Application of thermodynamics

Classical ideal gas

From the equation of state

$$pV = Nk_BT$$

we obtain the mechanical response functions

$$\begin{aligned}\alpha_p &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{Nk_B}{Vp} = \frac{1}{T}\\ \kappa_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{Nk_BT}{Vp^2} = \frac{1}{p}.\end{aligned}$$

Thermal response functions cannot be derived from the equation of state. Empirically we have

$$C_V = \frac{1}{2}fk_BN.$$

Here $\frac{1}{2}fk_B$ is the specific heat capacity/molecule and f is the number of degrees of freedom of the molecule.

Atoms/molecule	f	translations	rotations
1	3	3	0
2	5	3	2
poly	6	3	3

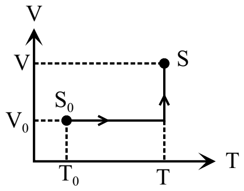
For real gases $f = f(T,p)$.

Entropy

$$\begin{aligned}dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\\ &= \frac{1}{T}C_V dT + \left(\frac{\partial p}{\partial T}\right)_V dV,\end{aligned}$$

since according to Maxwell relations

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



Integrating we get

$$\begin{aligned}S &= S_0 + \int_{T_0}^{T} dT\,\frac{C_V}{T} + \int_{V_0}^{V} dV\,\frac{Nk_B}{V}\\ &= S_0 + C_V\ln\frac{T}{T_0} + Nk_B\ln\frac{V}{V_0}\end{aligned}$$

or

$$S = S_0 + Nk_B\ln\left[\left(\frac{T}{T_0}\right)^{f/2}\frac{V}{V_0}\right].$$

Note A contradiction with the third law: $S \to -\infty$, when $T \to 0$.

Internal energy

We substitute into the firs law

$$dU = T\,dS - p\,dV$$

the differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

and get

$$dU = C_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV.$$

According to a Maxwell relations and to the equation of state we have

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

so

$$dU = C_V dT$$

and

$$U = U_0 + C_V(T - T_0) = U_0 + \frac{1}{2}fk_BN(T - T_0).$$

If we choose $U_0 = C_VT_0$, we get for the internal energy

$$U = \frac{1}{2}fk_BNT.$$

Now

$$C_p = C_V + VT\,\frac{\alpha_p^2}{\kappa_T}$$

or

$$C_p = Nk_B\left(\frac{1}{2}f + 1\right)$$

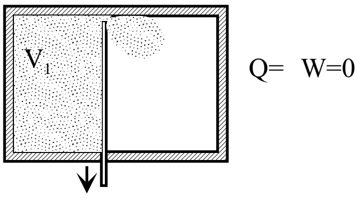
or

$$C_p = \gamma C_V,$$

where γ is the *adiabatic constant*

$$\gamma = C_p/C_V = (f+2)/f.$$

Free expansion of gas



In the process $V_1 \to V_2$ and $\Delta Q = \Delta W = 0$, so $\Delta U = 0$. Process is irreversible.

a) Ideal gas
Now

$$U = \frac{1}{2}fk_BTN,$$

so $T_1 = T_2$, because $U_1 = U_2$. The cange in the entropy is thus

$$\Delta S = Nk_B\ln\frac{V_2}{V_1}.$$

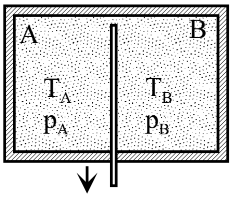
b) Other material
The internal energy (and the number of particle) being constant ($dU = 0$) we obtain from the expression

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

for the *Joule coefficient* $\left(\frac{\partial T}{\partial V}\right)_{U,N}$ the form

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_{U,N} &= -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} \\ &= \frac{1}{C_V}\left(p - T\,\frac{\alpha_p}{\kappa_T}\right).\end{aligned}$$

Mixing entropy



Suppose that initially $p_A = p_B = p$ and $T_A = T_B = T$.
The process is adiabatic so $\Delta Q = 0$.
In a mixture of ideal gases every component satisfies the state equation

$$p_j V = N_j k_B T.$$

The concentration of the component j is

$$x_j = \frac{N_j}{N} = \frac{p_j}{p},$$

where the total pressure p is

$$p = \sum_j p_j.$$

Tapa 1
Each constituent gas expands in turn into the volume V. Since $p_A = p_B$ and $T_A = T_B$, we have $V_j = V x_j$. The change in the entropy is (see the free expansion of a gas)

$$\Delta S = \sum_j N_j k_B \ln \frac{V}{V_j}$$

or

$$\Delta S_{\text{sek}} = -N k_B \sum_j x_j \ln x_j.$$

Now $\Delta S_{\text{sek}} \geq 0$, since $0 \leq x_j \leq 1$.
Way 2
For a process taking place in constant pressure and temperature the Gibbs function is the suitable potential:

$$\begin{aligned}G &= U - TS + pV \\ &= \frac{1}{2} f k_B T N - TS + pV = \cdots \\ &= N k_B T[\phi(T) + \ln p] = N\mu(p,T),\end{aligned}$$

where

$$\phi(T) = \frac{\mu^0}{k_B T} - \xi - (\frac{f}{2} + 1)\ln T.$$

Before mixing

$$G_{(\mathrm{b})} = \sum_j N_j k_B T[\phi_j(T) + \ln p]$$

and after mixing

$$G_{(\mathrm{a})} = \sum_j N_j k_B T[\phi_j(T) + \ln p_j],$$

so the change in the Gibbs function is

$$\begin{aligned}\Delta G_{(\mathrm{mix})} &= G_{(\mathrm{a})} - G_{(\mathrm{b})} = \sum_j N_j k_B T \ln \frac{p_j}{p} \\ &= \sum_j N_j k_B T \ln x_j.\end{aligned}$$

Because

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\{N_j\}},$$

we get for the mixing entropy

$$\Delta S_{\text{mix}} = S_{(\mathrm{a})} - S_{(\mathrm{b})} = -\sum_j N_j k_B \ln x_j.$$

Gibbs' paradox: If $A \equiv B$, i.e. the gases are identical no changes take place in the process. However, according to the former discussion, $\Delta S > 0$. The contradiction can be removed by employing quantum statitics of identical particles.

Chemical reaction

Consider for example the chemical reaction

$$2\,\mathrm{H_2S} + 3\,\mathrm{O_2} \rightleftarrows 2\,\mathrm{H_2O} + 2\,\mathrm{SO_2}.$$

In generall the *chemical reaction formula* is written as

$$0 = \sum_j \nu_j M_j.$$

Here $\nu_j \in \mathcal{I}$ are the *stochiometric coefficient* and M_j stand for the molecular species.

Example

j	A	B	C	D
M_j	H_2S	O_2	H_2O	SO_2
ν_j	-2	-3	2	2

We define the *degree of reaction* ξ so that

$$dN_j = \nu_j d\xi.$$

When ξ increments by one, one reaction of the reaction formula from left to right takes place.
Convention: When $\xi = 0$ the reaction is as far left as it can be. then

$$\xi \geq 0.$$

We suppose that p and T are constant in the reaction. Then a suitable potential is the Gibbs function

$$G = \sum_j \mu_j N_j.$$

Its differential is

$$dG = \sum_j \mu_j dN_j = d\xi \sum_j \nu_j \mu_j .$$

We define

$$\Delta_{\mathrm{r}} \equiv \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_j \nu_j \mu_j .$$

Δ_{r} is thus the change in the Gibbs function per one reaction.
Since (p,T) is constant G has a minimum at an equilibrium. The equilibrium condition is thus

$$\Delta_{\mathrm{r}} G^{\mathrm{eq}} = \sum_j \nu_j \mu_j^{\mathrm{eq}} = 0.$$

In a nonequilibrium $dG/dt < 0$, so if $\Delta_{\mathrm{r}} > 0$ we must have $d\xi/dt < 0$, i.e. the reaction proceeds to left and vice versa.
We assume that the components obey the state equation of the ideal gas. Then

$$\mu_j = k_B T[\phi_j(T) + \ln p + \ln x_j],$$

where

$$\phi_j(T) = \frac{\mu_j^0}{k_B T} - \eta_j - (1 + \frac{1}{2} f_j)\ln T.$$

So

$$\Delta_{\mathrm{r}} G = k_B T \sum_j \nu_j \phi_j(T) + k_B T \ln\left(p^{\sum \nu_j} \prod x_j^{\nu_j}\right).$$

The equilibrium condition can now be written as

$$\prod_j x_j^{\nu_j} = p^{-\sum_j \nu_j} K(T),$$

where

$$K(T) = e^{-\sum_j \nu_j \phi_j(T)}$$

is the *equilibrium constant* of the reaction. The equilibrium condition is call the *law of mass action.*
The *reaction heat* is the change of heat $\Delta_{\mathrm{r}} Q$ per one reaction to right. A reaction is

- *Endothermic*, if $\Delta_{\mathrm{r}} Q > 0$ i.e. the reaction takes heat.
- *Exothermic*, if $\Delta_{\mathrm{r}} Q < 0$ i.e. the reaction releases heat.

We write $\Delta_{\mathrm{r}} G$ as

$$\Delta_{\mathrm{r}} G = -k_B T \ln K(T) + k_B T \sum_j \nu_j \ln p x_j .$$

Now

$$\begin{aligned} \Delta Q &= \Delta U + \Delta W = \Delta U + p\,\Delta V = \Delta(U + pV) \\ &= \Delta H, \end{aligned}$$

since $\Delta p = 0$.
When the total amount matter is constant

$$dG = -S\,dT + V\,dp$$

holds in a reversible process and

$$\begin{aligned} d\left(\frac{G}{T}\right) &= \frac{1}{T}dG - \frac{G}{T^2}dT = -\left(\frac{G}{T^2} + \frac{S}{T}\right)dT + \frac{V}{T}dp \\ &= -\frac{H}{T^2}dT + \frac{V}{T}dp, \end{aligned}$$

because $G = H - TS$. We see that

$$H = -T^2\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_{p,N}.$$

Now

$$\frac{\partial}{\partial T}\left(\frac{\Delta_{\mathrm{r}} G}{T}\right) = -k_B \frac{d}{dT}\ln K(T),$$

so that

$$\Delta_{\mathrm{r}} H = k_B T^2 \frac{d}{dT}\ln K(T).$$

This expression is known as the *reaction heat.*

Phase equilibrium

In a system consisting of several phases the equilibrium conditions for each pair (A and B) of phases are

$$\begin{aligned} T_A &= T_B = T \\ p_A &= p_B = p \\ \mu_{jA} &= \mu_{jB},\ j = 1, \ldots, H, \quad (*) \end{aligned}$$

where H is the number of particle species in the system.
Let us assume that the number of phases is F, so for each species there are $F-1$ independent conditions $(*)$. Now $\mu_{i\alpha} = \mu_{i\alpha}(p,T,\{N_{j\alpha}\})$. Because the chemical potential is an intensive quantity it depends only on relative fractions, so

$$\mu_{j\alpha} = \mu_{j\alpha}(p,T,x_{1\alpha},\ldots,x_{H-1,\alpha}),$$

and the conditions $(*)$ take the form

$$\begin{aligned} &\mu_{1A}(p,T,x_{1A},\ldots,x_{H-1,A}) = \\ &\qquad \mu_{1B}(p,T,x_{1B},\ldots,x_{H-1,B}) \\ &\vdots \\ &\mu_{HA}(p,T,x_{1A},\ldots,x_{H-1,A}) = \\ &\qquad \mu_{HB}(p,T,x_{1B},\ldots,x_{H-1,B}). \end{aligned}$$

There are

- $M = (H-1)F + 2$ variables,
- $Y = H(F-1)$ equations.

The simultaneous equations can have a solution only if $M \geq Y$ or

$$F \leq H + 2.$$

This condition is know as the *Gibbs phase rule.*
For *pure matter* the equilibrium condition

$$\mu_A(p,T) = \mu_B(p,T)$$

defines in the (p, T)-plane a *coexistence curve*. If the phase B is in equilibrium with the phase C we get another curve

$$\mu_B(p, T) = \mu_C(p, T).$$

The phases A, B can C can be simultaneously in equilibrium in a crossing point, so called *triple point*, of these curves.

Phase transitions

In a phase transition the chemical potential

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

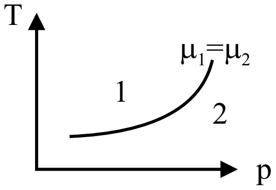
is continuous. Instead

$$S = -\left(\frac{\partial G}{\partial T}\right)_p$$

and

$$V = \left(\frac{\partial G}{\partial p}\right)_T$$

are not necessarily continuous.
A transition is of *first order*, if the first order derivatives (S, V) of G are discontinuous and of *second order*, if the second order derivatives are discontinuous. Otherwise the transition is *continuous*



In a first order transition from a phase 1 to a phase 2

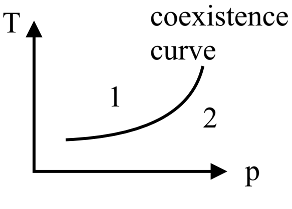
$$\begin{aligned}\Delta S &= -\left(\frac{\partial G}{\partial T}\right)_p^{(2)} + \left(\frac{\partial G}{\partial T}\right)_p^{(1)}\\ \Delta V &= \left(\frac{\partial G}{\partial p}\right)_T^{(2)} - \left(\frac{\partial G}{\partial p}\right)_T^{(1)}.\end{aligned}$$

When we cross a coexistence curve p and T stay constant, so

$$\begin{aligned}\Delta Q &= T\,\Delta S = \Delta U + p\,\Delta V = \Delta(U + pV)\\ &= \Delta H.\end{aligned}$$

ΔQ is called the *phase transition heat* or the*latent heat.*
Note First order transitions are associated with the heat of phase transitions but not the higher order transitions.

Coexistence



On the coexistence curve

$$G_1(p, T, N) = G_2(p, T, N)$$

and

$$dG = -S\,dT + V\,dp$$

when the number of particles N is constant. Along the curve

$$G_1(p + dp, T + dT, N) = G_2(p + dp, T + dT, N),$$

so that

$$-S_1 dT + V_1 dp = -S_2 dT + V_2 dp$$

or on the curve

$$\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} = \frac{T^{-1}\Delta H}{\Delta V}$$

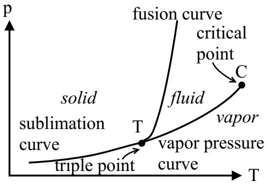
and we end up with the *Clausius-Clapeyron equation*

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{1}{T}\frac{\Delta H}{\Delta V}.$$

Here $\Delta H = H_2 - H_1$ and $\Delta V = V_2 - V_1$.

Examples

a) Vapor pressure curve



We consider the transition

$$\text{liquid} \to \text{vapor}.$$

Supposing that we are dealing with ideal gas we have

$$\Delta V = V_{\text{v}} = \frac{Nk_BT}{p},$$

since

$$V_{\text{l(iquid)}} \ll V_{\text{v(apor)}}.$$

Because the vaporization heat (the phase transition heat) ΔH_{lv} is roughly constant on the vapor pressure curve we have

$$\frac{dp}{dT} = \frac{\Delta H_{\text{lv}}p}{Nk_BT^2}.$$

Integration gives us

$$p = p_0 e^{-\Delta H_{\text{lv}}/Nk_BT}.$$

b) Fusion curve
Now

$$\Delta V_{\text{ls}} = V_{\text{l(iquid)}} - V_{\text{s(olid)}}$$

can be positive or negative (for example H_2O).

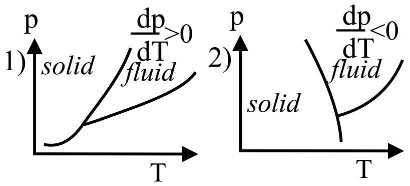
According to the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{\mathrm{ls}}}{T\,\Delta V_{\mathrm{ls}}}$$

we have

$$\frac{dp}{dT} > 0, \quad \text{if } \Delta V_{\mathrm{ls}} > 0 \qquad 1)$$

$$\frac{dp}{dT} < 0, \quad \text{if } \Delta V_{\mathrm{ls}} < 0 \qquad 2) \quad .$$



We see that when the pressure is increased in constant temperature the system

1) drifts "deeper" into the solid phase,

2) can go from the solid phase to the liquid phase.

c) Sublimation curve
Now

$$dH = T\,dS + V\,dp = C_p dT + V(1 - T\alpha_p)\,dp,$$

since $S = S(p,T)$ and using Maxwell relations and definitions of thermodynamic response functions

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT = -\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{C_p}{T}\,dT.$$

The vapor pressure is small so $dp \approx 0$, and

$$\begin{aligned} H_{\mathrm{s}} &= H_{\mathrm{s}}^0 + \int_0^T C_p^{\mathrm{s}} dT && \text{solid phase} \\ H_{\mathrm{v}} &= H_{\mathrm{v}}^0 + \int_0^T C_p^{\mathrm{v}} dT && \text{vapor (gas).} \end{aligned}$$

Let us suppose that the vapor satisfies the ideal gas state equation. Then

$$\Delta V_{\mathrm{vs}} = \frac{Nk_BT}{p} - V_{\mathrm{s}} \approx \frac{Nk_BT}{p},$$

so

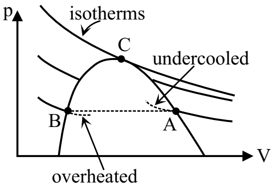
$$\frac{dp}{dT} = \frac{\Delta H_{\mathrm{vs}}}{T\,\Delta V_{\mathrm{vs}}} \approx \frac{p\,\Delta H_{\mathrm{vs}}}{Nk_BT^2},$$

where $\Delta H_{\mathrm{vs}} = H_{\mathrm{s}} - H_{\mathrm{v}}$.
For a mono atomic ideal gas $C_p = \frac{5}{2}k_BN$, so that

$$\ln p = -\frac{\Delta H_{\mathrm{vs}}^0}{Nk_BT} + \frac{5}{2}\ln T - \frac{1}{k_BN}\int \frac{\int_0^T C_p^{\mathrm{s}} dT'}{T^2}\,dT + \text{constant}.$$

Here ΔH_{vs}^0 is the sublimation heat at 0 temperature and pressure.

Coexistence range



Matter is mechanically stable only if $\frac{dV}{dp} < 0$. Thus the range of stability lies outside of the points A and B. Overheated liquid and undercooled vapor are metastable. According to the Gibbs-Duhem relation

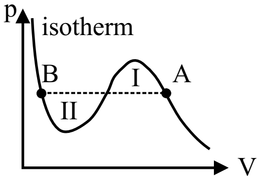
$$d\mu = -\frac{S}{N}\,dT + \frac{V}{N}\,dp$$

we have on an isotherm

$$d\mu = \frac{V}{N}\,dp.$$

Thus, when the phases A and B are in equilibrium,

$$\mu_A - \mu_B = \int_A^B \frac{V}{N}\,dp = 0.$$



Maxwell's construction: The points A and B have to be chosen so that the area I = area II.