

Type of work	dw	Comments	Units [†]
Expansion	$-p_{\text{ex}}dV$	p_{ex} is the external pressure dV is the change in volume	Pa m ³
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area	N m ⁻¹ m ²
Extension	$f dl$	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge	V C
	$Q d\phi$	$d\phi$ is the potential difference Q is the charge transferred	V C

Reversible change : can be reversed by an infinitesimal modification of a variable

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature
transfer of energy as heat between the two is reversible because

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because
if temperature of either system is lowered infinitesimally

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because
if temperature of either system is lowered infinitesimally
then energy flows into the system with the lower temperature

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because

if temperature of either system is lowered infinitesimally

then energy flows into the system with the lower temperature

If temperature of either system at thermal equilibrium is raised infinitesimally

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because

if temperature of either system is lowered infinitesimally

then energy flows into the system with the lower temperature

If temperature of either system at thermal equilibrium is raised infinitesimally

then energy flows out of the hotter system

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because

if temperature of either system is lowered infinitesimally

then energy flows into the system with the lower temperature

If temperature of either system at thermal equilibrium is raised infinitesimally

then energy flows out of the hotter system

There is a very close relationship between reversibility and equilibrium:

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because

if temperature of either system is lowered infinitesimally

then energy flows into the system with the lower temperature

If temperature of either system at thermal equilibrium is raised infinitesimally

then energy flows out of the hotter system

There is a very close relationship between reversibility and equilibrium:

systems at equilibrium are poised to undergo reversible change

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

If external pressure is reduced infinitesimally, the gas expands slightly

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

If external pressure is reduced infinitesimally, the gas expands slightly

If the external pressure is increased infinitesimally, the gas contracts slightly

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

If external pressure is reduced infinitesimally, the gas expands slightly

If the external pressure is increased infinitesimally, the gas contracts slightly

In either case the change is reversible in the thermodynamic sense

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

If external pressure is reduced infinitesimally, the gas expands slightly

If the external pressure is increased infinitesimally, the gas contracts slightly

In either case the change is reversible in the thermodynamic sense

If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process.

Suppose a gas is confined by a piston and external pressure, p_{ex} is set equal to the pressure, p , of the confined gas

Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

If external pressure is reduced infinitesimally, the gas expands slightly

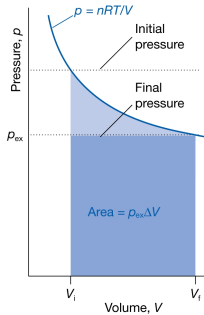
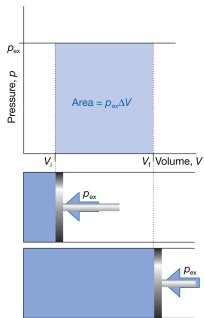
If the external pressure is increased infinitesimally, the gas contracts slightly

In either case the change is reversible in the thermodynamic sense

If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process.

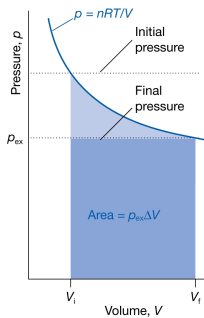
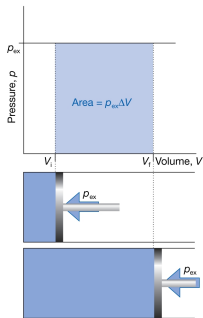
Such a system is **not** in mechanical equilibrium

Calculating work :



For a perfect gas, reversible work of expansion =

Calculating work :



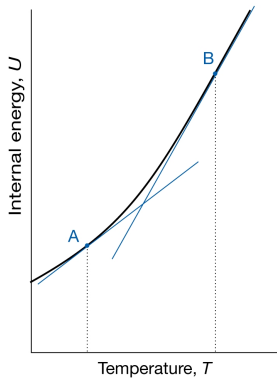
For a perfect gas, reversible work of expansion =

$$\begin{aligned}
 - \int_{V_i}^{V_f} p_{\text{ext}} dV &= - \int_{V_i}^{V_f} p dV \\
 &= -nRT \ln \frac{V_f}{V_i}
 \end{aligned}$$

for spontaneous expansion :

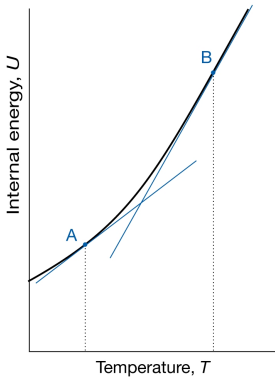
$$\text{work} = -p_{\text{ext}} (V_f - V_i)$$

Internal energy (U) as a function of temperature : $U(V, T)$



internal energy of a system
increases as temperature is raised

Internal energy (U) as a function of temperature : $U(V, T)$

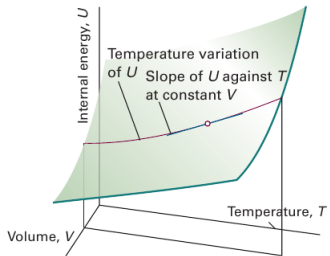


internal energy of a system
increases as temperature is raised
slope of tangent at any
temperature = heat capacity, C

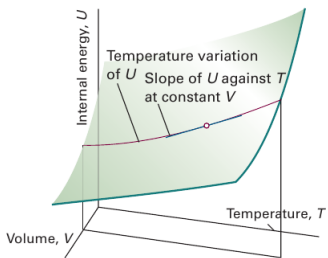
in the Fig.,

$$C \text{ at A} < C \text{ at B}$$

$$U(V, T)$$

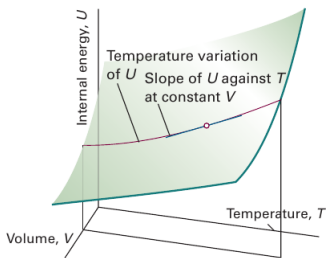


$$U(V, T)$$



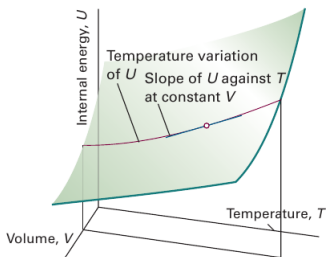
$$C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$U(V, T)$$



$$C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$
$$\Rightarrow dU = C_V dT$$

$$U(V, T)$$

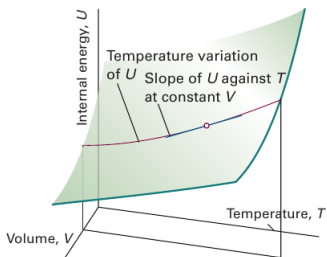


$$C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\Rightarrow dU = C_V dT$$

If heat capacity is independent of temperature over range of temperatures of interest

$$U(V, T)$$



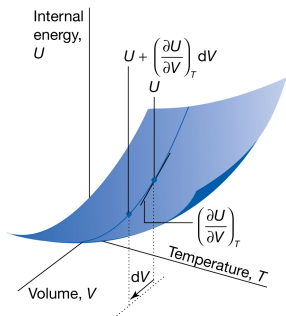
$$C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\Rightarrow dU = C_V dT$$

If heat capacity is independent of temperature over range of temperatures of interest
then $\Delta U = C_V \Delta T$

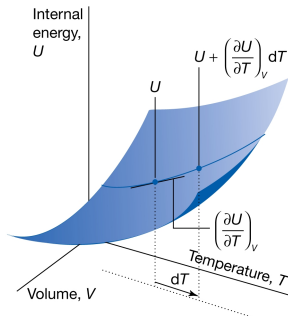
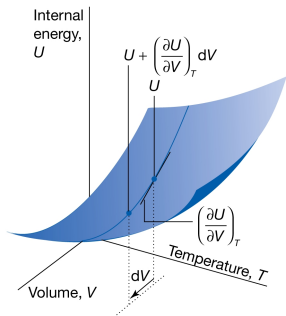
for $f \equiv f(x, y)$

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$



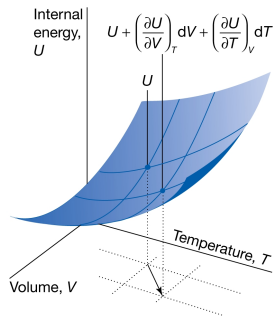
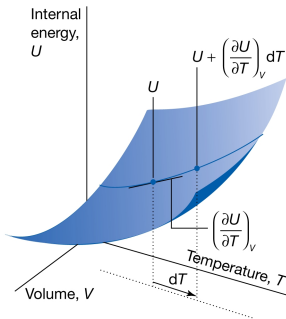
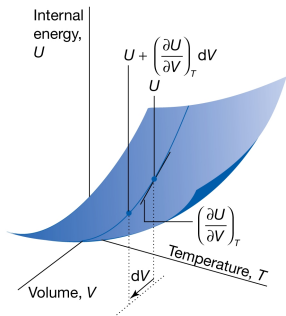
for $f \equiv f(x, y)$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$



for $f \equiv f(x, y)$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$



- ▶ large heat capacity \Rightarrow for given quantity of energy transferred as heat, a small increase in temperature

- ▶ large heat capacity \Rightarrow for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

- ▶ large heat capacity \implies for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

mean energy of a molecule due to its translational motion $= \frac{3}{2}k_B T$

\therefore contribution to molar energy $= \frac{3}{2}RT$

- ▶ large heat capacity \Rightarrow for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

mean energy of a molecule due to its translational motion $= \frac{3}{2}k_B T$

\therefore contribution to molar energy $= \frac{3}{2}RT$

\Rightarrow considering only translational contribution to internal energy

$$U_m(T) = U_m(0) + \frac{3}{2}RT$$

- ▶ large heat capacity \Rightarrow for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

mean energy of a molecule due to its translational motion $= \frac{3}{2}k_B T$

\therefore contribution to molar energy $= \frac{3}{2}RT$

\Rightarrow considering only translational contribution to internal energy

$$U_m(T) = U_m(0) + \frac{3}{2}RT$$

For polyatomics, rotational and vibrational contributions must be added :

- ▶ large heat capacity \Rightarrow for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

mean energy of a molecule due to its translational motion $= \frac{3}{2}k_B T$

\therefore contribution to molar energy $= \frac{3}{2}RT$

\Rightarrow considering only translational contribution to internal energy

$$U_m(T) = U_m(0) + \frac{3}{2}RT$$

For polyatomics, rotational and vibrational contributions must be added :

e.g., for CO_2 , $U_m(T) = U_m(0) + \frac{3}{2}RT + RT + \dots$

Thermodynamic definition of a perfect gas :

Thermodynamic definition of a perfect gas :
no intermolecular interactions in a perfect gas

Thermodynamic definition of a perfect gas :

no intermolecular interactions in a perfect gas

\therefore distance between molecules has no effect on energy

Thermodynamic definition of a perfect gas :

no intermolecular interactions in a perfect gas

∴ distance between molecules has no effect on energy

⇒ internal energy of a perfect gas is independent of the volume it occupies

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

generally, we consider only w_{exp} , $dU = dq_V$

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

generally, we consider only w_{exp} , $dU = dq_V$

Heat and work are equivalent ways of changing a system's internal energy

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

generally, we consider only w_{exp} , $dU = dq_V$

Heat and work are equivalent ways of changing a system's internal energy
A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

generally, we consider only w_{exp} , $dU = dq_V$

Heat and work are equivalent ways of changing a system's internal energy
A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy

First Law : internal energy of an isolated system is constant

$$\Delta U = q + w$$

Heat :

$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↗ ↑ ↑
upper lower expansion extra
case case

generally, we consider only w_{exp} , $dU = dq_V$

Heat and work are equivalent ways of changing a system's internal energy
A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy

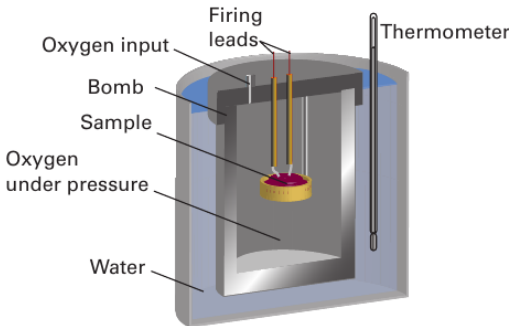
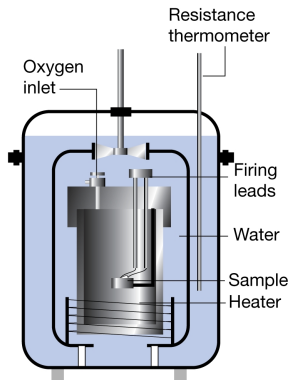
First Law : internal energy of an isolated system is constant

$$\Delta U = q + w$$

$$dU = dq + dw$$

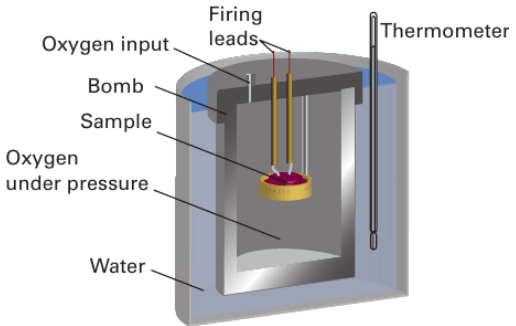
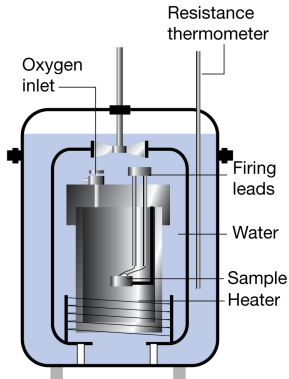
Calorimetry

- Constant volume bomb calorimeter : measurement of q_V



Calorimetry

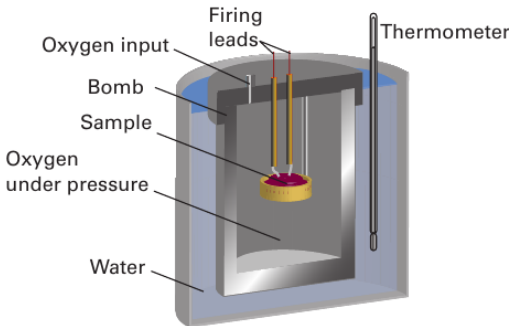
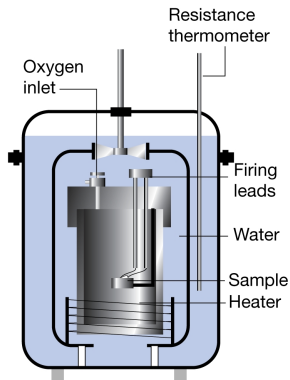
- Constant volume bomb calorimeter : measurement of q_V



‘bomb’ : central vessel, strong enough to withstand high pressures

Calorimetry

- Constant volume bomb calorimeter : measurement of q_V



‘bomb’ : central vessel, strong enough to withstand high pressures

To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion

change in calorimeter temperature, $\Delta T \propto$ energy released or absorbed in reaction

change in calorimeter temperature, $\Delta T \propto$ energy released or absorbed in reaction

measure $\Delta T \implies q_V$ and hence ΔU

change in calorimeter temperature, $\Delta T \propto$ energy released or absorbed in reaction

measure $\Delta T \implies q_V$ and hence ΔU

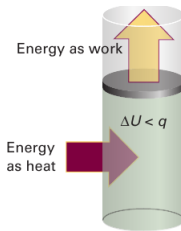
Calibration : use a process of known energy output and determine calorimeter constant

$$q = C\Delta T$$

Enthalpy

$\Delta \text{energy} \neq$ energy transferred as heat
when system is free to change its volume

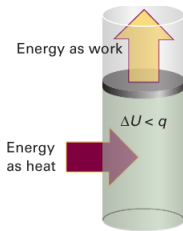
Under these circumstances some of the
energy supplied as heat to system is
returned to surroundings as expansion
work, so $dU < dq$



Enthalpy

$\Delta \text{energy} \neq \text{energy transferred as heat}$
when system is free to change its volume

Under these circumstances some of the energy supplied as heat to system is returned to surroundings as expansion work, so $dU < dq$



def. $H = U + pV$, a state function

$$dH = d(U + pV) = dU + pdV + Vdp = dq + Vdp \implies dq_p = dH$$

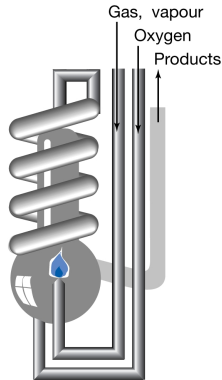
$$\text{def. } c_p = \left(\frac{dq}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p \implies dH = C_p dT$$

$$\overbrace{\int_i^f dH}^{H_f - H_i} = \overbrace{\int_i^f dq_p}^{q_p}$$

$$\overbrace{\int_i^f dH}^{H_f - H_i} = \overbrace{\int_i^f dq_p}^{q_p}$$

Part of a **constant-pressure**
adiabatic flame calorimeter

it is immersed in a stirred
waterbath

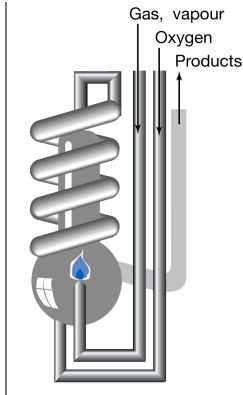


$$\underbrace{H_f - H_i}_f = \underbrace{q_p}_f$$

$$\int_i^f dH = \int_i^f dq_p$$

Part of a **constant-pressure**
adiabatic flame calorimeter

it is immersed in a stirred
waterbath



Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

$$\begin{aligned}\blacktriangleright \Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

$$\begin{aligned}\blacktriangleright \Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for } \text{CaCO}_3 (100 \text{ g}) = \frac{34(\text{a})}{37(\text{c})} \text{ cm}^3$$

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

$$\begin{aligned}\blacktriangleright \Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for } \text{CaCO}_3 (100 \text{ g}) = \frac{34(\text{a})}{37(\text{c})} \text{ cm}^3$$

$$\blacktriangleright \therefore p\Delta V = 10^5 \text{ Pa} \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

$$\begin{aligned}\blacktriangleright \Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for } \text{CaCO}_3 (100 \text{ g}) = \frac{34(\text{a})}{37(\text{c})} \text{ cm}^3$$

$$\blacktriangleright \therefore p\Delta V = 10^5 \text{ Pa} \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

$$\blacktriangleright \therefore \Delta H - \Delta U = -0.3 \text{ J} (\approx 0.15\% \text{ of } \Delta U)$$

solved problem :

when 1.0 mol CaCO_3 as calcite converts to aragonite, $\Delta U = 0.21 \text{ kJ}$

Calculate $\Delta H - \Delta U$ when $p = 1 \text{ bar}$ given densities of solids : 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively

$$\begin{aligned}\blacktriangleright \Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for } \text{CaCO}_3 (100 \text{ g}) = \frac{34(\text{a})}{37(\text{c})} \text{ cm}^3$$

$$\blacktriangleright \therefore p\Delta V = 10^5 \text{ Pa} \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

$$\blacktriangleright \therefore \Delta H - \Delta U = -0.3 \text{ J} (\approx 0.15\% \text{ of } \Delta U)$$

\blacktriangleright usually justifiable to ignore $\Delta H - \Delta U$ for condensed phases, except at very high pressures, when pV is no longer negligible

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = 2.1 \text{ kJ}$

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = 2.1 \text{ kJ}$

$$\begin{aligned}\blacktriangleright \Delta[H(\text{w}) - H(\text{g})] &= [U + pV](\text{w}) - [U + pV](\text{g}) \\ &= \Delta U + p[V(\text{w}) - V(\text{g})] = \Delta U + p\Delta V\end{aligned}$$

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = 2.1 \text{ kJ}$

$$\begin{aligned}\blacktriangleright \Delta[H(\text{w}) - H(\text{g})] &= [U + pV](\text{w}) - [U + pV](\text{g}) \\ &= \Delta U + p[V(\text{w}) - V(\text{g})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for Sn (118.71 g)} = \frac{20.65(\text{g})}{16.24(\text{w})} \text{ cm}^3$$

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = 2.1 \text{ kJ}$

$$\begin{aligned}\blacktriangleright \Delta[H(\text{w}) - H(\text{g})] &= [U + pV](\text{w}) - [U + pV](\text{g}) \\ &= \Delta U + p[V(\text{w}) - V(\text{g})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for Sn (118.71 g)} = \frac{20.65(\text{g})}{16.24(\text{w})} \text{ cm}^3$$

$$\blacktriangleright \therefore p\Delta V = 10 \times 10^5 \text{ Pa} \times (16.24 - 20.65) \times 10^{-6} \text{ m}^3 = -4.4 \text{ J}$$

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = 2.1 \text{ kJ}$

$$\begin{aligned}\blacktriangleright \Delta[H(\text{w}) - H(\text{g})] &= [U + pV](\text{w}) - [U + pV](\text{g}) \\ &= \Delta U + p[V(\text{w}) - V(\text{g})] = \Delta U + p\Delta V\end{aligned}$$

$$\blacktriangleright V_m \text{ for Sn (118.71 g)} = \frac{20.65(\text{g})}{16.24(\text{w})} \text{ cm}^3$$

$$\blacktriangleright \therefore p\Delta V = 10 \times 10^5 \text{ Pa} \times (16.24 - 20.65) \times 10^{-6} \text{ m}^3 = -4.4 \text{ J}$$

$$\blacktriangleright \therefore \Delta H - \Delta U = -0.44 \text{ J } (\approx 0.2\% \text{ of } \Delta U)$$

enthalpy of a perfect gas:

$$H = U + pV = U + nRT \quad \Rightarrow \quad \Delta H = \Delta U + \Delta nRT$$

solved problem :

Water is heated to boiling under $p = 1.0$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it,

0.798 g of water is vaporized. Calculate ΔU_m and ΔH_m at the boiling point (373.15 K)

solved problem :

Water is heated to boiling under $p = 1.0$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it,

0.798 g of water is vaporized. Calculate ΔU_m and ΔH_m at the boiling point (373.15 K)

$$\Delta H = q_p = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}$$

$$\Delta H_m = q_p = \frac{0.50 \times 12 \times 300}{\frac{0.798}{18}} = 41 \text{ kJ mol}^{-1}$$

solved problem :

Water is heated to boiling under $p = 1.0$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it,

0.798 g of water is vaporized. Calculate ΔU_m and ΔH_m at the boiling point (373.15 K)

$$\Delta H = q_p = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}$$

$$\Delta H_m = q_p = \frac{0.50 \times 12 \times 300}{\frac{0.798}{18}} = 41 \text{ kJ mol}^{-1}$$

$$\Delta U_m = \Delta H_m - RT = 38 \text{ kJ mol}^{-1} [\because p(V_g - V_l) \approx pV_g = RT]$$

solved problem :

Water is heated to boiling under $p = 1.0$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it,

0.798 g of water is vaporized. Calculate ΔU_m and ΔH_m at the boiling point (373.15 K)

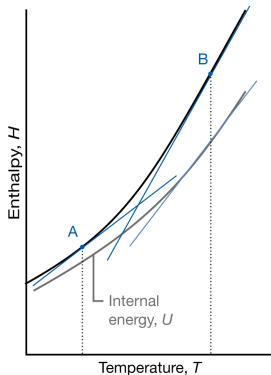
$$\Delta H = q_p = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}$$

$$\Delta H_m = q_p = \frac{0.50 \times 12 \times 300}{\frac{0.798}{18}} = 41 \text{ kJ mol}^{-1}$$

$$\Delta U_m = \Delta H_m - RT = 38 \text{ kJ mol}^{-1} [\because p(V_g - V_l) \approx pV_g = RT]$$

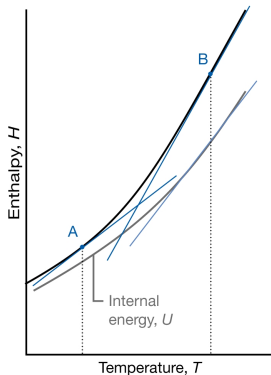
Notice $\Delta U_m < \Delta H_m$ because energy has been used to drive back surrounding atmosphere to make room for vapour

Enthalpy (H) as a function of temperature :



internal energy and enthalpy of system increase as temperature is raised

Enthalpy (H) as a function of temperature :



internal energy and enthalpy of system increase as temperature is raised

at constant pressure, slope of tangent at any temperature = heat capacity, C_p

For gases, at a given temperature the slope is steeper than that of internal energy versus temperature

$$C_{p,m} > C_{v,m}$$

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

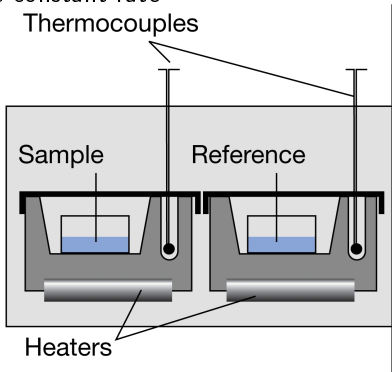
Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change
'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

'scanning' : temperatures are increased, or scanned, during the analysis

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

'scanning' : temperatures are increased, or scanned, during the analysis

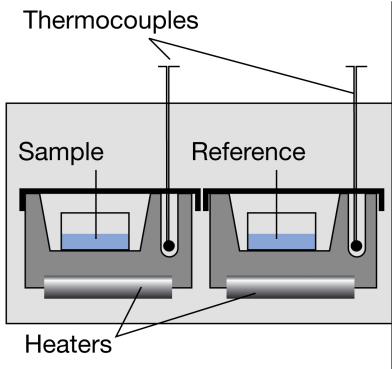
DSC consists of two small, separate but identical compartments heated electrically at constant rate



Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

'scanning' : temperatures are increased, or scanned, during the analysis

DSC consists of two small, separate but identical compartments heated electrically at constant rate

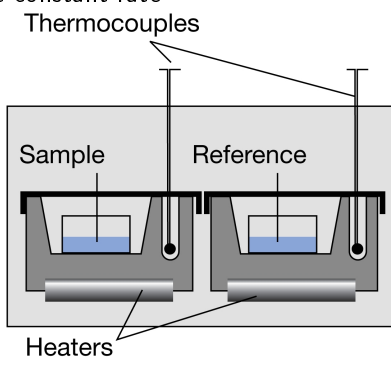


output : difference in power needed to maintain heat sinks at equal temperatures as temperature rises.

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

'scanning' : temperatures are increased, or scanned, during the analysis

DSC consists of two small, separate but identical compartments heated electrically at constant rate



output : difference in power needed to maintain heat sinks at equal temperatures as temperature rises. $T(t) = T_0 + \alpha t$, where T_0 = initial temperature
 α = temperature scan rate (in Ks^{-1})

A computer controls electrical power to maintain same temperature in sample and reference compartments

sample temperature changes significantly relative to that of reference material
if transfer of energy as heat occurs in the sample during the scan

sample temperature changes significantly relative to that of reference material if transfer of energy as heat occurs in the sample during the scan

To maintain same temperature in both compartments, excess energy is transferred as heat to or from sample during the process

an endothermic process lowers sample temperature relative to that of reference
and, as a result, the sample must be heated more strongly than reference in order
to maintain equal temperatures
if transfer of energy as heat occurs in the sample during the scan

an endothermic process lowers sample temperature relative to that of reference
and, as a result, the sample must be heated more strongly than reference in order
to maintain equal temperatures

if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample, $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

an endothermic process lowers sample temperature relative to that of reference and, as a result, the sample must be heated more strongly than reference in order to maintain equal temperatures

if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample, $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

The chemical or physical process requires the transfer of $q_p + q_{p, ex}$

where $q_{p, ex}$ = excess energy transferred as heat, to attain same change in temperature of the sample

an endothermic process lowers sample temperature relative to that of reference and, as a result, the sample must be heated more strongly than reference in order to maintain equal temperatures

if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample, $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

The chemical or physical process requires the transfer of $q_p + q_{p, ex}$

where $q_{p, ex}$ = excess energy transferred as heat, to attain same change in temperature of the sample

$q_{p, ex}$ = apparent change in heat capacity at constant pressure, C_p during temperature scan

an endothermic process lowers sample temperature relative to that of reference and, as a result, the sample must be heated more strongly than reference in order to maintain equal temperatures

if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample, $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

The chemical or physical process requires the transfer of $q_p + q_{p, ex}$

where $q_{p, ex}$ = excess energy transferred as heat, to attain same change in temperature of the sample

$q_{p, ex}$ = apparent change in heat capacity at constant pressure, C_p during temperature scan

heat capacity = $C_p + C_{p, ex}$ and $q_p + q_{p, ex} = (C_p + C_{p, ex}) \Delta T$

an endothermic process lowers sample temperature relative to that of reference and, as a result, the sample must be heated more strongly than reference in order to maintain equal temperatures

if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample, $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

The chemical or physical process requires the transfer of $q_p + q_{p, ex}$

where $q_{p, ex}$ = excess energy transferred as heat, to attain same change in temperature of the sample

$q_{p, ex}$ = apparent change in heat capacity at constant pressure, C_p during temperature scan

heat capacity = $C_p + C_{p, ex}$ and $q_p + q_{p, ex} = (C_p + C_{p, ex}) \Delta T$

$\therefore C_{p, ex} = \frac{q_{p, ex}}{\Delta T} = \frac{q_{p, ex}}{\alpha t} = \frac{P_{ex}}{\alpha}$; P_{ex} = excess electrical power necessary to equalize the temperature of sample and reference compartments

DSC trace - a thermogram : plot
of P_{ex} or C against T

Broad peaks in thermogram
indicate processes requiring
transfer of energy as heat

DSC trace - a thermogram : plot
of P_{ex} or C against T

Broad peaks in thermogram
indicate processes requiring
transfer of energy as heat

$$\Delta H = \int_{T_1}^{T_2} C_{p, \text{ex}} dT$$

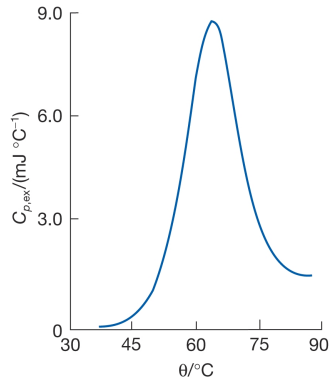
DSC trace - a thermogram : plot of P_{ex} or C against T

Broad peaks in thermogram indicate processes requiring transfer of energy as heat

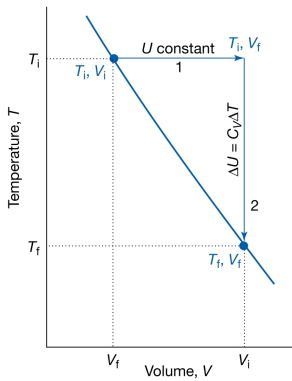
$$\Delta H = \int_{T_1}^{T_2} C_{p, \text{ex}} dT$$

thermogram for protein ubiquitin at pH = 2.45

native structure up to $\approx 45^\circ\text{C}$ and then endothermic conformational change

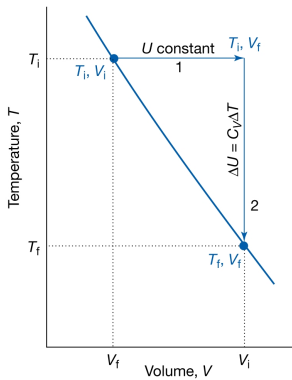


Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$



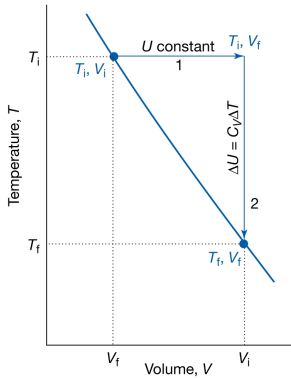
Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$

when a perfect gas expands adiabatically

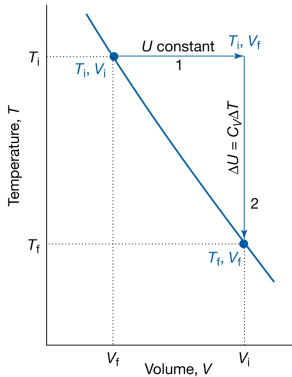


Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$

when a perfect gas expands adiabatically
work is done but no heat enters the system

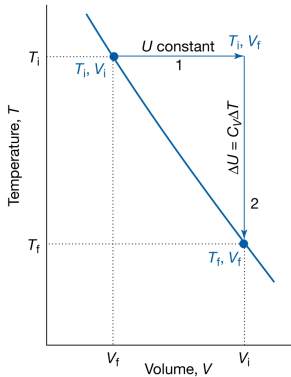


Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$



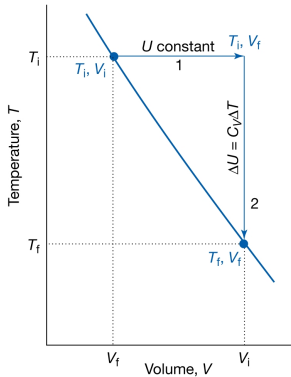
when a perfect gas expands adiabatically
work is done but no heat enters the system
internal energy falls - kinetic energy of
molecules falls, average speed decreases

Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$



when a perfect gas expands adiabatically
work is done but no heat enters the system
internal energy falls - kinetic energy of
molecules falls, average speed decreases
∴ temperature falls

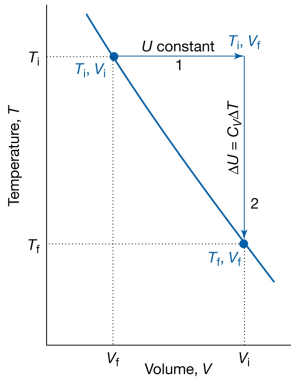
Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$



when a perfect gas expands adiabatically
work is done but no heat enters the system
internal energy falls - kinetic energy of
molecules falls, average speed decreases
 \therefore temperature falls

ΔU for temperature change from T_i to T_f and
the volume change from V_i to V_f can be seen
as the sum of two steps

Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$

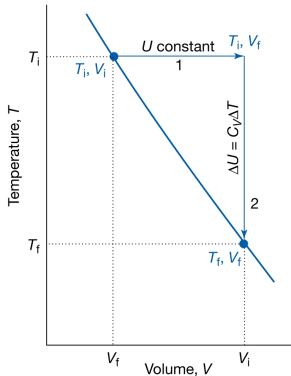


when a perfect gas expands adiabatically
work is done but no heat enters the system
internal energy falls - kinetic energy of
molecules falls, average speed decreases
 \therefore temperature falls

ΔU for temperature change from T_i to T_f and
the volume change from V_i to V_f can be seen
as the sum of two steps

1st step : only volume changes and
temperature is constant

Adiabatic expansion : $T_i, V_i \longrightarrow T_f, V_f$



when a perfect gas expands adiabatically
work is done but no heat enters the system
internal energy falls - kinetic energy of
molecules falls, average speed decreases
 \therefore temperature falls

ΔU for temperature change from T_i to T_f and
the volume change from V_i to V_f can be seen
as the sum of two steps

1st step : only volume changes and
temperature is constant

U for perfect gas is independent of volume of
molecules, the overall ΔU arises solely from
second step, the change in temperature at
constant volume

$$\Delta U = C_v (T_f - T_i) = w_{ad}$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -p dV$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

$$C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

$$C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

$$\text{or, } \ln \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \ln \left(\frac{V_1}{V_2} \right) \text{ or, } \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \frac{V_1}{V_2}$$

Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

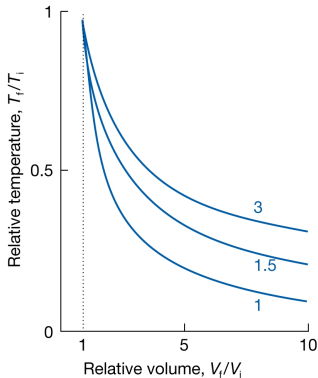
$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

$$C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

$$\text{or, } \ln \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \ln \left(\frac{V_1}{V_2} \right) \text{ or, } \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \frac{V_1}{V_2}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_v}} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \text{ or, } TV^{\gamma-1} = \text{const.}$$

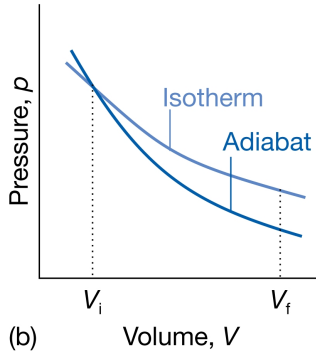
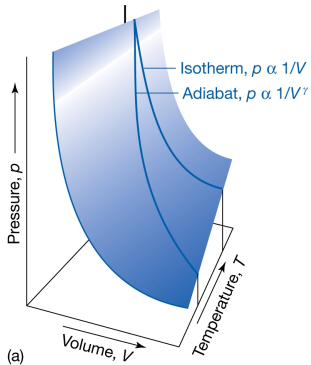
show: $pV^\gamma = \text{const}$



label : $\frac{C_v}{R}$

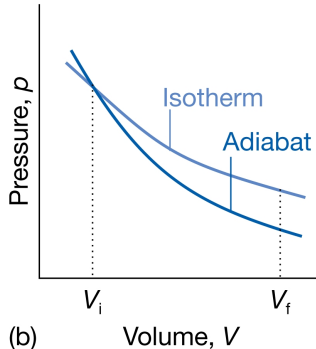
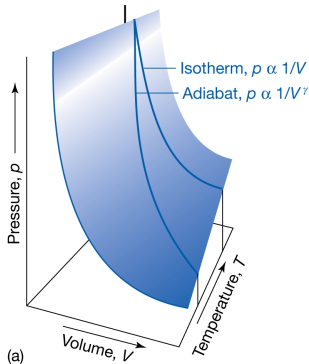
p-V-T plots : isotherms and adiabats

pressure declines more steeply for an adiabat than for an isotherm



p-V-T plots : isotherms and adiabats

pressure declines more steeply for an adiabat than for an isotherm



in isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, pressure does not fall as much as in adiabatic expansion

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48 + 8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48 + 8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

$$\text{Using } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48 + 8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

$$\text{Using } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$\text{we have } T_f = 298 \times \left(\frac{0.50}{1} \right)^{0.666} = 188 \text{ K}$$

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48+8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

$$\text{Using } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$\text{we have } T_f = 298 \times \left(\frac{0.50}{1}\right)^{0.666} = 188 \text{ K}$$

$$\Delta T = 188 - 298 = -110 \text{ K and } w_{ad} = nC_V \Delta T = -0.020 \times 12.48 \times 110 = -27 \text{ J}$$

ex. :

adiabatic, reversible expansion of 0.020 mol Ar
initially at 25°C, from 0.50 dm³ to 1.00 dm³

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48+8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

$$\text{Using } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$\text{we have } T_f = 298 \times \left(\frac{0.50}{1}\right)^{0.666} = 188 \text{ K}$$

$$\Delta T = 188 - 298 = -110 \text{ K and } w_{ad} = n C_V \Delta T = -0.020 \times 12.48 \times 110 = -27 \text{ J}$$

Note : ΔT is independent of the amount of gas but the work is not

Thermochemistry

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

identify $q_V = \Delta U$ or $q_p = \Delta H$

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

identify $q_V = \Delta U$ or $q_p = \Delta H$

Conversely, if we know ΔU or ΔH for a reaction, predict the energy (transferred as heat) the reaction produces

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

identify $q_V = \Delta U$ or $q_p = \Delta H$

Conversely, if we know ΔU or ΔH for a reaction, predict the energy (transferred as heat) the reaction produces

exothermic process at constant pressure : $\Delta H < 0$

Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

identify $q_V = \Delta U$ or $q_p = \Delta H$

Conversely, if we know ΔU or ΔH for a reaction, predict the energy (transferred as heat) the reaction produces

exothermic process at constant pressure : $\Delta H < 0$

endothermic process at constant pressure : $\Delta H > 0$

Standard state :

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

solid iron at 500 K is pure iron at 500 K and 1 bar

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change, $\Delta H^\ominus =$

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change, $\Delta H^\ominus =$

enthalpy of products_{standard states} — enthalpy of reactants_{standard states}

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

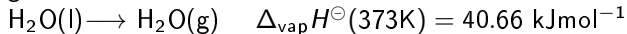
solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change, $\Delta H^\ominus =$

enthalpy of products_{standard states} — enthalpy of reactants_{standard states}

standard enthalpy of vaporization :

$\Delta_{\text{vap}}H^\ominus =$ enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar



Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

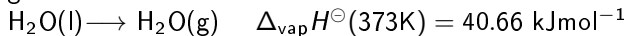
solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change, $\Delta H^\ominus =$

enthalpy of products_{standard states} — enthalpy of reactants_{standard states}

standard enthalpy of vaporization :

$\Delta_{\text{vap}}H^\ominus$ = enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar



standard enthalpy of fusion :

$\Delta_{\text{fus}}H^\ominus$ = enthalpy change per mole when a pure liquid at 1 bar condenses to solid at 1 bar



Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

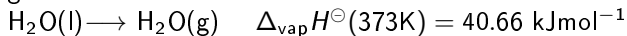
solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change, $\Delta H^\ominus =$

enthalpy of products_{standard states} — enthalpy of reactants_{standard states}

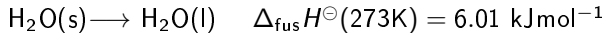
standard enthalpy of vaporization :

$\Delta_{\text{vap}}H^\ominus =$ enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar



standard enthalpy of fusion :

$\Delta_{\text{fus}}H^\ominus =$ enthalpy change per mole when a pure liquid at 1 bar condenses to solid at 1 bar



standard enthalpies may be reported for any temperature

enthalpy is a state function

enthalpy is a state function

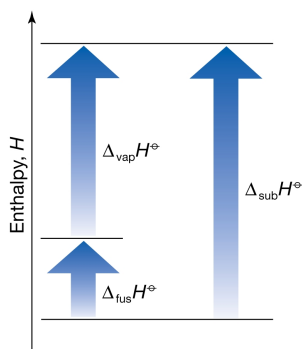
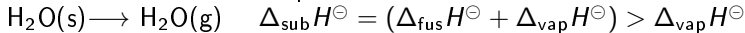
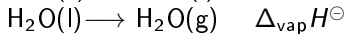
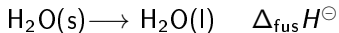
ΔH is independent of path between the two states

enthalpy is a state function

ΔH is independent of path between the two states

same ΔH^\ominus for change brought about between same initial and final states

e.g., conversion of a solid to a vapour either as occurring by sublimation

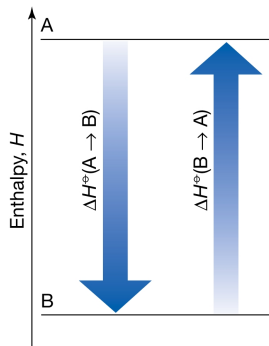


ΔH^\ominus for a forward process and its reverse
differ in sign

ΔH^\ominus for a forward process and its reverse differ in sign

e.g., conversion of a solid to a vapour either as occurring by sublimation

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A)$$



Transition	Process	Symbol
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{\text{trs}}H$
Fusion	$s \rightarrow l$	$\Delta_{\text{fus}}H$
Vaporization	$l \rightarrow g$	$\Delta_{\text{vap}}H$
Sublimation	$s \rightarrow g$	$\Delta_{\text{sub}}H$
Mixing	Pure \rightarrow mixture	$\Delta_{\text{mix}}H$
Solution	Solute \rightarrow solution	$\Delta_{\text{sol}}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\text{hyd}}H$
Atomization	Species(s, l, g) \rightarrow atoms(g)	$\Delta_{\text{at}}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{\text{ion}}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{\text{eg}}H$
Reaction	Reactants \rightarrow products	Δ_rH
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	Δ_cH
Formation	Elements \rightarrow compound	Δ_fH
Activation	Reactants \rightarrow activated complex	$\Delta^{\ddagger}H$

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

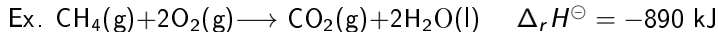
pure, separate products in standard states

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

pure, separate products in standard states

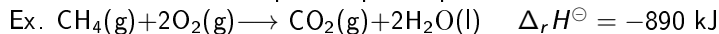


Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

pure, separate products in standard states



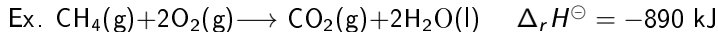
For the reaction $2\text{A} + \text{B} \longrightarrow 3\text{C} + \text{D}$

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

pure, separate products in standard states



For the reaction $2\text{A} + \text{B} \longrightarrow 3\text{C} + \text{D}$

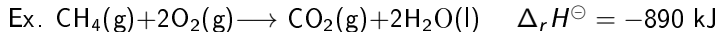
$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\}$$

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

pure, separate products in standard states



For the reaction $2\text{A} + \text{B} \longrightarrow 3\text{C} + \text{D}$

$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\}$$

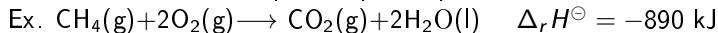
$$\text{generally, } \Delta_r H^\ominus = \sum_{\text{products}} \nu H_m^\ominus - \sum_{\text{reactants}} \nu H_m^\ominus$$

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states \longrightarrow

pure, separate products in standard states



For the reaction $2\text{A} + \text{B} \longrightarrow 3\text{C} + \text{D}$

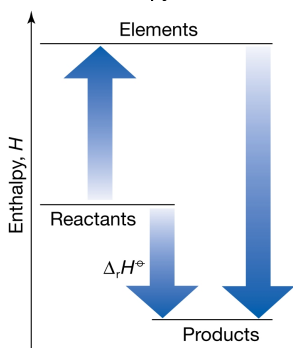
$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\}$$

generally,
$$\Delta_r H^\ominus = \sum_{\text{products}} \nu H_m^\ominus - \sum_{\text{reactants}} \nu H_m^\ominus$$

standard enthalpy of combustion, $\Delta_c H^\ominus$ = standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid water if the compound contains C, H, and O, and to N_2 gas if N is also present

reaction enthalpy in terms of enthalpies of formation

reaction enthalpy in terms of enthalpies of formation



$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

Can we construct $\Delta_f H^\ominus$ from a knowledge of chemical constitution of the species?

Can we construct $\Delta_f H^\ominus$ from a knowledge of chemical constitution of the species?

no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds

$$dH = C_p dT \quad \implies \quad H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT \quad \text{assuming no phase transition in}$$

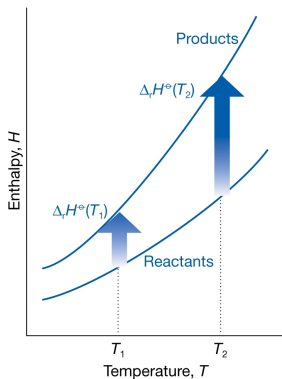
temperature range of interest

$dH = C_p dT \implies H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$ assuming no phase transition in temperature range of interest

Kirchhoff's law :

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

where $\Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$



solved prob.: $\Delta_f H^\ominus(\text{H}_2\text{O(g)}; 298 \text{ K}) = -241.82 \text{ kJ mol}^{-1}$

Estimate $\Delta_f H^\ominus$ at 100°C

given $C_{p,m}(\text{H}_2\text{O,g}) = 33.58 \text{ J K}^{-1}\text{mol}^{-1}$; $C_{p,m}(\text{H}_2,\text{g}) = 28.84 \text{ J K}^{-1} \text{ mol}^{-1}$;

$C_{p,m}(\text{O}_2,\text{g}) = 29.37 \text{ J K}^{-1} \text{ mol}^{-1}$

solved prob.: $\Delta_f H^\ominus(\text{H}_2\text{O}(\text{g}); 298 \text{ K}) = -241.82 \text{ kJ mol}^{-1}$

Estimate $\Delta_f H^\ominus$ at 100°C

given $C_{p,m}(\text{H}_2\text{O}, \text{g}) = 33.58 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_{p,m}(\text{H}_2, \text{g}) = 28.84 \text{ J K}^{-1} \text{ mol}^{-1}$;

$C_{p,m}(\text{O}_2, \text{g}) = 29.37 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta_r C_p^\ominus = C_{p,m}(\text{H}_2\text{O}, \text{g}) - \{C_{p,m}(\text{H}_2, \text{g}) + \frac{1}{2} C_{p,m}(\text{O}_2, \text{g})\} = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$

solved prob.: $\Delta_f H^\ominus(\text{H}_2\text{O}(\text{g}); 298 \text{ K}) = -241.82 \text{ kJ mol}^{-1}$

Estimate $\Delta_f H^\ominus$ at 100°C

given $C_{p,m}(\text{H}_2\text{O}, \text{g}) = 33.58 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_{p,m}(\text{H}_2, \text{g}) = 28.84 \text{ J K}^{-1} \text{ mol}^{-1}$;

$C_{p,m}(\text{O}_2, \text{g}) = 29.37 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta_r C_p^\ominus = C_{p,m}(\text{H}_2\text{O}, \text{g}) - \{C_{p,m}(\text{H}_2, \text{g}) + \frac{1}{2} C_{p,m}(\text{O}_2, \text{g})\} = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$

$\therefore \Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + (T_2 - T_1) \Delta_r C_p^\ominus$
 $= -241.82 - 75 \times 9.94 \times 10^{-3} = -242.6 \text{ kJ mol}^{-1}$