

Lecture Notes 10

1. Brayton Cycle



Figure 1: George Brayton (1830-1892) American engineer

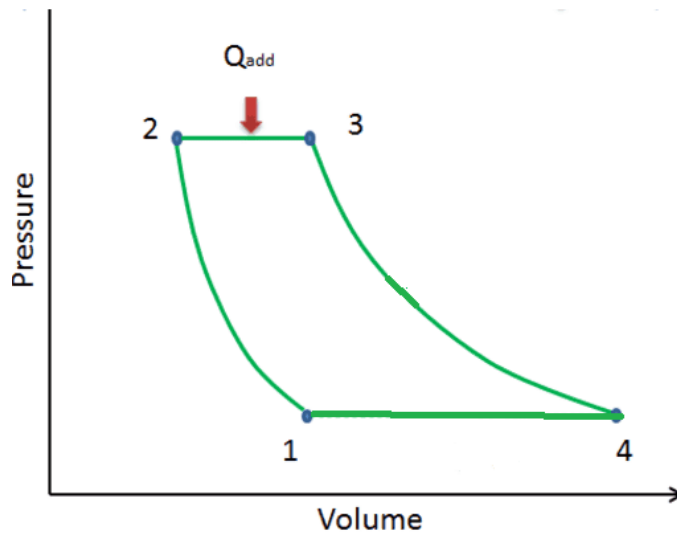


Figure 2: Brayton cycle

The Brayton cycle is the used by gas turbines. It contains two adiabats and two isobars. The fluid is a mixture of air and fuel that we will assume to be an ideal gas. The equation of state is: $pV = NRT$ and the energy is: $U = (i/2)NRT$, where i is number of degrees of freedom for a molecule.

Step 1 to 2 is adiabatic compression:

$$Q_{12} = 0 \quad (1)$$

$$W_{12} = U_2 - U_1 - Q_{12} = N \frac{i}{2} R(T_2 - T_1) \quad (2)$$

Step 2 to 3 is isobaric heating (combustion):

$$W_{23} = -p_2(V_3 - V_2) = -NR(T_3 - T_2) \quad (3)$$

$$Q_{23} = U_3 - U_2 - W_{23} = N \frac{i+2}{2} R(T_3 - T_2) \quad (4)$$

Step 3 to 4 is adiabatic expansion:

$$Q_{34} = 0 \quad (5)$$

$$W_{34} = U_4 - U_3 - Q_{34} = N \frac{i}{2} R(T_4 - T_3) \quad (6)$$

Step 4 to 1 is isobaric cooling:

$$W_{41} = -p_1(V_1 - V_4) = -NR(T_1 - T_4) \quad (7)$$

$$Q_{41} = U_1 - U_4 - W_{41} = N \frac{i+2}{2} R(T_1 - T_4) \quad (8)$$

The total work done on the fluid is: $W = W_{12} + W_{23} + W_{34} + W_{41}$. Using Eqs. (2), (3), (6), and (7) we find:

$$W = N \frac{i}{2} R(T_2 - T_1 + T_4 - T_3) - NR(T_3 - T_2 + T_1 - T_4) = N \frac{i+2}{2} R(T_2 - T_1 + T_4 - T_3) \quad (9)$$

The efficiency is $e = -W/Q_{23}$. Using Eqs (4) and (9) we find:

$$e = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (10)$$

On adiabats we have the Poisson equation: $pV^\gamma = \text{constant}$, where $\gamma = (i+2)/i$. Using the equation of state $pV/T = \text{constant}$, we find: $Tp^{(1-\gamma)/\gamma} = \text{constant}$. For the adiabat 1 to 2:

$$T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}} \quad (11)$$

For the adiabat 3 to 4 we get:

$$T_3 p_2^{\frac{1-\gamma}{\gamma}} = T_4 p_1^{\frac{1-\gamma}{\gamma}} \quad (12)$$

Equations (11) and (12) yield:

$$\frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}} \quad (13)$$

The efficiency is obtained from (10) and (13):

$$e = 1 - \left(\frac{p_1}{p_2}\right)^{\frac{\gamma-1}{\gamma}} \quad (14)$$

The power in Eq. (14) is equal to: $2/(i+2)$.

READING: Set 9: Callen 4.10.3, HRW 20.32.

2. Joule Experiment

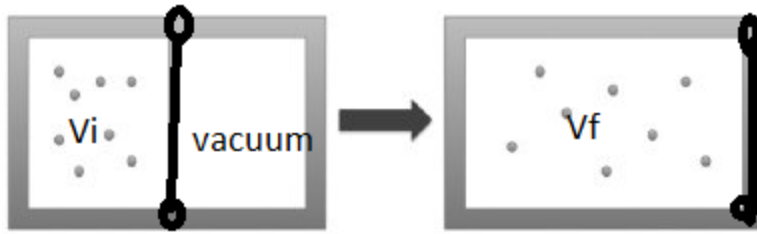


Figure 3: Free expansion experiment

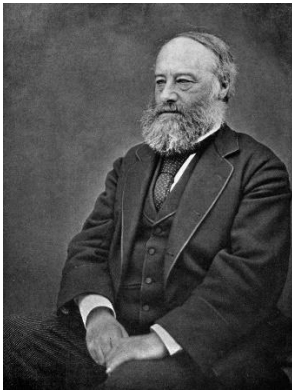


Figure 4: James Prescott Joule (1818-1889), English physicist

In the free expansion experiment (Figure 3), the gas is initially on the left compartment. In the right compartment there is vacuum. The gas is allowed to expand freely. Since the external walls are rigid and adiabatic, there is no work or heat exchange with external world. Hence the energy is conserved. We assume the fluid to be an ideal van der Waals fluid (see Lecture notes 5). The molar energy is:

$$u = \frac{i}{2}RT - \frac{a}{v} \quad (15)$$

and the equation of state is:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (16)$$

Since in the free expansion the molar energy is conserved, Eq. (15) gives:

$$u = \frac{i}{2}RT_i - \frac{a}{v_i} = \frac{i}{2}RT_f - \frac{a}{v_f} \quad (17)$$

The change in temperature follows from Eq. (17):

$$T_f - T_i = -\frac{2a}{iR} \left(\frac{1}{v_i} - \frac{1}{v_f} \right) \quad (18)$$

Since $v_i < v_f$, the right hand side of Eq. (18) is negative. Thus for the ideal van der Waals fluid, the free expansion experiment results in a drop in temperature:

$$T_f < T_i \quad (19)$$

The physical cause for this drop in temperature is the attraction between molecules which is proportional to a . For the ideal gas $a = 0$ so that the temperature remains unchanged $T_f = T_i$.

READING: Callen pg. 192; Set 4 Callen 3.4.8.

3. Electromagnetic Radiation

A container with walls maintained at a temperature T contains electromagnetic radiation which can be described as gas of photons. A photon travels with a speed equal to the speed of light and has an energy equal to hf , where h is the Planck constant and f is the frequency of the radiation.



Figure 5: Max Planck (1858-1947) German physicist who discovered in 1900 the quantum nature of radiation.

The photons can be created and destroyed without an energetic price. Hence the chemical potential $\mu = 0$. The number of photons is fluctuating quantity and it cannot be fixed. The fundamental equation in terms of intensive variables is $0 = \mu(T,p)$. Hence the pressure is a function of T only:

$$p = p(T) \quad (20)$$

The gas of photons is an ideal gas Then the energy is expected to be proportional to pV :

$$U = 3p(T)V \quad (21)$$

The factor of 3 is the spatial dimension. Note the absence of $\frac{1}{2}$ factor present in monatomic ideal gas is due to energy-momentum relation being linear $\varepsilon = pc$, in contrast to matter particles that have a quadratic dependence $\varepsilon = p^2/2m$.

The first law in differential form, with $\mu = 0$, is:

$$dU = TdS - pdV \quad (22)$$

Substitute in (22): $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$:

$$dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - p\right)dV \quad (23)$$

We can evaluate derivatives of U using Eq. (21):

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = 3 \frac{dp}{dT} V \quad (24)$$

$$T\left(\frac{\partial S}{\partial V}\right)_T - p = \left(\frac{\partial U}{\partial V}\right)_T = 3p \quad (25)$$

It follows:

$$\left(\frac{\partial S}{\partial T}\right)_V = 3 \frac{dp}{dT} \frac{V}{T} \quad (26)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = 4 \frac{p}{T} \quad (27)$$

Use the Maxwell relation:

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V} \quad (28)$$

Calculate the left hand side of (28) by using Eq.(26) and the right hand side of (28) by using

Eq.(27):

$$\frac{3}{T} \frac{dp}{dT} = \frac{4}{T} \frac{dp}{dT} - \frac{4p}{T^2} \quad (29)$$

Or

$$\frac{dp}{dT} = \frac{4p}{T} \quad (30)$$

Integrate Eq. (30) by separating variables:

$$p = \frac{a}{3} T^4 \quad (31)$$

In Eq. (31) a is a constant, called the Stefan constant. Its value is: $a = 7.56 \cdot 10^{-16} \text{Pa/K}^4$. Equation (31) gives the fundamental equation in terms of intensive variables.



Figure 6: Josef Stefan (1835-1893) was a Slovene physicist

From Eqs.(21) and (31) we get:

$$U = aVT^4 \quad (32)$$

The entropy can be calculated from the Euler equation: $U = TS - pV$, where I used $\mu = 0$.

$$S = (4/3)aVT^3 \quad (33)$$

Note at $T = 0$ the entropy is $S = 0$. This is a manifestation of the third law of thermodynamics.

The isochoric heat capacity is:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aVT^3 \quad (34)$$

The fundamental equation in terms of extensive variables is obtained by eliminating T between Eqs. (32) and (33):

$$U = aV(3S/4aV)^{4/3} = (3/4)^{4/3}a^{-1/3}V^{-1/3}S^{4/3} \quad (35)$$

Reading

Callen Ch. 3 Sec. 6

Problem Set 10

Lecture Notes 11

A. Thermodynamic Potentials, Maxwell Relations

The thermodynamic potentials are Legendre transforms of the energy U . They arise naturally in statistical mechanics.



Figure 1: Adrien-Marie Legendre (1752 – 1833), French mathematician, (caricature by Boilly)

1. The Helmholtz Free Energy



Figure 2: Hermann von Helmholtz (1821-1894) German physicist and physician

This potential, denoted by F , is defined as:

$$F = U - TS \quad (1)$$

To calculate its differential form, I will use the first law of thermodynamics:

$$dU = TdS - pdV + \mu dN \quad (2)$$

Then:

$$dF = dU - TdS - SdT = TdS - pdV + \mu dN - TdS - SdT \quad (3)$$

or

$$dF = -SdT - pdV + \mu dN \quad (4)$$

Expressing the free energy F as a function of T, V, N is a fundamental equation.

$$F = F(T, V, N) \quad (5)$$

Derivatives of F are identified using (4):

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad (6)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \quad (7)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad (8)$$

We next write the Maxwell relations associated with F. They follow from the fact that second order mixed derivatives are invariant under change of the order of differentiation.

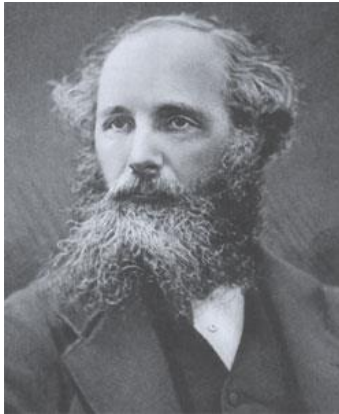


Figure 2: James Clerk Maxwell (1831 – 1879), Scottish physicist.

Using:

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \quad (9)$$

we get:

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N} \quad (10)$$

The other Maxwell relations associated with F are:

$$\left(\frac{\partial p}{\partial N}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N} \quad (11)$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{V,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} \quad (12)$$

2. Enthalpy

Enthalpy is denoted by H and is defined as:

$$H = U + pV \quad (13)$$

The differential of H is:

$$dH = dU + pdV + Vdp = TdS + Vdp + \mu dN \quad (14)$$

To get the last form of Eq. (14), I used the first law of thermodynamics, Eq. (2).

Using:

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p} \quad (15)$$

We get:

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \quad (16)$$

The other two Maxwell relations associated with the enthalpy are:

$$\left(\frac{\partial T}{\partial N}\right)_{p,S} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \quad (17)$$

$$\left(\frac{\partial \mu}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial N}\right)_{p,S} \quad (18)$$

3. Gibbs Potential

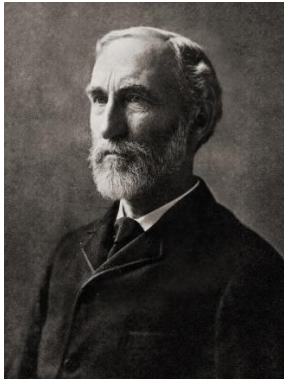


Figure 3: Josiah Willard Gibbs (1839 – 1903), American physicist, who developed statistical mechanics.

This potential is denoted by G.

$$G = U - TS + pV \quad (19)$$

Its differential is obtained using Eqs. (13) and (2):

$$dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp + \mu dN \quad (20)$$

The Maxwell relations associated with G are:

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} \quad (21)$$

$$\left(\frac{\partial V}{\partial N}\right)_{p,T} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} \quad (22)$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{p,T} \quad (23)$$

4. Thermodynamic Identities

I next sketch the derivation of a couple of thermodynamic identities:

(a) $C_p = C_v + \alpha^2 VT/k_T$ and (b) $k_T = k_S + \alpha^2 VT/C_p$

(a) Start with $S = S(T, V(T, p)) = S(T, p)$ and use Maxwell relation Eq.(10).

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \quad (24)$$

But: $\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$, so Eq. (24) becomes:

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V - \frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} \quad (25)$$

But:

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad (26)$$

$$C_v = T \left(\frac{\partial S}{\partial T}\right)_V \quad (27)$$

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (28)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad (29)$$

Using Eqs.(25) to (29) we find:

$$C_p = C_v + \alpha^2 VT/k_T \quad (30)$$

(b) Start with $V = V(p, S(p, T)) = V(p, T)$ and use Maxwell relation Eq.(16).

$$\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_S + \left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_S + \left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial S}{\partial p}\right)_T \quad (31)$$

But: $\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}$, so Eq. (31) becomes:

$$\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_S - \frac{\left(\frac{\partial S}{\partial p}\right)_T^2}{\left(\frac{\partial S}{\partial T}\right)_p} \quad (32)$$

Using the Maxwell relation Eq (21), Eq.(32) becomes:

$$\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{\partial V}{\partial p}\right)_S - \frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial S}{\partial T}\right)_p} \quad (33)$$

$$k_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S \quad (34)$$

Using Eqs.(26), (28), (29), (34) and (33) we find:

$$k_T = k_S + \alpha^2 VT/C_p \quad (35)$$

Application: Using the identities (a) and (b) show that: $C_p/C_v = k_T/k_S$

Treat the two identities, Eqs.(30) and (35) as a system of 2 equations with 2 unknowns: C_p and C_v . We find: $C_p = \alpha^2 VT/(k_T - k_S)$ and $C_v = (k_S/k_T)[\alpha^2 VT/(k_T - k_S)]$. It follows that:

$$C_p/C_v = k_T/k_S \quad (36)$$

Application: Check identities (30), (35), (36) for the ideal gas.

Use: $C_p = N[(i+2)/2]R$; $C_v = N[i/2]R$; $\alpha = 1/T$; $k_T = 1/p$; $k_S = [i/(i+2)]/p$.

B. Third Law of Thermodynamics

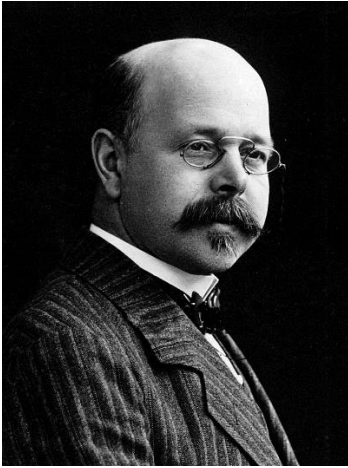


Figure 4 Walther Nernst (1864-1941), German chemist

The third law of thermodynamics, also known as Nernst postulate, states that at $T = 0\text{K}$ the entropy is zero $S = 0\text{J/K}$. This law is related to quantum mechanics. For instance blackbody radiation which is an intrinsically quantum mechanical system satisfies this law. As a consequence, the thermal expansion of any material is also zero at $T = 0\text{K}$. Indeed using Maxwell relation (21): $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left(\frac{\partial S}{\partial p} \right)_T$. Since $S = 0$ at $T = 0$, it follows $\alpha = 0$.

Reading

Callen Ch. 5; Ch.7, Ch.11

Problem Set 11;

Computer Lab 11.

Lecture Notes 12

1. Phase Transitions

Water under atmospheric pressure at 0°C undergoes a transition from a solid phase (ice) to a liquid phase. At 100°C and under atmospheric pressure water boils transitioning from the liquid phase to the gas phase. The classical explanation of a phase transition involves a violation of thermodynamic stability. We will study this topic by using the van der Waals equation of state and the Maxwell construction



Figure 1: Jaohannes Diderik van der Waals (1837-1923) Dutch physicist

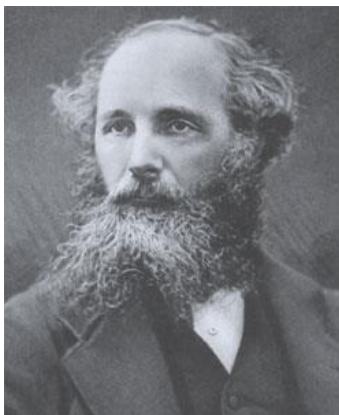


Figure 2: James Clerk Maxwell (1831 – 1879), Scottish physicist.

The van der Waals equation of state is:

$$(p + a/v^2)(v - b) = RT \quad (1)$$

The constants a and b depend on which chemical we study. The values for water are:

$a = 0.544 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 30.5 \cdot 10^{-6} \text{ m}^3/\text{mol}$.

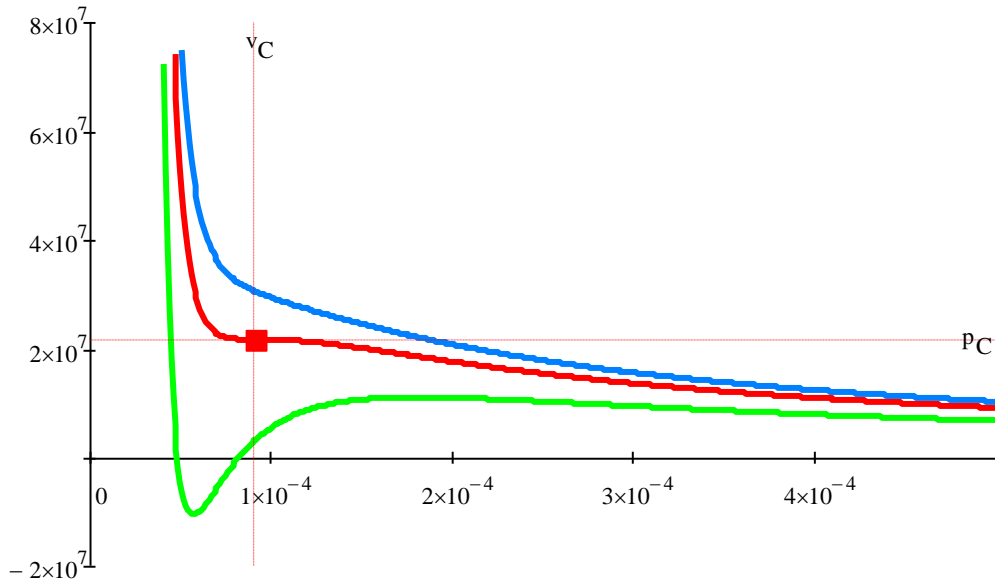


Figure 3: Water isotherms. Blue $T = 700\text{K}$, Green $T = 500\text{K}$, Red $T = 635.646\text{K}$ (critical isotherm). Red symbol critical point $p_C = 216.6 \cdot 10^5 \text{ Pa}$, $v_C = 0.0915 \cdot 10^{-3} \text{ m}^3/\text{mole}$. Pressure in Pa is on y axis; Molar volume in m^3/mole is on x axis.

High temperature isotherms, blue line in Figure 3, exhibit a monotonically decreasing pressure vs volume. This is what one expects. It is needed for thermodynamic stability: the isothermal compressibility is positive. $k_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T > 0$. However, on the low temperature isotherm (green line) the dependence is not monotonic. The system is unstable for a particular segment where the compressibility is negative. Maxwell interpreted this as the system separates in two phases, liquid and gas. The Maxwell construction is a horizontal segment chosen so that the two areas between the horizontal line and the $p(v)$ curve are equal. This is equivalent to the equality of the chemical potential in the liquid and gas phases. Indeed, since $d\mu = -sdT + vdp$, the equality of chemical potentials $\mu_L = \mu_G$ implies $\int v dp = 0$, or:

$$0 = \int_{v_L}^{v_G} v \frac{dp}{dv} dv = \int_{v_L}^{v_G} \left[\frac{dpv}{dv} - p \right] dv = \hat{p} (v_G - v_L) - \int_{v_L}^{v_G} p dv .$$

The first term is area of rectangle under p^{hat} between v_G and v_L and the second term is the area under the $p(v)$ curve between v_G and v_L . Thus, in Figure 4, the area I and are II are equal.

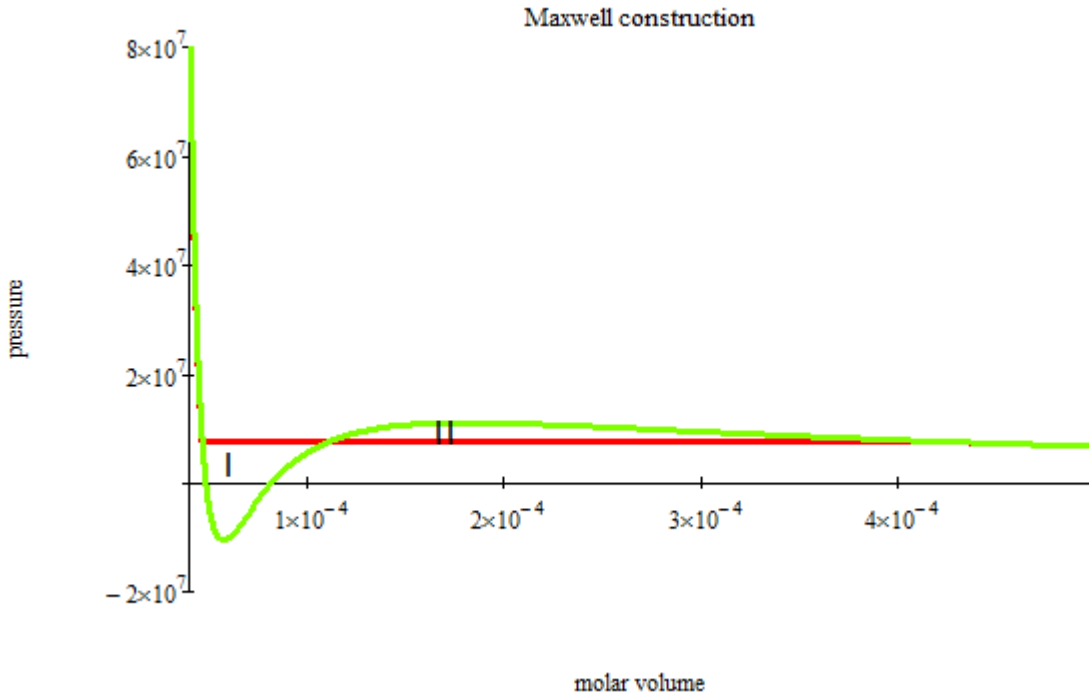


Figure 4: Maxwell construction: areas I and II are equal.

In between the high and low temperature isotherms is the critical isotherm, red line in Figure 3. The critical point is an inflexion point:

$$0 = \frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \quad (2)$$

$$0 = \frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \quad (3)$$

We solve Eqs (2) and (3) for temperature and volume. Then we substitute those values in the equation of state Eq (1) to calculate the pressure. We find:

$$v_c = 3b; RT_c = 8a/(27b); p_c = a/(27b^2). \quad (4)$$

In view of Eq. (2), at the critical point the isothermal compressibility is infinite: $k_T = \infty$.

We can rewrite the equation of state (1) by using dimensionless pressure, volume and temperature: $p^* = p/p_c; v^* = v/v_c; T^* = T/T_c$. We find:

$$(p^* + 3/v^{*2})(3v^* - 1) = 8T^* \quad (5)$$

Equation (5) expresses the law of corresponding states. The equation of state (5) written with the scaled quantities is universal, independent of chemistry.

Exercise: Calculate the critical point coordinates for water.

$a = 0.544 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 30.5 \cdot 10^{-6} \text{ m}^3/\text{mol}$. We find by substituting a, b in Eqs. (4):

$v_C = 9.15 \cdot 10^{-5} \text{ m}^3/\text{mole}$; $p_C = 216.6 \cdot 10^5 \text{ Pa}$; $T_C = 635.646 \text{ K}$.

We calculate the isothermal compressibility k_T from $p^* = 8T^*/(3v^* - 1) - 3/v^{*2}$

$$k_T = -\frac{1}{v^*} \left(\frac{\partial v^*}{\partial p^*} \right)_T = \frac{-1}{v^* \left(\frac{\partial p^*}{\partial v^*} \right)_T} = \frac{1}{6 \left(\frac{4T^* v^*}{(3v^* - 1)^2} - \frac{1}{v^{*2}} \right)} \quad (6)$$

We calculate the thermal expansion α from: $T^* = (1/8)(p^* + 3/v^{*2})(3v^* - 1)$.

$$\alpha = \frac{1}{v^*} \left(\frac{\partial v^*}{\partial T^*} \right)_{p^*} = \frac{1}{v^* \left(\frac{\partial T^*}{\partial v^*} \right)_{p^*}} = \frac{8}{3 \left(\frac{8T^* v^*}{3v^* - 1} - \frac{6}{v^*} + \frac{2}{v^{*2}} \right)} \quad (7)$$

Note at the critical point, $v^* = T^* = 1$, Eqs. (6) and (7) give infinite compressibility and thermal expansion: $k_T = \alpha = \infty$.

2. Clausius-Clapeyron Equation

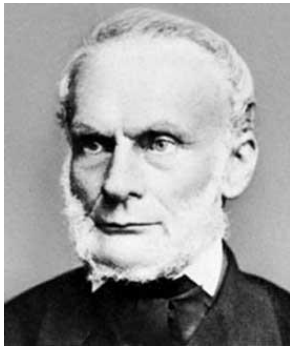


Figure 5: Rudolf Clausius (1822 – 1888), German physicist



Figure 6: Benoit Clapeyron (1799-1864), French physicist

The Clapeyron equation relates the slope of the coexistence curve $p = p(T)$ to the jumps in entropy and density at the coexistence line. For sake of being explicit, we will assume the two coexisting phases are a liquid and a gas phase. The second law, entropy maximization, implies the equality of the intensive variables in the coexisting phases:

$$\mu_G(p,T) = \mu_L(p,T) \quad (8)$$

Equation (8) determines the coexistence curve $p = p(T)$. Then we differentiate (8) with respect to T:

$$\left(\frac{\partial \mu_G}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial \mu_G}{\partial T}\right)_p = \left(\frac{\partial \mu_L}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial \mu_L}{\partial T}\right)_p \quad (9)$$

But the differential of the chemical potential, using the Gibbs-Duhem equation, is:

$d\mu = -sdT + vdp$. Hence equation (9) becomes:

$$v_G \frac{dp}{dT} - s_G = v_L \frac{dp}{dT} - s_L \quad (10)$$

Solving equation (10), we get the slope dp/dT :

$$\frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} \quad (11)$$

One defines the latent heat: $l = T(s_G - s_L)$. This heat is needed to be delivered to the liquid to boil into the gas, at fixed pressure and temperature.

$$\frac{dp}{dT} = \frac{l}{T(v_G - v_L)} \quad (12)$$

Equation (12) is the Clausius equation. A useful approximation of the Clausius equation, due to Clapeyron, is valid far from the critical point where $v_G \gg v_L$ and the gas can be treated as an ideal gas: $v_G = RT/p$. Equation (12) becomes:

$$\frac{dp}{dT} \cong \frac{l}{Tv_G} \cong \frac{lp}{RT^2} \quad (13)$$

Application: Compute the slope of the coexistence curve dp/dT for water in the following cases:

- (a) boiling under atmospheric pressure $T = 100^\circ\text{C}$, latent heat $l = 540\text{cal/g}$, $v_G = 1.6729\text{l/g}$, $v_L = 1.044 \cdot 10^{-3}\text{l/g}$; (b) freezing under atmospheric pressure $T = 0^\circ\text{C}$, latent heat $l = 80\text{cal/g}$, $v_S = 1.25\text{cm}^3/\text{g}$; $v_L = 1.0\text{cm}^3/\text{g}$.

We use Eq. (11).

(a) $dp/dT = (540 \cdot 4.184 \cdot 1000) / [373 \cdot (1.6729 - 0.001044)] = 3.6 \cdot 10^3 \text{Pa/K}$.

(b) $dp/dT = (80 \cdot 4.184 \cdot 1000) / [273 \cdot (0.001 - 0.00125)] = -4.9 \cdot 10^6 \text{Pa/K}$.

Note the slope of the melting line is negative and it is, in magnitude, much larger than the slope of the boiling line.

3. Gibbs Phase Rule

Here is generic phase diagram of a pure chemical substance. It includes the coexistence lines for liquid-gas (boiling), solid-liquid (melting) and solid-gas (sublimation). The intersection of the three coexistence line is the triple point. For water it occurs at $p = 0.00611 \cdot 10^5 \text{ Pa}$, $T = 273.16 \text{ K}$.

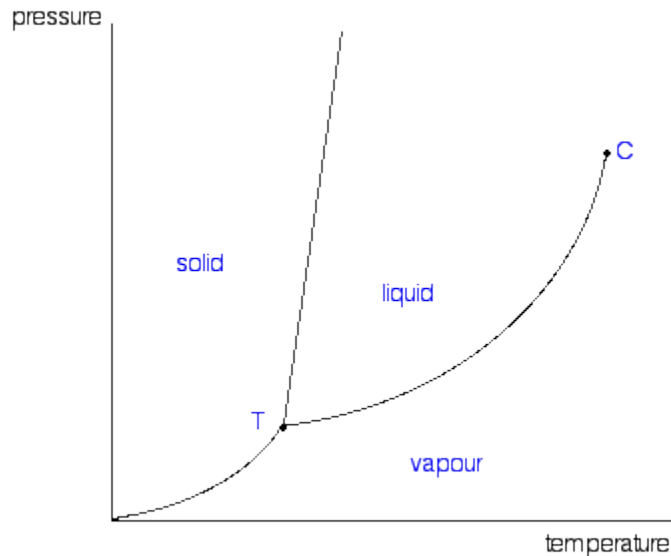


Figure 7: Generic phase diagram

At the triple point the chemical potentials of the 3 phases are equal: $\mu_s(T,p) = \mu_l(T,p) = \mu_g(T,p)$. Those are 2 equations with 2 un-knowns: T and p, the triple point coordinates.

Gibbs has generalized this to a mixture of c chemicals and coexisting in r phases. The fundamental equation $\mu_c = \mu_c(T, p, \mu_1, \dots, \mu_{c-1})$ The equality of the r values of the chemical potential $\mu_c, \mu_c^{(1)} = \mu_c^{(2)} = \dots = \mu_c^{(r)}$, results in r - 1 equations with c + 1 un-knowns. To have a solution the number of equations should be smaller or equal to the number of un-knowns: $r - 1 \leq c + 1$ or $r \leq c + 2$. This is the Gibbs phase rule. For a pure substance c = 1 and thus $r \leq 3$.

Reading

Callen Ch. 9;
Problem Set 12;
Computer Lab 10.

Lecture Notes 13

Overview of Thermodynamics

The first law, the energy conservation law, states that a change in the energy of the system equals the sum of the heat added to the system, the work done on the system and the chemical work done on the system: $\Delta U = Q + W + W_C$ Its differential form is:

$$dU = TdS - pdV + \mu dN \quad (1)$$

The heat capacities measure the heat needed to raise temperature by 1K.

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (2)$$

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (3)$$

The compressibility measures the fractional change in volume when we decrease pressure by one unit.

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (3)$$

$$k_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S \quad (4)$$

The thermal expansion measures the fractional change in volume when we raise isobarically the temperature by 1K.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (5)$$

The second law states that when a constrained is released the system evolves to a state of maximum entropy consistent with remaining constraints. The first consequence of the maximization of entropy is: in equilibrium the intensive variables, temperature, pressure, chemical potential, are uniform. Mathematically this is the result of setting the first derivative of entropy equal to zero.

The second consequence of the maximization process is that at equilibrium second derivatives of entropy are negative. This results in convexity properties of thermodynamic potentials. This is called thermodynamics stability. The entropy S is concave function of U, V, N . The energy $U(S, V, N)$ is convex function. The Helmholtz free energy $F(T, V, N)$ is concave function of T and is convex function V and N . The enthalpy $H(S, p, N)$ is concave function of p and convex

function of S, N. The Gibbs potential $G(T, p, N)$ is concave function of T and p and convex of N.

Here are some consequences.

$$0 \geq \left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} = \left(\frac{\partial \left(\frac{1}{T}\right)}{\partial U}\right)_{V,N} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_{V,N} = -\frac{1}{T^2 C_V} \quad (6)$$

Hence the isochoric heat capacity is positive.

$$0 \leq \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} = -\left(\frac{\partial p}{\partial V}\right)_{S,N} = \frac{1}{V k_S} \quad (7)$$

Hence the adiabatic compressibility is positive.

$$0 \geq \left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = -\left(\frac{\partial S}{\partial T}\right)_{p,N} = -\frac{C_p}{T} \quad (8)$$

Hence the isobaric heat capacity is positive.

We have proved the following thermodynamic identities:

$$C_p = C_v + \alpha^2 VT/k_T \quad (9)$$

$$k_T = k_S + \alpha^2 VT/C_p \quad (10)$$

Since $C_p \geq 0$ and $k_S \geq 0$ it follows, from Eq. (10), that the isothermal compressibility is positive: $k_T \geq 0$. Furthermore, from Eqs. (9), (10), we find:

$$C_p \geq C_v \geq 0 \quad (11)$$

$$k_T \geq k_S \geq 0 \quad (12)$$

$$|\alpha| \leq \sqrt{\frac{k_T C_p}{VT}} \quad (13)$$

The third law (Nernst postulate) states that at absolute zero the entropy is zero:

$$T = 0; S = 0 \quad (14)$$

The validity of this law is connected to quantum mechanics. Intrinsic quantum systems, such as the electromagnetic radiation, satisfy it.