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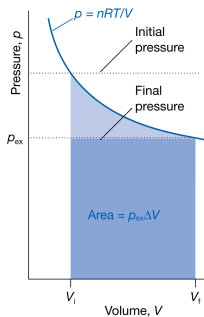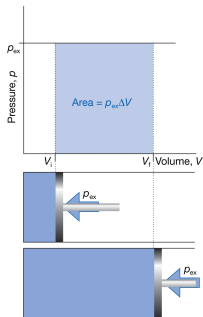
Calculating work :
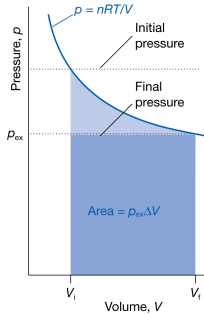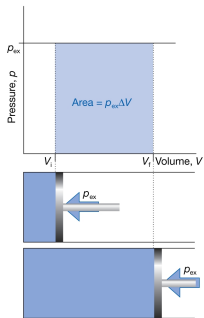
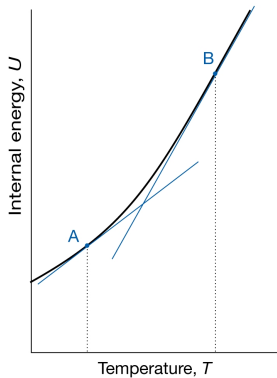For a perfect gas, reversible work of expansion =

Calculating work :

For a perfect gas, reversible work of expansion $=$

$$-\int_{V_i}^{V_f} p_{ext}\, dV = -\int_{V_i}^{V_f} p\, dV$$

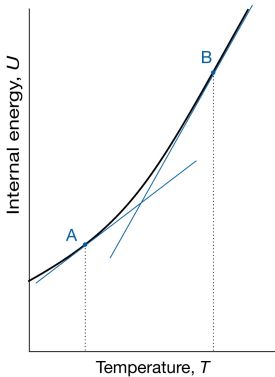$$= -nRT \ln \frac{V_f}{V_i}$$

for spontaneous expansion :

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

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

internal energy of a system
increases as temperature is raised

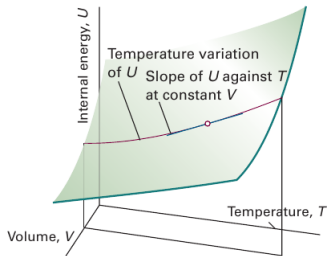Internal energy (U) as a function of temperature : $U(V, T)$

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slope of tangent at any
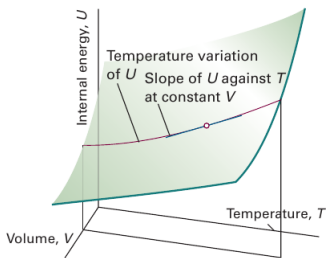temperature $=$heat capacity, C

in the Fig.,
    C at A $< C$ at B

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Internal energy, U

Temperature variation of U Slope of U against T at constant V

Temperature, T

Volume, V

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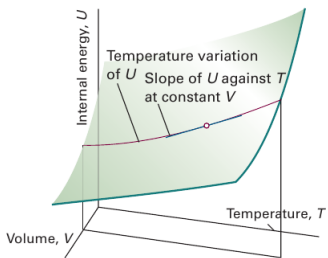Temperature variation of U Slope of U against T at constant V

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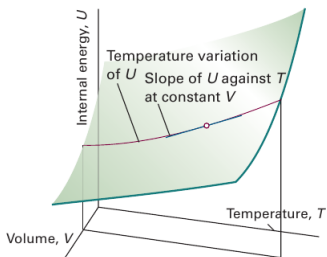$$C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

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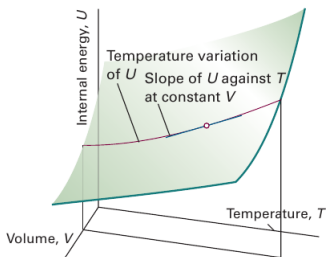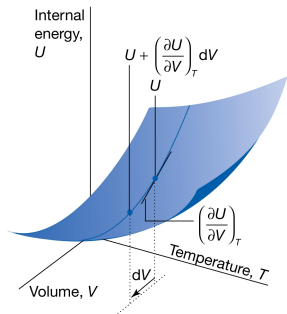If heat capacity is independent of temperature over range of temperatures of interest

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

for $f \equiv f(x, y)$ $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$
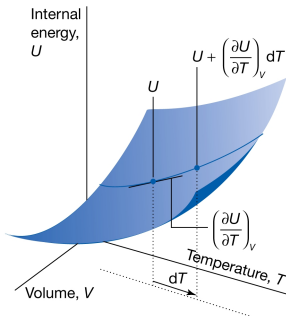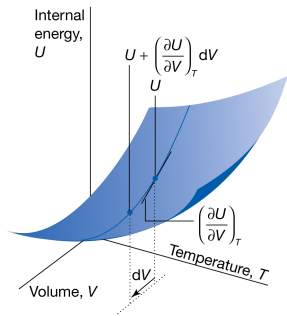
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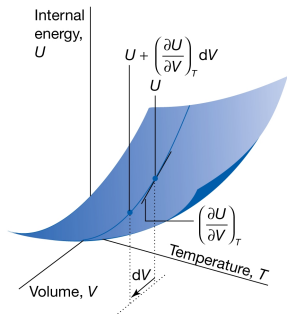
Internal energy, U

$U + \left(\frac{\partial U}{\partial V}\right)_T dV$

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Volume, V

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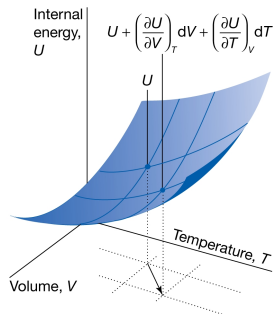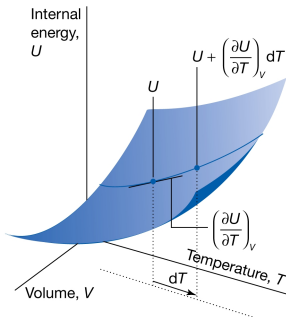
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e.g., for CO_2, $U_m(T) = U_m(0) + \frac{3}{2} RT + RT + \cdots$

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$\implies$ internal energy of a perfect gas is independent of the volume it occupies

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

Enthalpy

Δenergy $\neq$ 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 $dU < dq$

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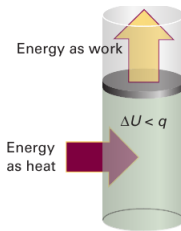
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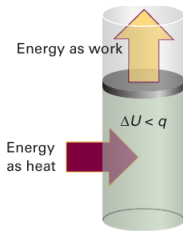
def. $H = U + pV$, a state function

$dH = d\left(U + pV\right) = dU + pdV + Vdp = dq + Vdp \implies dq_p = dH$
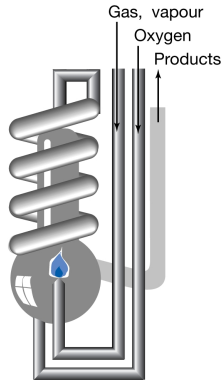
def. $c_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \implies dH = C_p\, dT$

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

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Part of a constant-pressure adiabatic flame calorimeter

it is immersed in a stirred waterbath

Gas, vapour
Oxygen
Products

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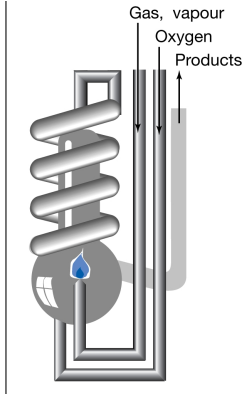
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Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

solved problem :

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

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► 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, $\Delta H = 2.1$ kJ

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▶ $\therefore \Delta H - \Delta U = -0.44$J $(\approx 0.2\%$ of $\Delta U)$

enthalpy of a perfect gas:

$$H = U + pV = U + nRT \implies \Delta H = \Delta U + \Delta nRT$$

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)

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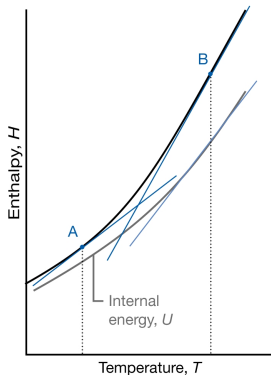
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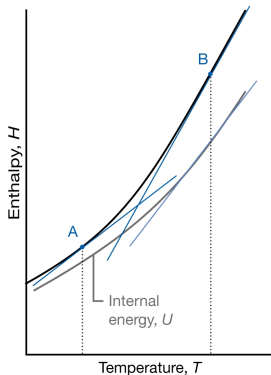
Notice $\Delta U_m < \Delta H_m$ because energy has been used to drive back surrounding atmosphere to make room for vapour

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

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

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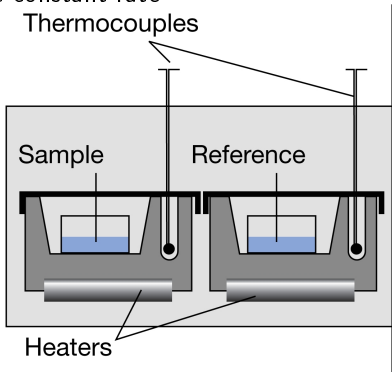'scanning' : temperatures are increased, or scanned, during the analysis

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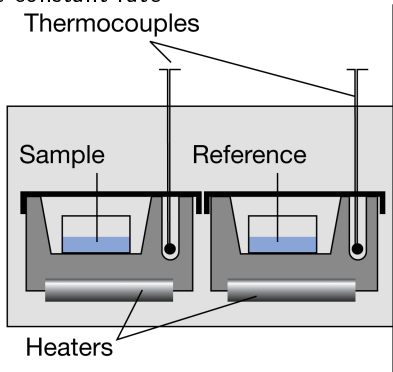'scanning' : temperatures are increased, or scanned, during the analysis
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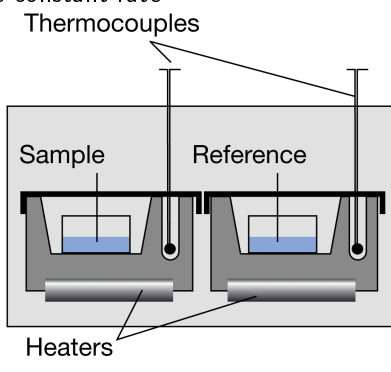at constant rate

Thermocouples

Sample   Reference

Heaters

output : difference in power needed to
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as temperature rises.

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Thermocouples
Sample
Reference
Heaters

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
$\alpha =$ 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

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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

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

$\therefore C_{p,\,ex} = \frac{q_{p,\,ex}}{\Delta T} = \frac{q_{p,\,ex}}{\alpha t} = \frac{P_{ex}}{\alpha}$; $\quad P_{ex}$ = 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

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

thermogram for protein ubiquitin
at pH = 2.45

native structure up to $\approx 45°$C
and then endothermic
conformational change

DSC trace - a thermogram : plot
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Broad peaks in thermogram
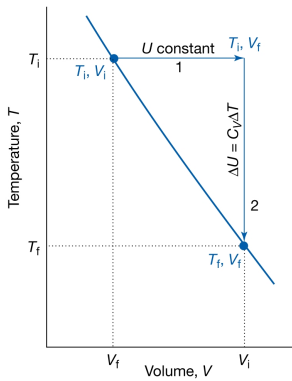indicate processes requiring
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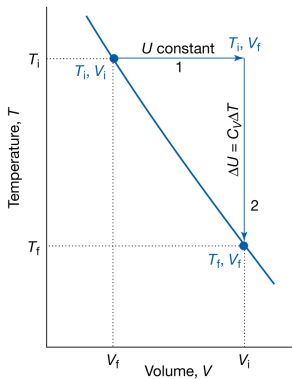$$\Delta H = \int\limits_{T_1}^{T_2} C_{p,\,ex}\,dT$$
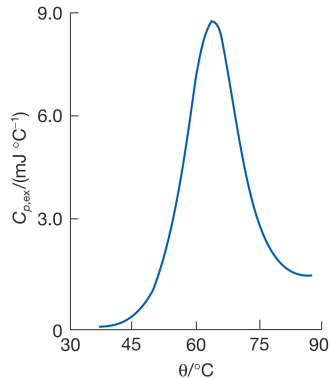
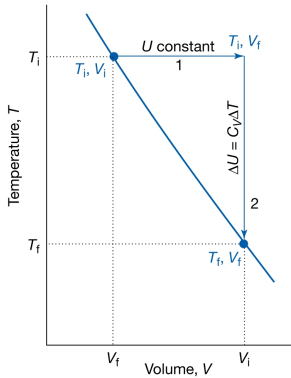Adiabatic expansion : T_i, $V_i \longrightarrow T_f$, V_f

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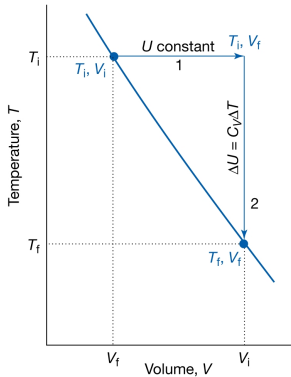Adiabatic expansion : T_i, $V_i \longrightarrow T_f$, V_f

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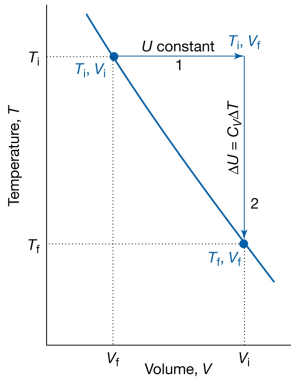$\therefore$ temperature falls

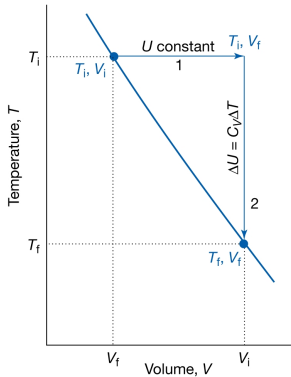Adiabatic expansion : T_i, $V_i \longrightarrow T_f$, V_f

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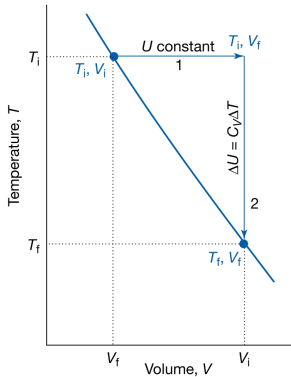temperature is constant

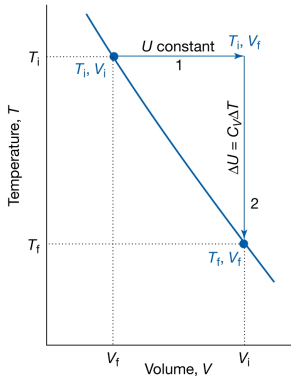Adiabatic expansion : T_i, $V_i \longrightarrow T_f$, V_f

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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

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

Temperature, T

T_i

U constant T_i, V_f

T_i, V_i 1

$\Delta U = C_v \Delta T$

2

T_f

T_f, V_f

V_f V_i

Volume, V

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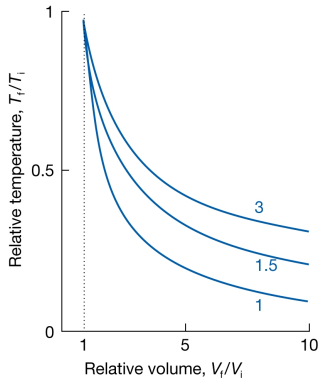
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$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{nR}{C_v}} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$ or, $TV^{\gamma - 1} = \text{const.}$
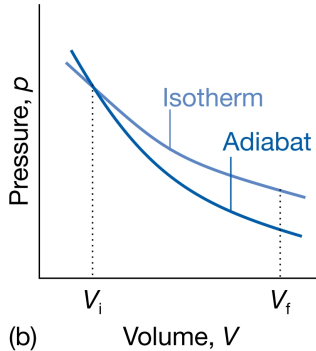
show: $pV^{\gamma} = \text{const}$

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

Relative temperature, T_f/T_i (vertical axis, values 0 to 1)

Relative volume, V_f/V_i (horizontal axis, values 1 to 10)

Curves labeled: 3, 1.5, 1

p-V-T plots : isotherms and adiabats
pressure declines more steeply for an adiabat than for an isotherm

Isotherm, $p \propto 1/V$
Adiabat, $p \propto 1/V^{\gamma}$

Pressure, p

Volume, V

Temperature, T

(a)

Pressure, p

Isotherm

Adiabat

V_i

V_f

Volume, V
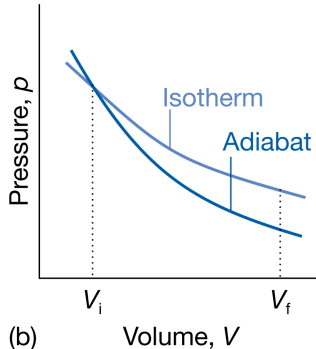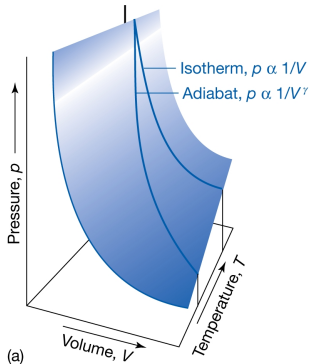
(b)

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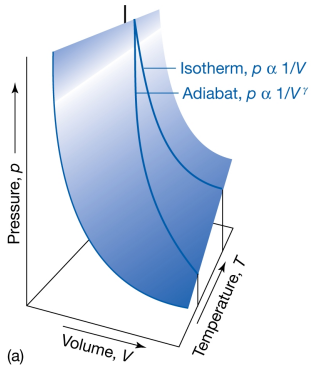
in isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, pressure does not fall as much as in adiabatic expansion

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

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

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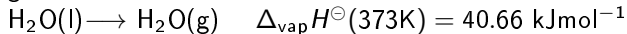ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar
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$H_2O(l) \longrightarrow H_2O(g)$ $\Delta_{\text{vap}} H^{\ominus}(373K) = 40.66 \text{ kJmol}^{-1}$

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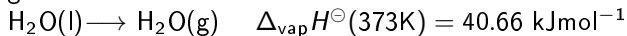ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar
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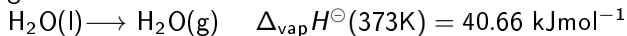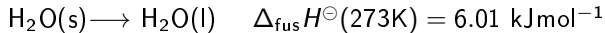ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar
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standard enthalpies may be reported for any temperature

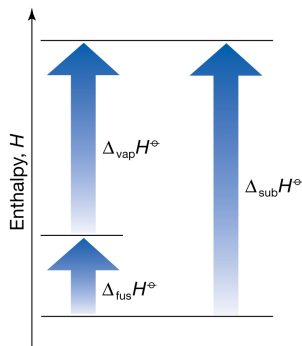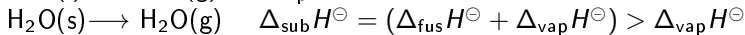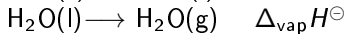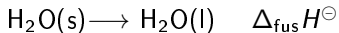enthalpy is a state function

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same $\Delta H^{\ominus}$ for change brought about between same initial and final states

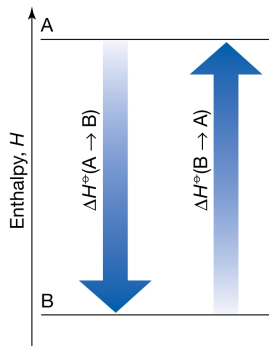e.g., conversion of a solid to a vapour either as occurring by sublimation

$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta_{fus}H^{\ominus}$

$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta_{vap}H^{\ominus}$

$H_2O(s) \longrightarrow H_2O(g) \qquad \Delta_{sub}H^{\ominus} = (\Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}) > \Delta_{vap}H^{\ominus}$

$\Delta H^{\ominus}$ for a forward process and its reverse differ in sign

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

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

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

Standard reaction enthalpy :
change in enthalpy for
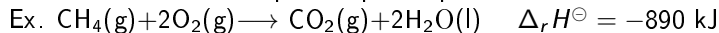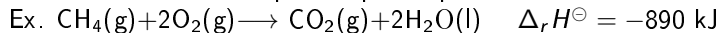Pure, separate reactants in standard states $\longrightarrow$
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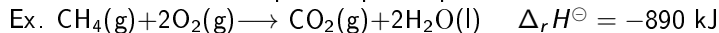   pure, separate products in standard states

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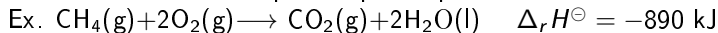　　　　　　　　　pure, separate products in standard states
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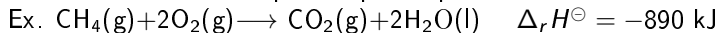
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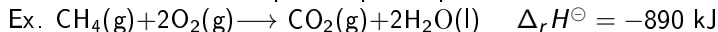
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generally, $\Delta_r H^{\ominus} = \sum_{products} \nu H_m^{\ominus} - \sum_{reactants} \nu H_m^{\ominus}$

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

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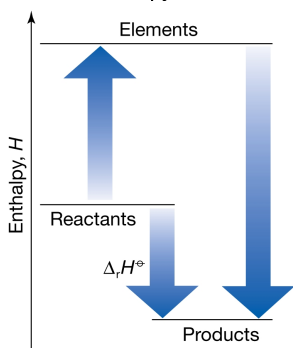
$$\Delta_r H^{\ominus} = \sum_{\text{products}} \nu \Delta_f H^{\ominus} - \sum_{\text{reactants}} \nu \Delta_f H^{\ominus}$$

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

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

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temperature range of interest

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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 $\Delta_r C_p^{\ominus} = \sum_{\text{products}} \nu C_{p,\,m}^{\ominus} - \sum_{\text{reactants}} \nu C_{p,\,m}^{\ominus}$
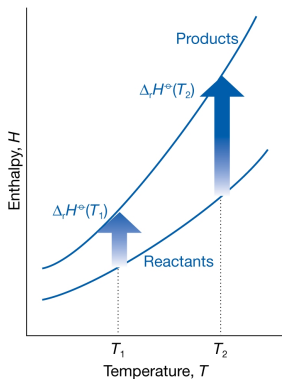
solved prob.: $\Delta_f H^{\ominus}(\text{H}_2\text{O(g)};298 \text{ K}) = -241.82 \text{ kJ mol}^{-1}$

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$\therefore \Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + (T_2 - T_1)\Delta_r C_p^{\ominus}$

$\qquad = -241.82 - 75 \times 9.94 \times 10^{-3} = -242.6kJ\ mol^{-1}$