

3. The first law of thermodynamics

(10)

Thermodynamics: abstract study of the transformations
of energy

↑
statistical physics: molecular interpretation

systems: open \rightarrow exchange of matter

closed \rightarrow no exchange

isolated \rightarrow no energy or matter transfer

The energy of a system is its capacity to do work. When work is done on an otherwise isolated system the capacity of the system ^{to do work} is increased, so the energy of the system is increased. When the system does work, the energy of the system is reduced and it can do less work.

When the energy of a system changes as a result of a temperature difference we say the energy has been transferred as heat.

diathermic \Rightarrow heat transfer possible

adiabatic \Rightarrow no heat transfer possible

exothermic: releases heat

endothermic: absorbs heat

molecular background

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heat transfer:

The disorderly molecular motion called thermal motion in the hot surroundings stimulates the molecules in the cooler system to move more and as a result the energy of the system is increased.

work:

work is the transfer of energy that makes use of organized motion e.g. motion of a piston.

Energy distribution = Boltzmann distribution

number of particles N in a sample of n particles that will be found in a state with an energy E_i when it is part of a system in thermal equilibrium at a temperature T

$$N = \frac{n e^{-E_i/kT}}{q}$$

partition function

$$k = 1.381 \cdot 10^{-23} \text{ J/K}$$

Boltzmann constant

$$q = \begin{cases} \int e^{-E/kT} dE & \text{classical} \\ \sum_i e^{-E_i/kT} & \text{quantum} \end{cases}$$

$$R = N_A k$$

Avogadro's number

- The work needed to change an adiabatic system from one specified state to another specified state is the same however the work is done.

$$\Delta W_{\text{adiabatic}} = U_f - U_i = \Delta U$$

$$q = W_{\text{ad}} - W$$

Reversibility and expansion work

$$dW = -F dz$$

$$= -p_{\text{ext}} A dz$$

$$= -p_{\text{ext}} dV$$

$$W = - \int_{V_i}^{V_f} p_{\text{ext}} dV$$

$$p = \text{const:} \quad W = -p_{\text{ext}} \int_{V_i}^{V_f} dV = -p_{\text{ext}} (V_f - V_i)$$

reversible change:

a system is in equilibrium with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state

$$p_{\text{ex}} \neq p \Rightarrow p_{\text{ex}} \pm dp \text{ not reversible} \Rightarrow \text{no equilibrium}$$

$$p_{\text{ex}} = p \Rightarrow p_{\text{ex}} \pm dp \text{ reversible} \Rightarrow \text{equilibrium}$$

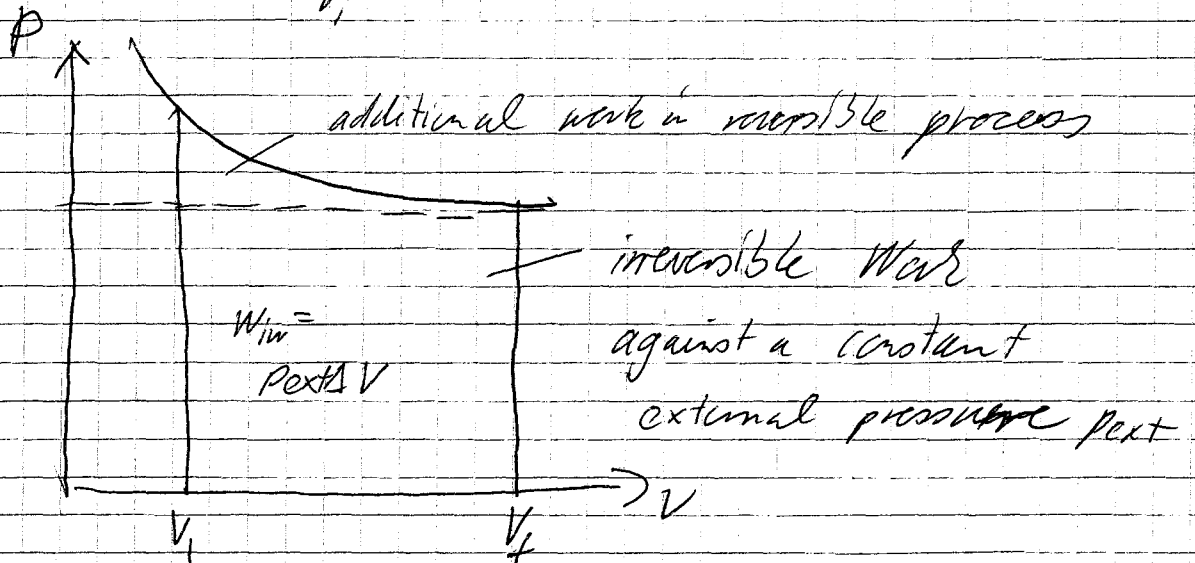
$$\Rightarrow dW = -p_{\text{ex}} dV = -p dV$$

ideal gas, reversible, $T = \text{const}$

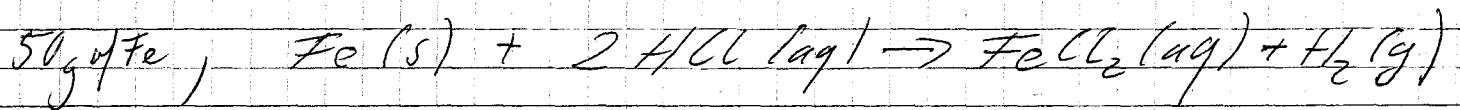
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$$p = nRT/V$$

$$\Rightarrow W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$



Work of gas production:



closed vessel $\Rightarrow V = \text{const} \Rightarrow W = 0$

open beaker \Rightarrow

$$W = -p_{\text{ext}} \Delta V \approx -p_{\text{ext}} \frac{nRT}{p_{\text{ext}}} = -nRT$$

$$W = \frac{50 \text{ g}}{55.85 \text{ g/mol}} \cdot R \cdot T = -2.2 \text{ kJ}$$

Heat changes

$$dU = dq + dW_{\text{expansion}} - dW'$$

$$V = \text{const}, \quad W' = 0$$

$$\Delta U = q_V \quad \Rightarrow \quad c_V = \frac{\Delta U}{\Delta T} \Big|_V \quad \text{heat capacity at constant volume}$$

$$\Rightarrow dU = c_V dT \quad \text{for } V = \text{const.}$$

material property: $c_V \rightarrow \infty \Rightarrow$ heat is absorbed but no temperature change, latent heat is used for a phase transition e.g. melting of ice

enthalpy H $H = U + pV$

change in enthalpy is equal to the heat supplied at constant pressure $dH = dq$ ($p = \text{const}$)

proof: infinitesimal change

$$H + dH = U + dU + (p + dp)(V + dV) = \underbrace{U + dU}_{=H} + p dV + V dp + \underbrace{dp dV}_{\approx 0}$$

$$H + dH = H + dU + p dV + V dp$$
$$\stackrel{H}{=} dq + dw$$

$$dH = dq + dw + p dV + V dp$$

~~$dW = -p dV$~~ $dW = -p dV$ equilibrium

$$dH = dq + V dp$$

$= 0$ for $p = \text{const}$

$\Delta H \leftrightarrow \Delta U$:

1 mol CaCO_3 calcite \rightarrow aragonite $\Delta U = 0.21 \text{ kJ}$
 $p = 1 \text{ bar}$ $\rho = 2.71 \text{ g/cm}^3$ $\rho = 2.93 \text{ g/cm}^3$

$$\Delta H = \Delta U + p(V(l) - V(c)) = \Delta U + p\Delta V$$

$$p\Delta V = -0.3 \text{ J}$$

$$\Rightarrow \Delta H \approx \Delta U$$

\Rightarrow usually the difference between enthalpy and internal energy of a condensed phase can be ignored

heat capacity at constant pressure

$$H = U + pV = U + nRT \quad \text{ideal gas}$$

$$\Delta H = \Delta U = \Delta n_g RT$$

$$C_p = \left. \frac{\partial H}{\partial T} \right|_p \quad \text{heat capacity at constant pressure}$$

$$\Rightarrow dH = C_p dT \quad \text{for } p = \text{const}$$

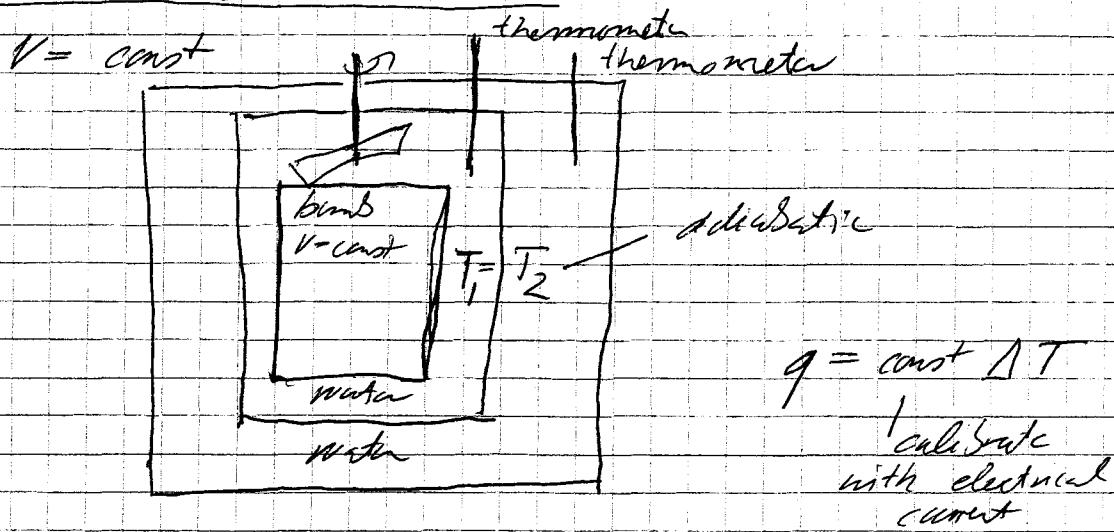
C_p is only independent of temperature for perfect monatomic gases (e.g. noble gases):

$$C_{p,m} \approx a + bT + \frac{c}{T^2}$$

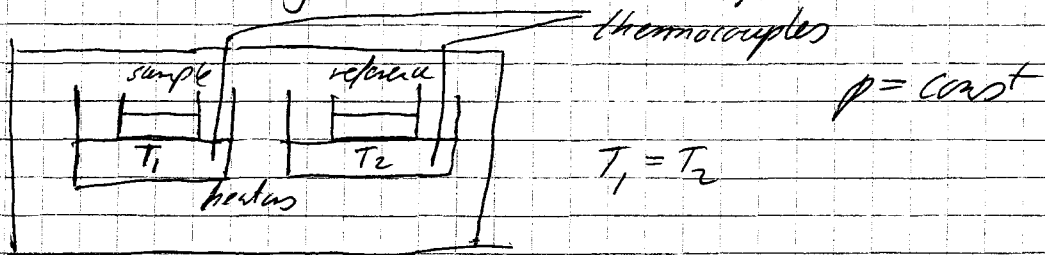
for a perfect gas: $C_p - C_v = nR$

Calorimetry (measuring heat changes)

(i) adiabatic bomb calorimeter



(ii) Differential scanning calorimeter (DSC)



Linear scan $T = T_0 + \alpha t$

e.g. a endothermic process in the sample requires more heating in the sample to maintain $T_1 = T_2$

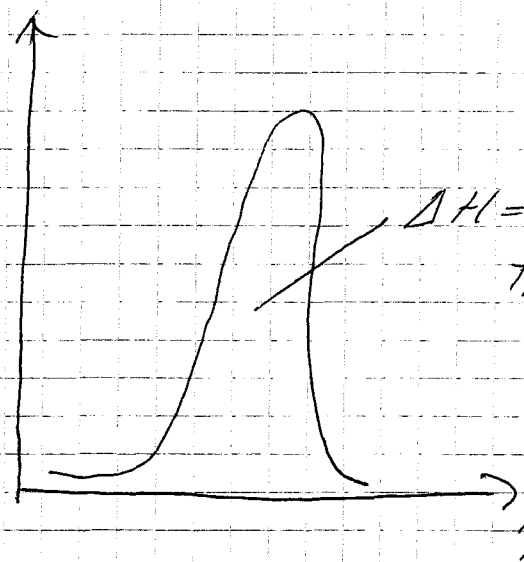
$$q_p + q_{prex} = (c_p + c_{prex}) \Delta T \Rightarrow$$

\uparrow physical or chemical change in sample \uparrow apparent change in heat capacity

$$\Rightarrow c_{prex} = \frac{q_{prex}}{\Delta T} = \frac{1}{\alpha} \frac{q_{prex}}{t}$$

= electrical power necessary to equalize the temperature

$C_{p,ex}/mg$
 $^{\circ}C$



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

enthalpy change associated with process

- assess the stability of proteins, nucleic acids and membranes
- large molecules attain complex three-dimensional structures due to intra- and inter-molecular interactions such as hydrogen bonding and hydrophobic interactions. disruption of these interactions is an endothermic process that can be studied with a DSC
- phase changes in lipid membranes, insertion of proteins, demixing of lipid mixtures \Rightarrow lipid rafts
- unfolding of protein, e.g. Tau protein and Alzheimer
- melting of DNA

adiabatic changes

$\Delta Q = 0$ perfect gas

$\Delta V \neq 0 \Rightarrow T_i \rightarrow T_f$

$\Delta U = C_V (T_f - T_i) = C_V \Delta T$

$\Delta U = q + w \xrightarrow{q=0} w_{ad} = C_V \Delta T$

$dw = -p dV \quad dU = C_V dT = dw \quad dq=0$

$\Rightarrow C_V dT = -p dV$

$\frac{C_V dT}{T} = \frac{nR dV}{V}$

$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$

$\Rightarrow \ln\left(\frac{T_f}{T_i}\right)^c = \ln\left(\frac{V_i}{V_f}\right) \quad c = \frac{C_V}{nR}$

$\Rightarrow V_f T_f^c = V_i T_i^c$

$\Rightarrow T_f = T_i \left(\frac{V_i}{V_f}\right)^{1/c}$

$\Rightarrow p_i V_i^\gamma = p_f V_f^\gamma \quad \gamma = 1 + \frac{R}{C_V}$

standard enthalpy of formation $\Delta_f H^\circ$:

Standard reactions enthalpy for the formation of the compound from its elements in their reference state (= most stable state at the specified temperature and 1 bar)

$$\Rightarrow \Delta H^\circ = \sum_{\text{Products}} \nu \Delta_f H^\circ - \sum_{\text{Reactants}} \nu \Delta_f H^\circ$$

Note!:

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

Kirchoff's laws:

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

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

with $\Delta C_p = \sum_{\text{products}} \nu C_{p,m} - \sum_{\text{reactants}} \nu C_{p,m}$

potential exercises:

2.7, 2.12, 2.16, 2.21, 2.22, 2.27, 2.32, 2.40

potential problems:

2.1, 2.9, 2.13, 2.16, 2.35, 2.31, 2.28