# Thermodynamics

#### **1.** Temperature Scales:

(a) The ideal gas temperature is defined through the equation of state

$$\theta = \frac{PV}{Nk_B}$$

The thermodynamic temperature is defined for a reversible Carnot cycle by

$$\frac{T_{hot}}{T_{cold}} = \frac{Q_{hot}}{Q_{cold}}$$

For an ideal gas, the internal energy is a function only of  $\theta$ , i.e.  $E = E(\theta)$ , and

$$dQ = dE - dW = \frac{dE}{d\theta} \cdot d\theta + PdV.$$



Consider the Carnot cycle indicated in the figure. For the segment 1 to 2, which undergoes an isothermal expansion, we have

$$d\theta = 0, \implies dQ_{hot} = PdV, \text{ and } P = \frac{Nk_B\theta_{hot}}{V}.$$

Hence, the heat input of the cycle is related to the expansion factor by

$$Q_{hot} = \int_{V_1}^{V_2} Nk_B \theta_{hot} \frac{dV}{V} = Nk_B \theta_{hot} \ln\left(\frac{V_2}{V_1}\right).$$

A similar calculation along the low temperature isotherm yields

$$Q_{cold} = \int_{V_4}^{V_3} N k_B \theta_{cold} \frac{dV}{V} = N k_B \theta_{cold} \ln\left(\frac{V_3}{V_4}\right),$$

and thus

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}} \frac{\ln\left(V_2/V_1\right)}{\ln\left(V_3/V_4\right)}.$$

(b) Next, we calculate the volume expansion/compression ratios in the adiabatic processes. Along an adiabatic segment

$$dQ = 0, \implies 0 = \frac{dE}{d\theta} \cdot d\theta + \frac{Nk_B\theta}{V} \cdot dV, \implies \frac{dV}{V} = -\frac{1}{Nk_B\theta} \frac{dE}{d\theta} \cdot d\theta.$$

Integrating the above between the two temperatures, we obtain

$$\begin{cases} \ln\left(\frac{V_3}{V_2}\right) = -\frac{1}{Nk_B} \int_{\theta_{cold}}^{\theta_{hot}} \frac{1}{\theta} \frac{dE}{d\theta} \cdot d\theta, & \text{and} \\ \ln\left(\frac{V_4}{V_1}\right) = -\frac{1}{Nk_B} \int_{\theta_{cold}}^{\theta_{hot}} \frac{1}{\theta} \frac{dE}{d\theta} \cdot d\theta. \end{cases}$$

While we cannot explicitly evaluate the integral (since  $E(\theta)$  is arbitrary), we can nonetheless conclude that

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}.$$

(c) Combining the results of parts (a) and (b), we observe that

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}}.$$

Since the thermodynamic temperature scale is defined by

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}},$$

we conclude that  $\theta$  and T are proportional. If we further define  $\theta(\text{triple point}_{H_20}) = T(\text{triple point}_{H_20}) = 273.16$ ,  $\theta$  and T become identical.

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## **2.** Equations of State:

(a) Since there is only one form of work, we can choose any two parameters as independent variables. For example, selecting T and V, such that E = E(T, V), and S = S(T, V), we obtain

$$dE = TdS - PdV = T\frac{\partial S}{\partial T}\Big|_{V}dT + T\frac{\partial S}{\partial V}\Big|_{T}dV - PdV,$$

resulting in

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - P.$$

Using the Maxwell's relation  $^{\dagger}$ 

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

we obtain

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P.$$

Since  $T \frac{\partial P}{\partial T}\Big|_{V} = T \frac{Nk_B}{V} = P$ , for an ideal gas,  $\frac{\partial E}{\partial V}\Big|_{T} = 0$ .

Thus E depends only on T, i.e. E = E(T).

(b) If E = E(T),

$$\left. \frac{\partial E}{\partial V} \right|_T = 0, \quad \Longrightarrow \quad T \left. \frac{\partial P}{\partial T} \right|_V = P.$$

The solution for this equation is P = f(V)T, where f(V) is any function of only V. (c) The van der Waals equation of state is given by

$$\left[P - a\left(\frac{N}{V}\right)^2\right] \cdot (V - Nb) = Nk_BT,$$

or

$$P = \frac{Nk_BT}{(V - Nb)} + a\left(\frac{N}{V}\right)^2.$$

From these equations, we conclude that

$$C_V \equiv \left. \frac{\partial E}{\partial T} \right|_V, \quad \Longrightarrow \quad \left. \frac{\partial C_V}{\partial V} \right|_T = \left. \frac{\partial^2 E}{\partial V \partial T} = \frac{\partial}{\partial T} \left\{ T \left. \frac{\partial P}{\partial T} \right|_V - P \right\} = T \left. \frac{\partial^2 P}{\partial T^2} \right|_V = 0.$$

#### **3.** Clausius-Clapeyron Equation:

The Clausius-Clapeyron equation describes the variation of boiling temperature with pressure. It is usually derived from the condition that the chemical potentials of the gas and liquid phases are the same at coexistence, i.e.

$$\mu_{liquid}(P,T) = \mu_{gas}(P,T),$$

<sup>†</sup> 
$$dL = X dx + Y dy + \cdots, \implies \frac{\partial X}{\partial y}\Big|_{x} = \frac{\partial Y}{\partial x}\Big|_{y} = \frac{\partial^{2} L}{\partial x \cdot \partial y}.$$

and

$$\mu_{liquid}(P+dP,T+dT) = \mu_{gas}(P+dP,T+dT).$$

From these equations, we conclude that along the coexistence line

$$\frac{dP}{dT}\Big|_{\rm coX} = \frac{\frac{\partial\mu_g}{\partial T}\Big|_P - \frac{\partial\mu_l}{\partial T}\Big|_P}{\frac{\partial\mu_l}{\partial P}\Big|_T - \frac{\partial\mu_g}{\partial P}\Big|_T}.$$

The variations of the Gibbs free energy,  $G = N\mu(P,T)$  from the extensivity condition, are given by

$$V = \frac{\partial G}{\partial P}\Big|_{T}, \quad S = -\frac{\partial G}{\partial T}\Big|_{P}.$$

In terms of intensive quantities

$$v = \frac{V}{N} = \left. \frac{\partial \mu}{\partial P} \right|_T, \quad s = \frac{S}{N} = -\left. \frac{\partial \mu}{\partial T} \right|_P,$$

where s and v are molar entropy and volume, respectively. Thus, the coexistence line satisfies the condition

$$\left. \frac{dP}{dT} \right|_{\rm coX} = \frac{S_g - S_l}{V_g - V_l} = \frac{s_g - s_l}{v_g - v_l}.$$

(a) If we approximate the adiabatic processes as taking place at constant volume V (vertical lines in the P - V diagram), we find

$$W = \oint PdV = PV - (P - dP)V = VdP.$$



Here, we have neglected the volume of liquid state, which is much smaller than that of the gas state. As the error is of the order of

$$\left. \frac{\partial V}{\partial P} \right|_S dP \cdot dP = O(dP^2),$$

we have

$$W = VdP + O(dP^2).$$

The efficiency of any Carnot cycle is given by

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H},$$

and in the present case,

$$Q_H = L$$
,  $W = VdP$ ,  $T_H = T$ ,  $T_C = T - dT$ .

Substituting these values in the universal formula for efficiency, we obtain the Clausius-Clapeyron equation

$$\frac{VdP}{L} = \frac{dT}{T}$$
, or  $\frac{dP}{dT}\Big|_{coX} = \frac{L}{T \cdot V}$ .

(b) The statement "At the sink L(T - dT) is supplied to condense one mole of water" is incorrect. In the P - V diagram shown, the state at "1" corresponds to pure water, "2" corresponds to pure vapor, but the states "3" and "4" have two phases coexisting. In going from the state 3 to 4 less than one mole of steam is converted to water. Part of the steam has already been converted into water during the adiabatic expansion  $2 \rightarrow 3$ , and the remaining portion is converted in the adiabatic compression  $4 \rightarrow 1$ . Thus the actual latent heat should be less than the contribution by one mole of water.

(c) For an ideal gas

$$V = \frac{Nk_BT}{P}, \implies \left. \frac{dP}{dT} \right|_{coX} = \frac{LP}{Nk_BT^2}, \text{ or } \frac{dP}{P} = \frac{L}{Nk_BT^2}dT.$$

Integrating this equation, the boiling temperature is obtained as a function of the pressure P, as

$$P = C \cdot \exp\left(-\frac{L}{k_B T_{Boiling}}\right).$$

(d) For  $T_C = -120^{\circ}F = 189^{\circ}K$ , and  $T_H = 80^{\circ}F = 300^{\circ}K$ , the limiting efficiency, as that of a Carnot engine, is

$$\eta_{max} = \frac{T_H - T_C}{T_H} = 0.37.$$

The output power, equal to (input power) x (efficiency), is

Power output = 
$$\frac{90 \times 10^6 tons}{hr} \cdot \frac{1hr}{3600sec} \cdot \frac{1000kg}{ton} \cdot \frac{2.3 \times 10^6 J}{kg} \times 0.37 = 2 \times 10^{13} watts.$$

### **4.** *Glass:*

(a) Since in the present context we are considering only chemical work, we can regard entropy as a function of two independent variables, e.g. E, and N, which appear naturally from  $dS = dE/T - \mu dN/T$ . Since entropy is an extensive variable,  $\lambda S = S(\lambda E, \lambda N)$ . Differentiating this with respect to  $\lambda$  and evaluating the resulting expression at  $\lambda = 1$ , gives

$$S(E,N) = \left. \frac{\partial S}{\partial E} \right|_N E + \left. \frac{\partial S}{\partial N} \right|_E N = \frac{E}{T} - \frac{N\mu}{T},$$

leading to

$$\mu = \frac{E - TS}{N}.$$

(b) Finite temperature entropies can be obtained by integrating dQ/T, starting from S(T = 0) = 0. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_{crystal} = \alpha T^3 = \frac{T}{N} \frac{dS_{crystal}}{dT}, \implies S_{crystal} = \frac{N\alpha T^3}{3}, \\ C_{glass} = \beta T = \frac{T}{N} \frac{dS_{glass}}{dT}, \implies S_{glass} = \beta NT. \end{cases}$$

(c) Since  $dE = TdS + \mu dN$ , for dN = 0, we have

$$\begin{cases} dE = TdS = \alpha NT^3 dT \quad (crystal), \\ dE = TdS = \beta NTdT \quad (glass). \end{cases}$$

Integrating these expressions, starting with the same internal energy  $E_o$  at T = 0, yields

$$\begin{cases} E = E_o + \frac{\alpha N}{4} T^4 & (crystal), \\ E = E_o + \frac{\beta N}{2} T^2 & (glass). \end{cases}$$

(d) From the condition of chemical equilibrium between the two phases,  $\mu_{crystal} = \mu_{glass}$ , we obtain

$$\left(\frac{1}{3} - \frac{1}{4}\right) \cdot \alpha T^4 = \left(1 - \frac{1}{2}\right) \cdot \beta T^2, \quad \Longrightarrow \quad \frac{\alpha T^4}{12} = \frac{\beta T^2}{2},$$

resulting in a transition temperature

$$T_{melt} = \sqrt{\frac{6\beta}{\alpha}}.$$

(e) From the assumptions of the previous parts, we obtain the latent heats for the glass to crystal transition as

$$L = T_{melt} \left( S_{glass} - S_{crystal} \right) = NT_{melt} \left( \beta T_{melt} - \frac{\alpha T_{melt}^3}{3} \right)$$
$$= NT_{melt}^2 \left( \beta - \frac{\alpha T_{melt}^2}{3} \right) = NT_{melt}^2 (\beta - 2\beta) = -N\beta T_{melt}^2 < 0.$$

(f) The above result implies that the entropy of the crystal phase is larger than that of the glass phase. This is clearly unphysical, and one of the assumptions must be wrong. The questionable step is the assumption that the glass phase is subject to the third law of thermodynamics, and has zero entropy at T = 0. In fact, glass is a non-ergodic state of matter which does not have a unique ground state, and violates the third law.

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