Thermodynamics

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Zeroth law

temperature scales

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6 Enthalpy

6.1 State function enthalpy

We define <u>enthalpy</u> as:
$$H = U + PV.$$

This state function greatly simplifies our C_P definition:
$$C_P = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

and its differential is:
$$\mathrm{d}H = \mathrm{d}U + V\mathrm{d}P + P\mathrm{d}V.$$

6.2 Latent heats

6.3 Constant pressure expansion

6.4 Filling empty tank

6.5 Chemical reactions

7   Heat engines

include hurricanes application

8   Entropy

8.1   State function entropy

Entropy is defined as:
$$S = \frac{Q}{T},$$
where Q is <u>heat from reservoir</u> and T the <u>reservoir temperature</u>.

Entropy has units JK^{-1}, and if we have a **reversible cyclic** heat engine:
$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}.$$

This is the differential form of entropy. Applying the first law under again **reversible** conditions gives:
$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

The entropy change of a system is:
$$\Delta S = \int_{(1)}^{(2)} \frac{\mathrm{d}U}{T} + \int_{(1)}^{(2)} P\mathrm{d}V$$
$$= \int_{(1)}^{(2)} \frac{\mathrm{d}Q}{T},$$

for a **reversible path**.

8.2   Entropy of ideal gases

Let's now assume an <u>ideal</u>, **monoatomic** gas. Then its heat capacity becomes:
$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T}.$$

So $C_V \mathrm{d}T = T\mathrm{d}S - P\mathrm{d}V$ and $C_V = \frac{3}{2}nR$. Combining these:
$$\mathrm{d}S = nR\left(\frac{3}{2}\frac{\mathrm{d}T}{T} + \frac{\mathrm{d}V}{V}\right)$$

which can be discretised to find ΔS. Rearranging we get $T\mathrm{d}S = C_V\mathrm{d}T + P\mathrm{d}V$. Integrating and using identity $C_P - C_V = nR$ we get:
$$\Delta S = nc_V \ln\left(\frac{P_2}{P_1}\right) + nc_P \ln\left(\frac{V_2}{V_1}\right)$$

for here n is moles and the heat capacities are in molar quantities.

8.3   Entropy of mixing

Consider a box with separator, containing n_A moles at V_A of gas A on one side and n_B moles at V_B of gas B on the other. We set $\Delta T = 0$, $\Delta P = 0$ and proceed to <u>mix</u> gases A and B.

The **entropy of mixing** is:

$$\Delta S = \Delta S_A + \Delta S_B$$

$$= n_i R \ln \left(\frac{V_f}{V_i} \right)$$

$$= n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) + n_B R \ln \left(\frac{V_A + V_B}{V_B} \right),$$

Since P and T are fixed, the ideal state equation $PV = nRT$ implies that:

$$\frac{V_A + V_B}{V_A} = \frac{n_A + n_B}{n_A}$$

and so we define **inverse mole fractions** as:

$$x_A = \frac{n_A}{n_A + n_B}$$

and

$$x_B = \frac{n_B}{n_A + n_B}.$$

After substituting and dividing through by $n_A + n_B$ we find the **molar specific entropy of mixing**:

$$\Delta s_{mix} = -R(x_A \ln x_A + x_B \ln x_B).$$

8.4   Measuring entropy

Practically, C_P is much easier to measure than C_V. Recall definition:

$$C_P = \frac{\mathrm{d}Q_p}{\mathrm{d}T} = \left(\frac{\mathrm{d}H}{\mathrm{d}T} \right)_p$$

where state function H is the enthalpy. Since $H = U + PV$:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$$

and dividing by $\mathrm{d}T$:

$$\frac{\mathrm{d}H}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T} + V\frac{\mathrm{d}P}{\mathrm{d}T}.$$

If $\Delta P = 0$ then:

$$C_P(T) = T\left(\frac{\mathrm{d}S}{\mathrm{d}T} \right)_P.$$

Rearranging and integrating gives us the change in entropy:

$$\Delta S = \int_{(1)}^{(2)} \frac{C_P(T)}{T}\mathrm{d}T.$$

9   Second law

9.1   Reversibility

9.2   Second law

include spontaneous process

sections 12 and 13

10   Helmholtz and Gibbs free energy

include chemical reactions and colloidal particles

sections 14 and 15

11   Maxwell relations

11.1   Derivation

So from previous sections we have the following four differential relations[1]:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V,$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P,$$

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V,$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P.$$

For equation of state $f(P, V, T) = 0$, the **Maxwell relations** are the following:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$

Notice how each equation relates entropy S to measurable quantities.

These relations are derived by taking **total differentials** and then applying **Clairaut's theorem**. We are only going to do the first relation:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

$$= \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

Therefore we have that:

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

and

$$P = -\left(\frac{\partial U}{\partial V}\right)_S.$$

Taking partials again and equating gives us the first relation.

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[1] Here U is the internal energy, H is enthalpy, F is the Helmholtz free energy and G is the Gibbs free energy.

11.2   Applications

We can define **isobaric expansivity** β with units K^{-1} as:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and **isothermal compressibility** κ_T with units Pa^{-1} as:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

These may be thought of as volume change per physical unit change.

The Maxwell relations can be used to find entropy. For example:

$$\Delta S = \int_{(1)}^{(2)} \mathrm{d}S$$

$$= -\int_{(1)}^{(2)} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P.$$

11.2.1   Ideal gas internal energy

Now we can show why $U = U(T)$ if we have an ideal gas. Beginning with:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

and dividing through by $\mathrm{d}V$ gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P$$

via a Maxwell relation. Finally our ideal gas assumption implies that:

$$P = \frac{nRT}{V}$$

and substituting this into the previous expression results in:

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

which means that $U = U(T)$.

11.2.2   Difference in heat capacities

We begin with the following expression:

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

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

$$= C_V + T\left(\frac{\partial P}{\partial T}\right)_V \beta V.$$

$$\therefore C_P - C_V = \beta T V \left(\frac{\partial P}{\partial T}\right)_V$$

Then using the following identities:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

$$\frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} = \left(\frac{\partial P}{\partial V}\right)_T$$

we get that the difference in heat capacities is:

$$C_P - C_V = \frac{\beta^2}{\kappa_T} T V$$

where β is the **isobaric expansivity** and κ_T is the **isothermal compress-ibility**. Furthermore it is clear that $C_P - C_V > 0$ for all cases.

11.2.3   Liquefying gases

12   Phase transitions

12.1   PT diagrams

phase transition diagrams (PT)

supercritical points

phase boundaries

triple point

clausius clapeyron equation

12.2   Van der Waals state equation

The Van der Waals equation is a modification of the ideal gas equation:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

and defines the volume V occupied by n moles of gas at pressure P and temperature T. The <u>molar</u> version of this is the following:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where we define the <u>molar volume</u> as $v = \frac{V}{n}$.

12.2.1   Helmholtz and Gibbs free energies

Since we have that $\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V$ at fixed temperatures:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

and integrating the molar version of this:

$$f = -\int P\,\mathrm{d}v$$
$$= \tau(T) - RT\ln(v - b) - \frac{a}{v}$$

where we have substituted the Van der Waals equation.

For the Gibbs free energy because $f = u - TS$ we then have that:

$$\begin{aligned}
g &= u + Pv - TS \\
&= f + Pv \\
&= \tau(T) - RT\ln(v - b) - \frac{a}{v} + Pv
\end{aligned}$$

12.3   PV diagrams

13   Chemical potentials

14   Third law