus

$$\Delta U_{(a \rightarrow f)} = 4.09 \times 1.5 \times 8.3144 \times (30 - 298) \text{ joules} = -13.67 \text{ kilojoules}$$

$$\Delta U_{(f \rightarrow c)} = q_p - w$$

$$= \int_f^c n c_p dT - P_f (V_c - V_f)$$

$$= [4.09 \times 2.5 \times 8.3144 \times (119 - 30)] - [1 \times (40 - 10) \times 101.3] \text{ joules}$$

$$= +7.566 - 3.039 \text{ kilojoules}$$

Thus

$$\begin{aligned} \Delta U_{(a \rightarrow c)} &= \Delta U_{(a \rightarrow f)} + \Delta U_{(f \rightarrow c)} = -13.67 + 7.566 - 3.039 \\ &= -9.143 \text{ kilojoules} \end{aligned}$$

(v) *A constant-pressure process followed by a constant-volume process* (the path $a \rightarrow g \rightarrow c$; that is, a constant-pressure step from a to g , followed by a constant-volume step from g to c).

$$\Delta U_{(a \rightarrow g)} = q_p - w$$

From the ideal gas law

$$T_g = \frac{P_g V_g}{nR} = \frac{10 \times 40}{4.09 \times 0.0821} = 1191^\circ \text{K}$$

and hence the state g lies on the 1191°K isotherm. Thus

$$\begin{aligned} \Delta U_{(a \rightarrow g)} &= [4.09 \times 2.5 \times 8.3144 \times (1191 - 298)] \text{ joules} \\ &\quad - [10 \times (40 - 10) \times 101.3] \text{ joules} \\ &= 75.918 - 30.39 \text{ kilojoules} \end{aligned}$$

$$\begin{aligned} \Delta U_{(g \rightarrow c)} &= q_v = 4.09 \times 1.5 \times 8.3144 \times (119 - 1191) \text{ joules} \\ &= -54.681 \text{ kilojoules} \end{aligned}$$

Thus

$$\begin{aligned} \Delta U_{(a \rightarrow c)} &= \Delta U_{(a \rightarrow g)} + \Delta U_{(g \rightarrow c)} = 75.918 - 30.39 - 54.681 \\ &= -9.153 \text{ kilojoules} \end{aligned}$$

The value of $\Delta U_{(a \rightarrow c)}$ is thus seen to be independent of the path taken by the process between the states a and c .

The change in enthalpy from a to c . The enthalpy change is most simply calculated from consideration of a path which involves an isothermal portion over which $\Delta H = 0$ and an isobaric portion over which $\Delta H = q_p = \int n c_p dT$. For example, consider the path $a \rightarrow b \rightarrow c$.

$$\Delta H_{(a \rightarrow b)} = 0$$

$$\begin{aligned} \Delta H_{(b \rightarrow c)} &= q_p = nc_p(T_c - T_b) \\ &= 4.09 \times 2.5 \times 8.3144 \times (119 - 298) \text{ joules} \\ &= -15.218 \text{ kilojoules} \end{aligned}$$

and hence

$$\Delta H_{(a \rightarrow c)} = -15.218 \text{ kilojoules}$$

or alternatively

$$\begin{aligned} \Delta H_{(a \rightarrow c)} &= \Delta U_{(a \rightarrow c)} + (P_c V_c - P_a V_a) \\ &= -9.14 \text{ kilojoules} + [(1 \times 40 - 10 \times 10) \times 101.3] \text{ joules} \\ &= -9.14 - 6.078 = -15.218 \text{ kilojoules} \end{aligned}$$

In each of the paths (i) to (v) the heat and work effects differ, although in each case the difference $q - w$ equals -9.14 kilojoules. In the case of the reversible adiabatic path, $q = 0$ and hence $w = +9.14$ kilojoules. If the processes (i) to (v) are carried out reversibly, then

for path (i) $q = -9.14 + \text{the area } aeih$

for path (ii) $q = -9.14 + \text{the area } dcih$

for path (iii) $q = -9.14 + \text{the area } abjh - \text{the area } cbji$

for path (iv) $q = -9.14 + \text{the area } fcih$

for path (v) $q = -9.14 + \text{the area } agih$

PROBLEMS

2.1 A quantity of an ideal gas occupies 10 liters at 10 atm and 100°K . Calculate (1) the final volume of the system, (2) the work done by the system, (3) the heat entering or leaving the system, and (4) the internal energy and enthalpy changes in the system if it undergoes

a. A reversible isothermal expansion to 1 atm

b. A reversible adiabatic expansion to 1 atm

For the gas, the molar heat capacity $c_v = 1.5 R$.

2.2 A system comprises 7.14 grams of Ne gas at 0°C and 1 atm. When 2025 joules of heat are added to the system at constant pressure, the resultant expansion causes the system to perform 810 joules of work. Calculate (a) the initial state, (b) the final state, (c) ΔU and ΔH for the process, and (d) c_p and c_v . The molecular weight of Ne is 20 grams and it can be assumed that Ne behaves as an ideal gas.