

Review of classical thermodynamics

Fundamental Laws, Properties and Processes (1)

First Law - Energy Balance

Thermodynamic functions of state

Internal energy, heat and work

Types of paths (isobaric, isochoric, isothermal, adiabatic, cyclic)

Enthalpy, heat capacity, heat of formation, phase transformations

Calculation of enthalpy as a function of temperature

Heats of reactions and the Hess's law

Reading: Chapters 2, 6.1, 6.4 of Gaskell
or the same material in any other textbook on thermodynamics

Thermodynamic variables

What are thermodynamics variables?

There are two approaches to describe properties and behavior of a material: 1. *Microscopic approach* - to describe the material in terms of microscopic variables (positions, velocities, charges, etc. of all particles in the system). But there are too many particles ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$) and this approach is unpractical in most cases.

2. *Classical (continuum) thermodynamics* – to describe the material in terms of average quantities, or **thermodynamic variables**, such as temperature, internal energy, pressure, etc.

Statistical thermodynamics provides the connection between the classical thermodynamics and the behavior of the microscopic constituents of matter (atoms and molecules). Although in this course we will focus on classical thermodynamics, we will also consider a few elements of statistical thermodynamics, in particular in our discussion of heat capacity and entropy.

What are state variables and functions?

System at equilibrium can be described by a number of thermodynamic variables that are *independent of the history of the system*. Such variables are called **state variables** or **state functions** depending on the context.

We can describe a system by a set of *independent state variables* and we can express other variables (*state functions*) through this set of independent variables. For example, we can describe ideal gas by P and T and use $V = RT/P$ to define molar volume V. For different applications we can choose different sets of independent variables that are the most convenient.

Thermodynamic variables

Intensive and extensive variables

Intensive properties – independent of the size of the system, e.g. T, P.

Extensive properties – proportional to the quantity of material, e.g. V, U, C, H, S, G.

Example: if $V_1 = V_2$
 $T_1 = T_2$
 $P_1 = P_2$ then $V_{12} = V_1 + V_2$ but $T_{12} = T_1 = T_2$

$$\boxed{1} + \boxed{2} = \boxed{1+2}$$

We can also consider “*derived intensive variables*,” e.g. Mass/Volume or Energy/Volume, that do not depend on the size of the system.

Internal energy, heat, and work: not very rigorous definitions:

It is impossible to give a rigorous definition of energy. (“...in physics today, we have no knowledge of what energy is.” - *the Feynman Lectures on Physics*). Thermodynamics laws do not define energy, thermodynamics is dealing with **transfer of energy**. In particular, the 1st law of thermodynamics **postulates the energy conservation**. In thermodynamics of materials we usually do not consider the kinetic energy of the center-of-mass motion of the system or gravitational energy (mgh), only **internal energy**, intrinsic to the body is considered.

Internal energy U is a sum of all potential and kinetic energies in the system (not only of mechanical origin). Thermodynamics is only dealing with change of U. The absolute value of U is not defined by the laws of thermodynamics, but an arbitrary zero point is often chosen for convenience.

Energy, heat, and work (continued)

Heat is the energy being transferred to a system as a result of temperature difference (work-less transfer of internal energy).

Work can be defined as the energy being transferred to a system as a result of a (generalized) force acting over a (generalized) distance.

Examples of work:

Mechanical work done by force \mathbf{F} on a body moving from \mathbf{r}_1 to \mathbf{r}_2 along a certain trajectory or path:

$$\delta w = \vec{F} \cdot d\vec{r} \qquad U_{1 \rightarrow 2} = \int_{\vec{r}_1}^{\vec{r}_2} \vec{F} \cdot d\vec{r}$$

path integral

Work due to the volume expansion of a fluid or gas done against an external pressure P .

$$\delta w = P \, dV$$

Electric polarization work, where the generalized force is the strength of the electric field, \mathbf{E} , and the generalized displacement is the polarization of the medium, \mathbf{D} .

$$\delta w = -\vec{E} \cdot d\vec{D}$$

Magnetic work, where the generalized force is the strength of the magnetic field, \mathbf{H} , and the generalized displacement is the total magnetic dipole moment, \mathbf{B} .

$$\delta w = -\vec{H} \cdot d\vec{B}$$

Work and heat are both functions of the path of the process – **they are not state functions.**

Systems never possess heat and work! Heat and work are transient phenomena – describe energy *being transferred* to/from the system.

1st Law – conservation of energy in a thermodynamic process

A state function, called the internal energy, exists for any physical system – and the change in the internal energy during any process is the sum of work done on/by the system and heat transferred to/from the system.

$$\Delta U = q - w \quad \text{or in differential form: } dU = \delta q - \delta w$$

U – internal energy (all potential and kinetic energies). It is a **state function** – depends only on thermodynamic state of the system (e.g. P, V, & T for a simple system).

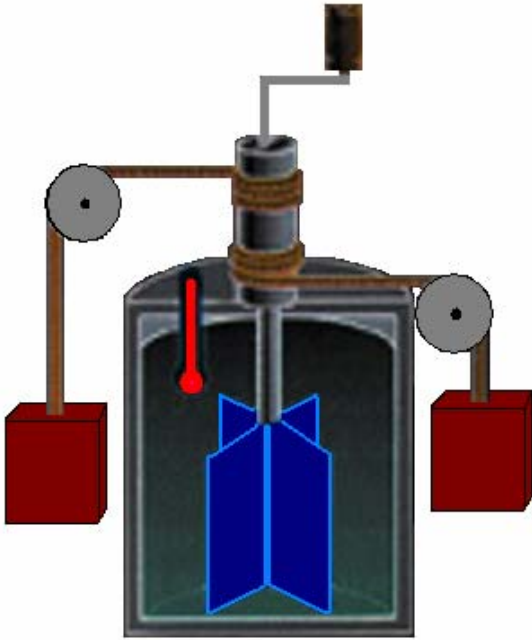
q – energy added into the system as heat. Positive (+) when the system gains heat from outside (**endothermic** process), negative (-) when heat flows out of the system (**exothermic** process).

w - work done by the system on its surroundings. Positive (+) when work is done by the system, and negative if work done on the system. If body does work, it expends energy and the internal energy of the body must decrease.

Note, that in some textbooks you will find a plus sign in front of δw (work done on the body) or minus sign in front of δq (heat flow out of the body). We use notation adapted in Gaskell.

Example: gas expands, mechanical work is done against an external pressure: $w = \int_1^2 P_{\text{ext}} dV > 0$ - cooling by adiabatic expansion

Equivalence of heat and work: Joule experiment



In Joule's experiment the mechanical energy can be measured simultaneously with temperature (thermal energy).

Joule found that

- the loss in mechanical energy is proportional to an increase in temperature of the water and the amount of water used.
- the constant or proportionality is 4.4 J/g °C (modern data is 4.186 J/g °C)

Heat and work can independently produce identical changes in the system.

T is not a good measure of heat but heat can be measured through work, and heat capacity can be determined.

J. P. Joule, On the existence of an equivalent relation between heat and the ordinary forms of mechanical power, *Phil. Mag.* **27**, 205, 1845.

Types of paths

A simple one-component system can be described by T, P, and V. They are connected by **equation of state**, e.g. $V=V(P,T)$. Therefore, **two independent variables** describe the system and define the state functions, e.g. $U = U(P,T)$.

Let's consider processes when one of the two independent variables is fixed.

V = const – isochoric process

No work is done ($w = \int PdV = 0$) and the 1st law takes form:

$$dU = \delta q \quad \text{or} \quad \Delta U = q$$

(internal energy can be changed only by heat exchange)

P = const – isobaric process

$$w = \int_{V_1}^{V_2} PdV = P \int_{V_1}^{V_2} dV = P(V_2 - V_1) \quad \text{and the 1st law takes form:}$$

$$U_2 - U_1 = q_p - P(V_2 - V_1) \quad \text{or} \quad (U_2 + PV_2) - (U_1 + PV_1) = q_p$$

q_p is heat added at constant pressure.

H = U + PV – enthalpy - state function

(since U, P, V are state functions)

$H_2 - H_1 = \Delta H = q_p$ – change in enthalpy equals to heat added to the system at constant pressure

Types of paths (continued)

T = const – isothermal process

Example: ideal gas

$dT = 0$, therefore, $dU = \delta q - \delta w = 0$ (internal energy of an ideal gas is a function only of T).

Work done depends on the path, i.e. how the external pressure is changing during the transformation. For example:

- *Free expansion* (no external pressure): $w = 0$
- *Reversible isothermal expansion* ($P_{\text{ext}} = P_{\text{gas}}$ at all times)
(reversible process – system is always at equilibrium)

$$\delta q = \delta w = PdV = RTdV/V \text{ per mole of gas}$$

Integration between states 1 and 2 gives

$$q = w = RT \ln(V_2/V_1) = RT \ln(P_1/P_2)$$

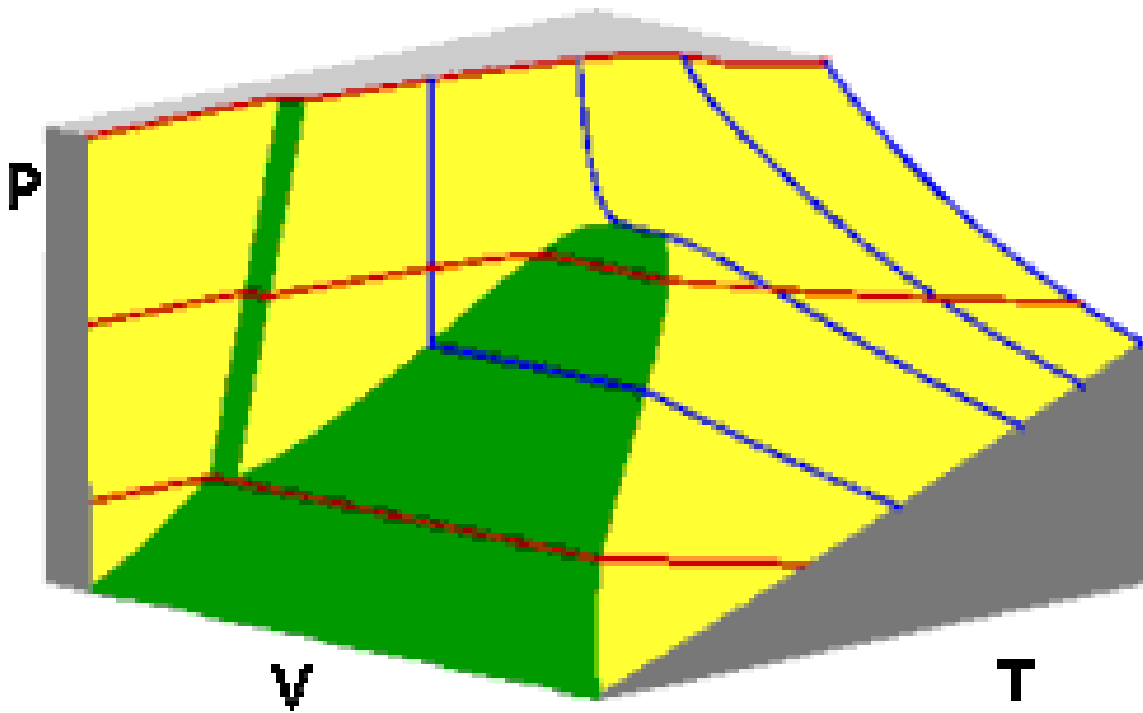
Work done by the system = heat absorbed by the system

Q = 0 - adiabatic process

$\Delta U = -w$ - no heat exchange, the internal energy can be changed only by work.

Real processes are often complex – P, V, and T all are changing. In this case state functions can be calculated by breaking process into a series of reversible isothermal, isobaric, or isochoric processes that bring system to correct final state.

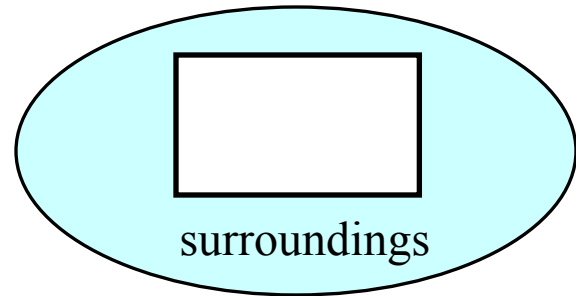
PVT Surface of a Pure Substance



Types of thermodynamic systems

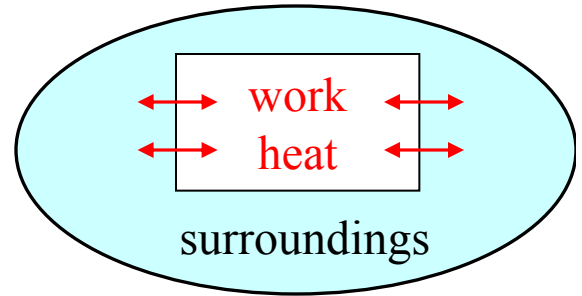
Isolated system

No energy and no matter can pass through the boundaries of the system.



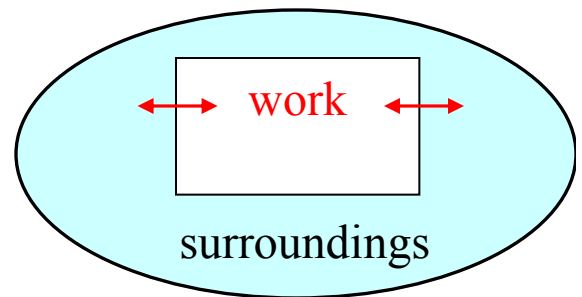
Closed system

Energy can pass through the boundaries (as heat and/or work), but matter cannot.



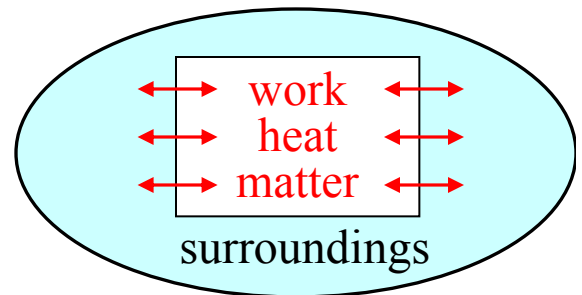
Adiabatic system

No heat can pass through the boundary (neither can matter that can carry heat) – ideal thermos. Work can be performed on or by the system.



Open system

Both energy and matter may pass through the boundaries.



An alternative formulation of the 1st law of thermodynamics:

The work done on a system during an adiabatic process is a state function and numerically equal to the change in internal energy of the system.

Heat Capacity

The heat capacity, C , of a system is the ratio of the heat added to the system, or withdrawn from the system, to the resultant change in the temperature: $C = q/\Delta T = \delta q/dT$ [J/deg]

- This definition is only valid in the absence of phase transitions
- Usually C is given as *specific heat capacity*, c , per gram or per mol
- New state of the system is not defined by T only, need to specify or constrain second variable:

$$C_v = \left(\frac{\delta q}{dT} \right)_v \quad \text{- heat capacity at constant volume}$$

$$C_p = \left(\frac{\delta q}{dT} \right)_p \quad \text{- heat capacity at constant pressure}$$

The fact that δq is not a state function and depends on the path is reflected in the dependence of the heat capacity on the path, $c_p \neq c_v$

(note that small c is used for the derived intensive quantity, per mass, per volume, or per mole, versus capital C for the extensive quantity. For a system containing n moles $C_p = nc_p$ and $C_v = nc_v$ where c_p and c_v are molar values).

c_v and c_p can be measured experimentally

isobaric process: $dH = \delta q = c_p dT$

isochoric process: $dU = \delta q = c_v dT$

H and U can be calculated from c_p and c_v

c_v vs. c_p

If material is allowed to expand during heating, how this affects its heat capacity?

$$c_p = \left(\frac{\delta q}{dT} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$c_v = \left(\frac{\delta q}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$c_p - c_v = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$$\text{since } U = U(V, T), \quad dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Differentiation with respect to T at constant P gives

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

therefore

$$c_p - c_v = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial V}{\partial T} \right)_P \left(P + \left(\frac{\partial U}{\partial V} \right)_T \right)$$

$$\left(\frac{\partial V}{\partial T} \right)_P P \quad \text{work of expansion at constant P due to the temperature increase by } dT$$

$$\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial U}{\partial V} \right)_T \quad \text{work of expansion against internal cohesive forces due to the temperature increase by } dT$$

Calculation of enthalpy from heat capacity

For $P = \text{const}$, $dH = c_p dT$ and integration gives:

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \int_{T_1}^{T_2} c_p dT \qquad H_2 = H_1 + \int_{T_1}^{T_2} c_p dT$$

Example:

Let us find enthalpy for copper at 500 K.

$c_p \approx 24.4 \text{ Jmol}^{-1}\text{K}^{-1}$ for copper at 1 atm.

From the 1st law can only calculate the difference ΔH - need a reference enthalpy. Enthalpy at 1 atm and 298 K is called **enthalpy of formation**, H_{298} . **For pure elements in their equilibrium states $H_{298} = 0$.**

$$H_{500} = H_{298} + \int_{298}^{500} c_p dT = 0 + \int_{298}^{500} 24.4 dT = 4.9 \text{ kJ/mol}$$

Enthalpy of substances other than pure elements can also be calculated. The enthalpy of a compound at 298 K = **standard heat of formation** of the substance from the elements.

Example:

For oxidation of copper at 25 C: $\text{Cu}^{\text{solid}} + \frac{1}{2} \text{O}_2^{\text{gas}} = \text{CuO}^{\text{solid}}$

$$\Delta H_{298}^{\text{CuO}} = H_{298}^{\text{CuO}} - H_{298}^{\text{Cu}} - \frac{1}{2} H_{298}^{\text{O}_2} = H_{298}^{\text{CuO}} = -156.1 \text{ kJ/mol}$$

The reaction is **exothermic** – heat and/or work are produced

Calculation of enthalpy from heat capacity (continued)

In general, heat capacity is a function of temperature. For example, for alumina, Al_2O_3 , the temperature dependence can be described by

$$c_p = 117.5 + 10.4 \times 10^{-3} T - 37.1 \times 10^{-5} T^{-2} \text{ Jmol}^{-1}\text{K}^{-1} \text{ in the range } 298\text{-}2325 \text{ K}$$

$$\begin{aligned} H_{500}^{\text{Al}_2\text{O}_3} &= H_{298}^{\text{Al}_2\text{O}_3} + \int_{298}^{500} c_p(T) dT = -1675.7 \text{ kJ/mol} + \\ &\int_{298}^{500} [117.5 + 10.4 \times 10^{-3} T - 37.1 \times 10^{-5} T^{-2}] dT = -1656.16 \text{ kJ/mol} \end{aligned}$$

The standard heat of formation, $H_{298}^{\text{Al}_2\text{O}_3}$, and heat capacity, $c_p(T)$, are measured experimentally and can be found in thermochemical tables, e.g. at <http://webbook.nist.gov/chemistry/> or at the end of Gaskell's textbook

In most cases, thermal treatment of materials is carried out under atmospheric pressure and no work other than work of expansion against the atmosphere is produced. Enthalpy change is used to describe such processes.

Enthalpy and phase transformations

If the system undergoes a phase transformation (or a chemical reaction) then the **enthalpy change due to the phase change**, ΔH_{trans} , has to be included into total enthalpy change.

Also, **different phases can have different heat capacities**, $c_p(T)$.

For example, let's find enthalpy for copper at 2000 K.

$c_p^{\text{solid}} = 17.7 + 28.1 \times 10^{-3} T - 31.2 \times 10^{-6} T^2 + 14.0 \times 10^{-9} T^3 + 6.86 \times 10^4 T^{-2}$ $\text{Jmol}^{-1}\text{K}^{-1}$ in the solid state for $T = 298 - 1358$ K (this formula for $c_p(T)$ is given at <http://webbook.nist.gov/chemistry/>)

Since this time we are considering a wide range of temperatures, we should account for the temperature dependence of c_p ($c_p \approx 24 \text{ Jmol}^{-1}\text{K}^{-1}$ at 298K, $26 \text{ Jmol}^{-1}\text{K}^{-1}$ at 500K, $33 \text{ Jmol}^{-1}\text{K}^{-1}$ at 1358K)

$c_p^{\text{liquid}} = 32.8 \text{ Jmol}^{-1}\text{K}^{-1}$ in the liquid state (nearly independent on T)

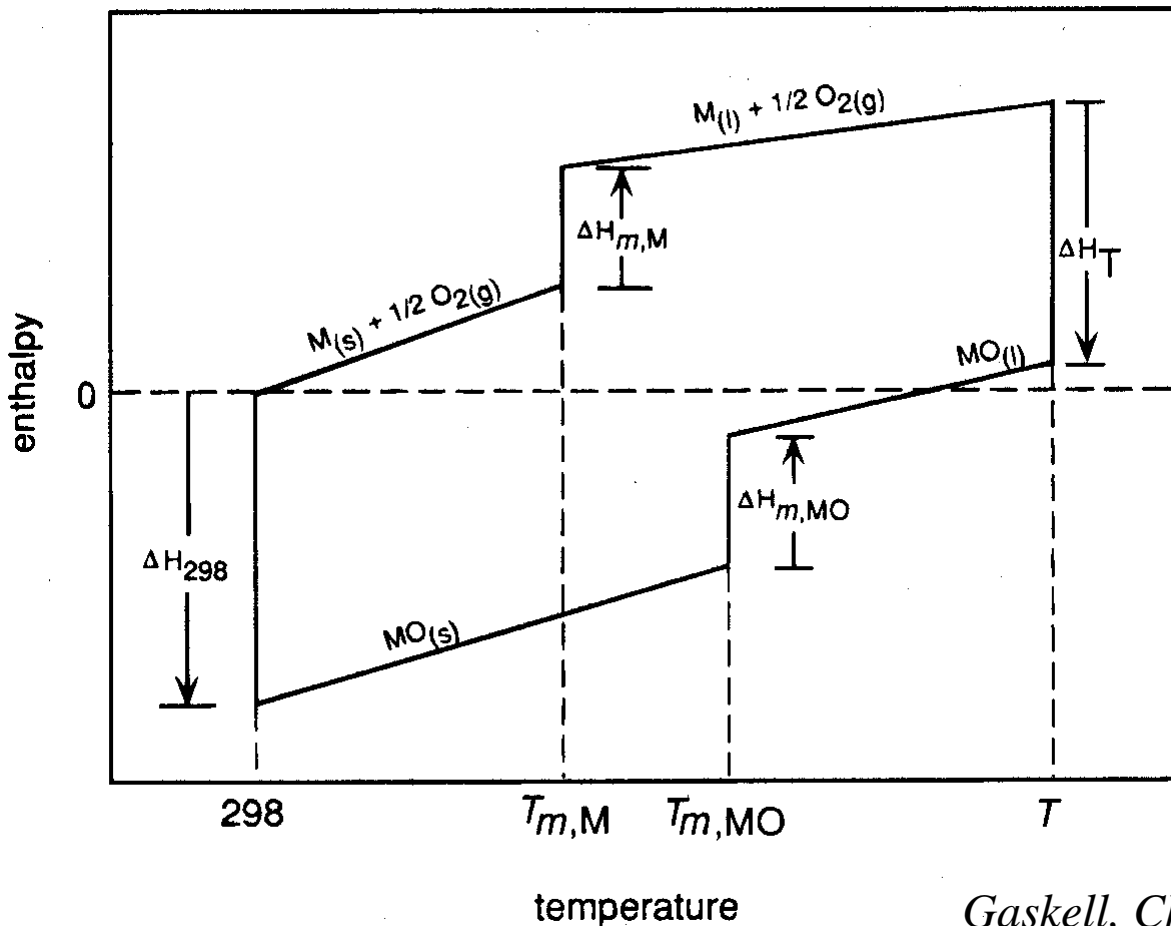
$\Delta H_m = 12 \text{ kJ mol}^{-1}$ – **latent heat of melting** – **always positive**

$$\begin{aligned} H_{2000} &= H_{298} + \int_{298}^{1358} c_p^{\text{solid}}(T) dT + \Delta H_m + \int_{1358}^{2000} c_p^{\text{liquid}} dT = \\ &= 0 + 30. + 12. + 21. = 63 \text{ kJ mol}^{-1} \end{aligned}$$

Heat of formation and phase transformations

If the temperature of interest is higher than the melting temperatures for both the metal and its oxide, the enthalpy change for $M^{\text{liquid}} + \frac{1}{2} O_2^{\text{gas}} = MO^{\text{liquid}}$ is then

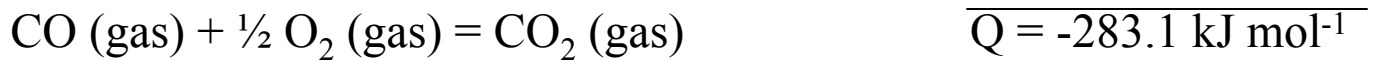
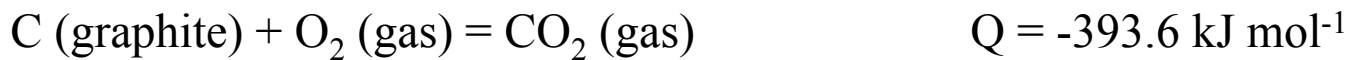
$$\begin{aligned} \Delta H_T = & \Delta H_{298} + \int_{298}^{T_m^M} \left[c_p^{\text{MO,solid}} - c_p^{\text{M,solid}} - \frac{1}{2} c_p^{\text{O}_2,\text{gas}} \right] dT - \\ & - \Delta H_m^M + \int_{T_m^M}^{T_m^{\text{MO}}} \left[c_p^{\text{MO,solid}} - c_p^{\text{M,liquid}} - \frac{1}{2} c_p^{\text{O}_2,\text{gas}} \right] dT + \\ & + \Delta H_m^{\text{MO}} + \int_{T_m^{\text{MO}}}^T \left[c_p^{\text{MO,liquid}} - c_p^{\text{M,liquid}} - \frac{1}{2} c_p^{\text{O}_2,\text{gas}} \right] dT \end{aligned}$$



Heats of Reactions –Hess’s Law

Heat absorbed or released in a given chemical reaction occurring under constant pressure conditions is the same whether the process occurs in one or several steps (Hess, 1840).

Example:



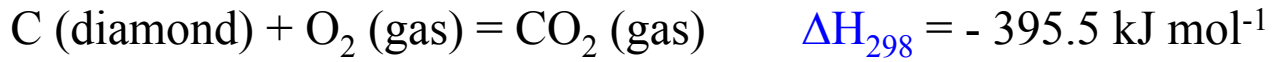
Total: $-393.6 \text{ kJ mol}^{-1}$

- Hess’s Law allows one to calculate Q for reactions that is hard to measure
- Presence of catalysts change the activation energy of reaction but not the net heat of reaction.

The Hess’s law is just a consequence of the 1st law of thermodynamics: for $P = \text{const}$, $\Delta H = Q$. Since H is a state function, total heat is independent of path.

Calculation of heat of transition from heats of reactions

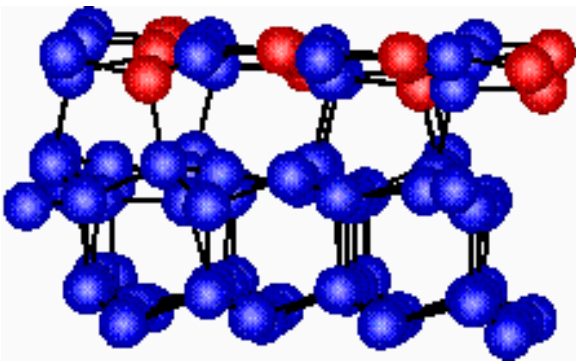
Let's find if an **allotropic** transition from diamond to graphite under ambient conditions results in the release or absorption of heat.



Then for reaction $\text{C (diamond)} \rightarrow \text{C (graphite)}$

$$\Delta H_{298} = 393.6 - 395.5 = -1.9 \text{ kJ mol}^{-1}$$

Transition of diamond to graphite is an exothermic reaction



Graphitization of a surface region of diamond at elevated temperature –
Figure from a computer simulation

Summary

Make sure you understand language and concepts:

Thermodynamic functions of state (no dependence on path/history):

- volume
- temperature
- pressure
- composition
- internal energy
- enthalpy

Heat and work are not state functions

Types of paths

- isobaric
- isochoric
- isothermal
- adiabatic

Types of systems

- open
- closed
- isolated
- adiabatic

Calculation of enthalpy as a function of temperature

Enthalpy and phase transformations

Heat of formation

Standard heat of formation

Heats of reactions and the Hess's law