

## 11/6 Lecture outline

- Recall,

$$\delta W_{mech} \leq |\delta W|_{max} = -d(U - T_0 S + P_0 V) \equiv -dA,$$

where we define

$$A(S, V) = U - T_0 S + P_0 V.$$

- Mention  $\delta W = \delta W_{mech} + P_0 dV$ , where  $\delta W_{mech}$  can also include other kinds of work,  $\delta W_{mech} = PdV + \mathcal{E}dq + \vec{B} \cdot d\vec{M} + \vec{E} \cdot dP + \mu dn + \dots$ . The above formula applies to **all** types of work, not just  $PdV$  work.

- Example: two identical blocks, with initial temperatures  $T_{1,i}$  and  $T_{2,i}$ . What is the maximum work that can be extracted? Solution: hook them up to a Carnot engine. Maximum work when everything is reversible. This means that the total entropy of the combined system of blocks, plus engine, should be constant. Since  $\Delta S_{engine} = 0$ , this means  $\Delta S_{total} = \Delta S_1 + \Delta S_2$  should be zero. Implies that  $T_1 T_2$  must be constant. Implies that  $T_{1,f} = T_{2,f} = \sqrt{T_{1,i} T_{2,i}}$ . The above formula, with  $S$  and  $V$  constant, implies  $\Delta W_{max} = -\Delta U = -(\Delta U_1 + \Delta U_2) = -C(2\sqrt{T_{1,i} T_{2,i}} - T_{1,i} - T_{2,i}) > 0$ .

- This illustrates a general kind of question that often comes up in thermodynamics. We start of being limited to consider equilibrium situations, because non-equilibrium processes are hard. But then broaden scope by consider bringing together two equilibrium subsystems, and study how the combined system reaches equilibrium. In general this happens such that

$$dA \leq 0, \quad \text{with } dA = 0 \quad \text{when equilibrium is restored.}$$

The above example had  $S$  constant and  $V$  constant, and so we get  $dU \leq 0$ , with  $dU = 0$  at equilibrium. In other words, for fixed  $S$  and  $V$ , the process reaches equilibrium when  $U$  is minimized.

We can instead impose  $U = U_1 + U_2$  fixed, with  $V = V_1 + V_2$  fixed, and then equilibrium is reached when  $S = S_1 + S_2$  is maximized.

- Connect to interpretation of other thermodynamic potentials,  $H = U + PV$ , and  $F = U - ST$ , and  $G = U + PV - ST$ . Suppose  $\Delta S = 0$  and  $P = P_0$ , then we get  $\Delta W_{mech} \leq -\Delta H$ . Or if  $T = T_0$  and  $\Delta V = 0$ , then  $\Delta W_{mech} \leq -\Delta F$ . Or if  $T = T_0$  and  $P = P_0$ , then  $\Delta W_{mech} \leq -\Delta G$ . Now Suppose no mechanical work,  $\delta W_{mech} = 0$ . Again,  $dA \leq 0$ . Processes occurring in the system tend to decrease  $A$ . It reaches its minimum at equilibrium. For fixed  $P_0 = P$  and  $T_0 = T$ , the process reaches equilibrium when  $G$

is a minimum. Likewise, for fixed  $T$  and  $V$ , the process reaches equilibrium when  $F$  is a minimum. Likewise, for fixed  $S$  and  $P$ , it reaches equilibrium when  $H$  is a minimum. For fixed  $S$  and  $V$ , the process reaches equilibrium when  $U$  is minimized. Equivalently, for fixed  $U$  and  $V$ , the process reaches equilibrium when  $S$  is maximized.

• Let's show in more detail that  $A$  decreases until it reaches its minimum, when the system is in equilibrium. Note that  $A$  is extremized if  $T = T_0$  and  $P = P_0$ :

$$\frac{\partial A}{\partial S} = \frac{\partial A}{\partial V} = 0 \quad \text{for} \quad T = T_0 \quad \text{and} \quad P = P_0.$$

To show that this extremum is a minimum of  $A$ , note that, expanding near  $T = T_0$  and  $P = P_0$ , and using  $T - T_0 = (\partial A / \partial S)_V$  and  $P - P_0 = -(\partial A / \partial V)_S$ , we get

$$A = A_0 + \frac{1}{2} \left( \frac{\partial T}{\partial S} \right)_V (\Delta S)^2 + \left( \frac{\partial T}{\partial V} \right)_S \Delta S \Delta V - \frac{1}{2} \left( \frac{\partial P}{\partial V} \right)_S (\Delta V)^2 + \dots$$

We see that  $A > A_0$  provided that

$$\left( \frac{\partial T}{\partial S} \right)_V > 0 \quad \text{which is equivalent to} \quad C_V > 0,$$

$$\left( \frac{\partial P}{\partial V} \right)_S < 0 \quad \text{which is equivalent to} \quad \kappa_S > 0,$$

$$\text{and} \quad \left( \frac{\partial T}{\partial V} \right)_S^2 < - \left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial P}{\partial V} \right)_S.$$

• Recall the  $P, T$  diagram of e.g.  $H_2O$ , with the solid, liquid, and gas phases. If we plot instead a  $P, V$  diagram, we see the phase changes as plateaus, along which  $V$  changes but  $T$  and  $P$  are constant. Because  $P$  and  $T$  are fixed, the useful quantity is  $G$ . The correct phase is the one which minimizes  $G$ . Consider phases 1 and 2, e.g. liquid and gas respectively. Convert an amount  $\delta n$  of the material from phase 1 to phase 2,  $\delta n_2 = -\delta n_1 = \delta n$ . Write  $G = n_1 g_1 + n_2 g_2$  (neglecting surface effects). Vary the parameters other than  $T$  and  $P$ ,

$$\delta G = -(g_1 - g_2) \delta n.$$

So the equilibrium phase boundary is when

$$g_1(T, P) = g_2(T, P).$$

Varying this, and using  $s = -(\partial g / \partial T)_V$  and  $v = (\partial g / \partial p)_T$ , we get

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP.$$

Write this as

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\ell}{T\delta v},$$

where  $\ell$  is the (specific) latent heat. This is called the “Clausius-Clapeyron” equation.

- Example: suppose  $v_2 \gg v_1$ , and  $Pv_2 = RT$ , then the above equation becomes

$$\frac{dP}{P} = \frac{\ell dT}{RT^2},$$

which integrates to  $P = P_0 \exp(-\ell/RT)$ . This is the vapor pressure, which rapidly increases with  $T$ .

- Next time: the above is a segue into discussing open systems, and chemical potential