Outline

- First Law of Thermodynamics
- Heat and Work
- Internal Energy
- Heat Capacity
- Enthalpy Standard State
- Heat of Formation
- Heat of Reaction
- Theoretical Calculations of Heat Capacity

Introduction

In thermodynamics, we would like to describe the material in terms of average quantities, or ***thermodynamic variables***, such as temperature, internal energy, pressure, etc.

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.**

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 V. For different applications, however, we can choose different sets of independent variables that are the most convenient.

Practical example: climbing a mountain by different means (*car, helicopter, cable car… etc*) – elevation is a **……** whereas displacement is **not**.

State Functions

There are *coefficient relations* that describe the change of state functions when other state functions change

Example:
Consider $Z=Z(X,Y,\ldots)$
$dZ = MdX + NdY + \ldots$

Then:

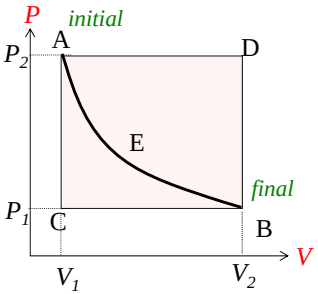
$$M = \left(\frac{\partial Z}{\partial X}\right)_{Y,\ldots} \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y}\right)_{X,\ldots}$$

And,

$$\left(\frac{\partial M}{\partial Y}\right)_{X,\ldots} = \left(\frac{\partial N}{\partial X}\right)_{Y,\ldots}$$ …… *relations*

Energy, Heat, and Work

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 that describe energy *being transferred* to the system.

Types of Work: there are many different ways that energy can be stored in a body by doing work on it: elastically by straining it; electrostatically by charging it, polarizing it in an electric field, magnetizing it in a magnetic field; chemically by changing its composition with a chemical potential.

Although these are examples for different types of work, *they all have the form that the (differential) work performed is the change in some …… variable of the system multiplied by an …… variable.*

Energy, Heat, and Work

Heat is energy being transferred to a system as a result of temp difference
Work can be defined as energy being transferred to a system as a result of a *generalized* force acting over a *generalized* distance.

Examples of work

1 Mechanical work done by force **F** on a body moving from $\mathbf{r}_1$ to $\mathbf{r}_2$ along a certain trajectory or path: $dw = \vec{F}\, d\vec{r}$ $\quad U_{1\to 2} = \int_{\vec{r}_1}^{\vec{r}_2} \vec{F}\, d\vec{r}$ path integral

2 Thermal work due to the volume expansion of a fluid or gas done against an external pressure P. $dw = P\, dV$

3 Electrical work, where the generalized force is the strength of the electric field, **E,** and the generalized displacement is the polarization of the medium, **D**. $dw = -\vec{E}\, d\vec{D}$

4 Magnetic work, where the generalized force is the strength of the magnetic field, **H**, and the generalized displacement is the total magnetic dipole moment, **B**. $dw = -\vec{H}\, d\vec{B}$

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 the work done on the system and the heat transferred to the system.

$\Delta U = q - w$ or in differential form: $dU = \delta q - \delta w$

U – internal energy (*all potential and kinetic energies*). ΔU is a state function depends only on thermodynamic state of the system (e.g. P, V, T for a simple system).
q – energy added to the system as heat. Positive (+) when the system gains heat from outside (**……** process), negative (-) when heat flows out of the system (**……** 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. (*analogy*: if body does work, it expends energy and the internal energy of the body must decrease.)

1st Law
conservation of energy in a thermodynamic process

$\Delta U = q - w$ or $dU = \delta q - \delta w$

In other words, the 1st law says that:

✓ heat and work have the same effect of increasing the internal energy of body AND the internal energy is a state function.

✓ Heat and work have the same units and there are ways of transferring energy from one entity to another.

It may seem obvious to you, but it was not obvious at the time of *Joule* and *Rumford* 200 years ago, that heat and work could be converted from one to another.

Types of Paths

A simple 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).

- **V = const → isochoric process** *(e.g. ……..)*
- **P = const → isobaric process** *(e.g. ……..)*
- **T = const → isothermal process** *(e.g. ……..)*
- **Q = 0 → adiabatic process**

Some properties are absolute, the rest are relative:

- P, T, V, and S are absolute: that is, *their zero values are* ……..
- U, H and G are relative; *they must be assigned a zero value at an* …… *"reference state"*.

Types of Paths

V = const → isochoric process

No work is done (w = +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

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

$U_2 - U_1 = q_p - P(V_2 - V_1)$ or $(U_2 + PV_2) - (U_1 + PV_1) = q_p$

q_p is heat added at constant pressure.

Enthalpy

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

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

It is useful to imagine a system that changes at constant pressure. In this case, the change in energy as a body is heated is not exactly the internal energy, but a new state function called enthalpy *H*. *H* represents the available **thermal** energy at constant pressure.

H is the first new derived state function we will discuss here.

Types of Paths

T = const → isothermal process

Example: ideal gas

dT = 0, therefore, dU = δq - δw = 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* ($P_{ext} = P_{gas}$ at all times)

(reversible process → system is always at equilibrium)

Work done by the system = heat absorbed by the system

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

Integration between states 1 and 2 gives

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

Types of Paths

Q = 0 → adiabatic process

Adiabatic - Greek word means not to be passed

ΔU = -w → no heat exchange, the internal energy can be changed only by work.

Example: Adiabatic heating and cooling are processes that commonly occur due to a change in the pressure of a gas.

Real processes are often complex where 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.

Types of Systems

Isolated system

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

Closed system

Energy can pass through the boundaries, but matter cannot.

Adiabatic system

No heat can pass through the boundary (neither can matter that can carry heat), e.g. ideal thermos.

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 ……. process is a state function and numerically equal to the change in *internal energy* of the system.

10 minutes *Break*

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:

$$C = q/\Delta T = \delta q/dT \text{ [J/deg]}$$

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

- constant-volume heat capacity $C_V = \left(\frac{\delta q}{dT}\right)_V$

- constant-pressure heat capacity $C_P = \left(\frac{\delta q}{dT}\right)_P$

Heat Capacity

$$C_V = \left(\frac{\delta q}{dT}\right)_V \qquad C_P = \left(\frac{\delta q}{dT}\right)_P$$

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: $dU = \delta q = c_V dT$

Hence, H and U can be calculated from c_P and c_V

Heat Capacity

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

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

Let us look at the difference between c_p and c_v.. Because this represents the effect of expansion.

$$c_v = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad c_P - c_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

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

Differentiation with respect to T at constant P gives

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

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

Note: $\left(\frac{\partial V}{\partial T}\right)_P P$ work of expansion against the **const.** ..... **P** due to the temp. increase by dT

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

Relation between Enthalpy and Heat Capacity

For P = const dH = c_P dT and integration gives:

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \int_{T_1}^{T_2} c_P dT \quad ➔ \quad H_2 = H_1 + \int_{T_1}^{T_2} c_P dT$$

Example:

What is the enthalpy for copper at 500K. Given that c_P = 24.4 J/mol.K for copper at 1 atm.

Solution:

From the 1st law, we can only calculate the difference ΔH. Therefore we need a reference enthalpy.

Enthalpy at 1 atm and 298 K is called ..... (H_{298}). *For pure elements in their equilibrium states, $H_{298} = 0$*

Relation between Enthalpy and Heat Capacity

Enthalpy of substances other than pure elements can also be calculated.

The enthalpy of a compound at 298 K is called: .... of the substance from the elements.

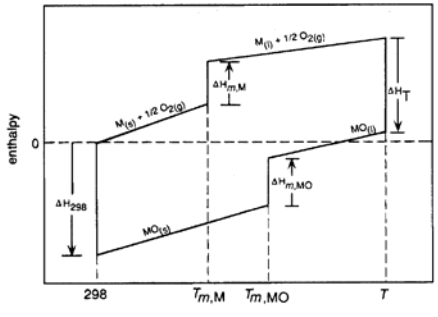
Example:

If you know that the heat capacity of alumina, Al_2O_3, is c_p = 117.5 + 10.4×10^{-3} T - 37.1×10^5 T^{-2} in the range 298-2325K, calculate its enthalpy at 500K. ($^{Al2O3}H_{298}$= -1675.7 kJ/mol)

Solution:

Heat of formation and phase transformations

If the temperature of interest is higher than the melting temp. for both the metal and its oxide, the enthalpy change for $M^{liquid} + ½\ O_2^{gas} = MO^{liquid}$ is then



$$\Delta H_T = \Delta H_{298} + \int_{298}^{T_m^M} \left[c_p^{MO,solid} - c_p^{M,solid} - \frac{1}{2} c_p^{O_2,gas}\right] dT$$
$$- \Delta H_m^M + \int_{T_m^M}^{T_m^{MO}} \left[c_p^{MO,solid} - c_p^{M,liquid} - \frac{1}{2} c_p^{O_2,gas}\right] dT +$$
$$+ \Delta H_m^{MO} + \int_{T_m^{MO}}^{T} \left[c_p^{MO,liquid} - c_p^{M,liquid} - \frac{1}{2} c_p^{O_2,gas}\right] dT$$

Heats of Reactions

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

Example:

C (graphite) + ½ O_2 (gas) = CO (gas)	Q = - 110.5 kJ mol^{-1}
CO (gas) + ½ O_2 (gas) = CO_2 (gas)	Q = -283.1 kJ mol^{-1}
	Total: -393.6 kJ mol^{-1}
C (graphite) + O_2 (gas) = CO_2 (gas)	Q = -393.6 kJ mol^{-1}

✐ Hess Law allows one to calculate Q for reactions that are hard to measure

✐ *Presence of catalysts change the activation energy of reaction but **not** the net heat of reaction.*

Hess's law is just a consequence of the 1st law of thermodynamics: for P = const, ΔH = Q. Since H is a state function, total heat is independent of path.

Theoretical Calculation of the Heat Capacity

• In 1819 Dulong and Petit found experimentally that for many pure elemental solids at room temperature, c_v = 3R = ……..

• Although c_v for many elements (*e.g. lead and copper*) at room temp. are indeed close to 3R, c_v values of silicon and diamond are significantly lower than 25 J/K.mol.

• Low temp. measurements showed a strong temperature dependence of c_v. Actually, c_v is zero at zero K.

• In 1865, Kopp introduced a rule saying that the molar heat capacity of a solid compound is approximately the sum of molar heat capacities of its constituent elements.

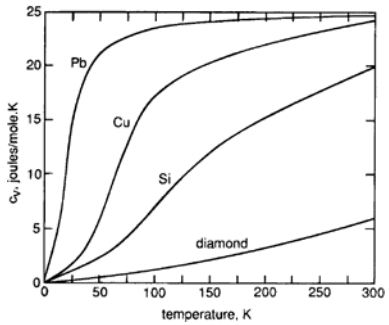


Figure 6.1: *Gaskell 3rd ed.*

Calculation of heat capacity of solids, as a *f(T)*, was one of the early driving forces of the quantum theory. *The first explanation was proposed by …… in 1906.*

Theoretical Calculation of the Heat Capacity

Einstein considered a solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency ν. Quantum theory gives the energy of ith level of a harmonic oscillator as

$\varepsilon_i = (i + ½)\, h\nu$ where i = 0,1,2….., and *h* is Planck's constant.

For a quantum harmonic oscillator the Einstein-Bose statistics must be applied (rather than Maxwell-Boltzmann statistics and equipartition of energy for classical oscillators) and the statistical distribution of energy in the vibrational states gives average energy (*refer to chapter 6 – Gaskell*) :

$$\langle U(t)\rangle = \frac{h\upsilon}{e^{h\upsilon/k_BT}-1}$$

For each atom, three coordinates have to be specified to describe the atom's position, so each atom has 3 degrees of freedom (dof) for its motion. A solid or a molecule composed of N_A atoms has $3N_A$ dof.

$$\therefore \quad U = \frac{3N_A h\upsilon}{e^{h\upsilon/k_BT}-1}$$

$$\because \quad c_V = \left[\frac{\partial U}{\partial T}\right]_V \Rightarrow \frac{3N_A k_B\left(\frac{h\upsilon}{k_BT}\right)^2 e^{h\upsilon/k_BT}}{\left(e^{h\upsilon/k_BT}-1\right)^2}$$

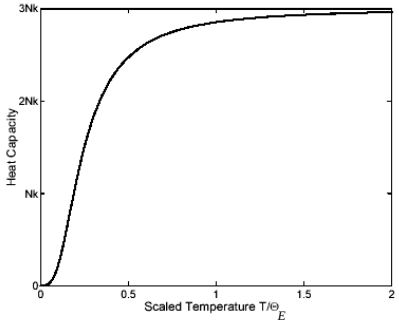
Theoretical Calculation of the Heat Capacity

Let's define Einstein temp. as $\theta_E = h\nu/k$

$$c_v = \frac{3N_A k_B\left(\frac{h\upsilon}{k_BT}\right)^2 e^{h\upsilon/k_BT}}{\left(e^{h\upsilon/k_BT}-1\right)^2}$$

$$c_v = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}}-1\right)^2}$$

Plot c_v versus T/θ_E



• It can be seen that c_v approaches 3R *(25 J/K.mol)* as T > θ_E *(high temp.)*
➔ this agrees with Dulog and Petit's observation
• and as T –> 0, c_v approaches 0 ➔ agrees with the experimental values.

Theoretical Calculation of the Heat Capacity

- Although Einstein's treatment agrees with the trend of the experimental values, it was not exact.
- Einstein formula predicts faster decrease of c_v as compared with experimental data.
- This discrepancy is caused by the fact that the oscillators do not vibrate with a single frequency.

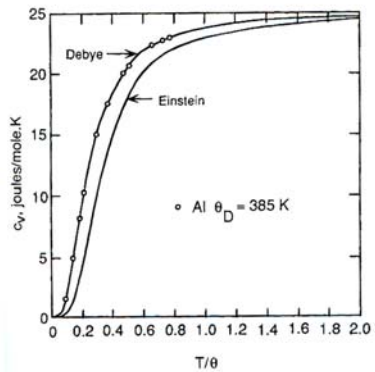
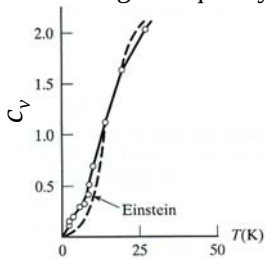


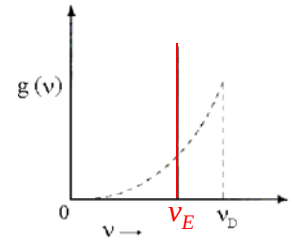
Figure 6.2: *Gaskell 3rd ed.*



Debye enhanced the model by treating the quantum oscillators as collective modes in the solid - *phonons*. And by considering that the oscillators vibrate with a range of frequencies.

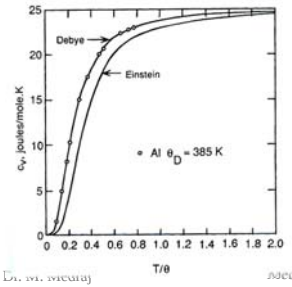
Heat capacity of solids – *Debye model*

Debye, however, assumed a continuum of frequencies with a distribution of $g(\nu) = a\nu^2$, up to a maximum frequency, ν_D, called the Debye frequency. This leads to the following expression for the Debye specific heat capacity:



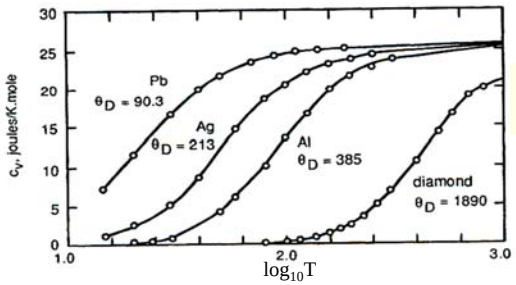
$$c_V = 9N_A k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where x = hν/kT and θ_D = hν$_D$/k (θ_D *is Debye characteristic temp.*)



It can be seen that For low temp., Debye's model predicts the experimental values well.

Theoretical Calculation of the Heat Capacity



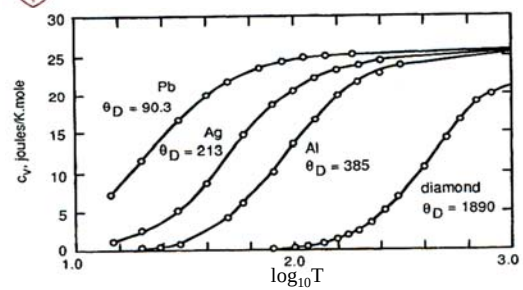
There is a horizontal shift between these curves

Figure 6.2: *Gaskell 3rd ed.*

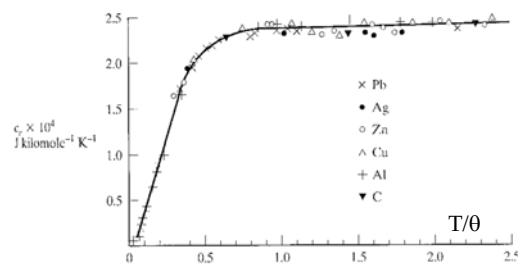
Heat capacity of gas, solid or liquid tends to increase with temperature, due to the increasing number of excited degrees of freedom, requiring more energy to cause the same temperature rise.

The discussed theoretical approaches to heat capacities are based on rather rough approximations (*anharmonicity is neglected, phonon spectrum is approximated by ν^2 in Debye model*). Consequently, in practice $c_p(T)$ is normally determined experimentally and the results are described analytically with equation as: Cp = A + BT + CT^{-2} for a certain temp. range.

Heat capacity of solids – Debye model



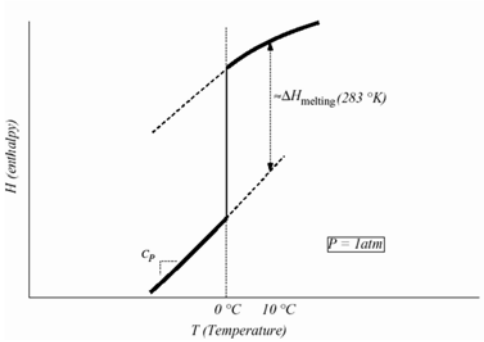
These curves are almost identical except for a horizontal displacement which is a measure of θ_D



As a consequence if we draw c_v versus T/θ all the data points fall on a single curve.

Extrapolation to Non-Stable States

We can calculate the enthalpies, entropies for substances at conditions that they are not stable by extrapolating data.



This is a useful trick as it allows us to make predictions about …….. changes in a system.

Next time:

Second Law of Thermodynamics