

## Thermodynamics – Lecture 8 Recap

- To be introduced to the thermodynamic potentials,  $U, H, F, G$ .
- To be introduced to the Maxwell Relations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p ; \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V ; \left(\frac{\partial T}{\partial V}\right) = -\left(\frac{\partial p}{\partial S}\right)_V ; \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

- To see the  $TdS$  and Energy equations;

$$S=S(V,T) \quad TdS = C_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV ; \quad TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_p dp;$$

$$dU = Tds - pdv \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p ; \quad \left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T$$

## Thermodynamics – Lecture 9 Aims

- To see how problems in thermodynamics can be solved.
- To look at some applications of entropy.
- To be introduced to the concept of Available Energy.
- To see how entropy change tells us about process irreversibility.

### Solve Problem

- 1) Write down appropriate potential
- 2) Substitute for Maxwell Relations
- 3) Apply Calculus [Reiprocal + Reciprocity]
- 4) Identified generalised quantities [Heat capacity, expansivity, ...]
- 5) Substitute for the equation of state + its derivatives
- 6) Separate variables (+ integrate)

Example 14.5 Calculate the isothermal heat transfer to a van der Waals gas

$$\delta Q = T ds \quad TdS = C_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$$

Equation of state is  $(V-b)(p + a/V^2) = RT$   
 Isothermal  $dT=0$   $T_0 ds = T_0 \left(\frac{\partial p}{\partial T}\right)_V dV$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\Delta Q = \int_{V_1}^{V_2} \frac{T_0 R}{V-b} dV = T_0 R \ln \left( \frac{V_2-b}{V_1-b} \right)$$

# Thermodynamics – Handout 8

Example 14.2, Show the Second Maxwell Relation

Comes from the Helmholtz function,  $F = U - TS$ .

Total derivative

$$dU = TdS - pdV$$

$$dF = dU - TdS - SdT$$

Chain rule

$$dF = -SdT - pdV. *$$

Have  $F = F(T, V)$

Other total differential

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

Compare terms  
\* and \*\*

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

Helmholtz is a function of state, so exact differential,

Order of 2nd derivatives  
doesn't matter

$$\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right)$$

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

Example 14.4: Relationship between Heat Capacities

$$TdS = C_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$$

$TdS$  ①

$$TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_p dp$$

$TdS$  ②

$TdS$  ② -  $TdS$  ①

$$(C_P - C_V) dT = T \left[ \left(\frac{\partial p}{\partial T}\right)_V dV + \left(\frac{\partial V}{\partial T}\right)_p dp \right].$$

Temperature is a function of state,  $T = T(p, V)$

Two independent variables

Total differential

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp.$$

Equate coefficients of either  $dV$  or  $dp$ ,

Compare + equate  
dp coefficients

$$\frac{T}{C_p - C_v} \left( \frac{\partial V}{\partial T} \right)_p \equiv \left( \frac{\partial T}{\partial p} \right)_v$$

$$\times \left( \frac{\partial p}{\partial T} \right)_v$$

Reciprocal  
theorem

$$C_p - C_v = T \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial p}{\partial T} \right)_v$$

Reciprocity theorem

$$\left( \frac{\partial p}{\partial T} \right)_v = - \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \Rightarrow C_p - C_v = -T \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p^2$$

Compressibility,  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$ , and expansivity,  $\beta_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ ,

$$C_p - C_v = \frac{-T(V\beta_p)^2}{\kappa_T V}$$

$$C_p - C_v = \frac{T\beta_p^2 V}{\kappa_T}$$

$\kappa_T > 0$  and  $\beta_p^2$  so RHS  $> 0$   $C_p > C_v$

$T \rightarrow 0$   $C_p \rightarrow C_v$

Note no internal energy dependence

Example 14.6: What does the first energy equation tell us about an ideal gas?

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

$$pV = RT$$

$$\left( \frac{\partial p}{\partial T} \right)_v = \frac{R}{V}$$

Required derivative

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

$U$  doesn't depend on volume!

$$\left( \frac{\partial u}{\partial v} \right)_T = 0$$

$$u = u(x, y)$$

$$x, y \neq V$$



## 15 Entropy Applications

Entropy is a measure of energy quality. 'Lower' entropy corresponds to higher energy quality [Higher temperature + more work potential]

Kelvin Statement - most important of an engine is the cold reservoir.

Add to heat cold reservoir (constant temperature), a large positive entropy change results

Real engines do less work than reversible ones, energy is turned to 'waste' heat and it is added to the cold environment, increases the environment entropy.

Entropy is irreversible change  $\Rightarrow$  less work possible.

Can Compare to Carnot cycle (totally reversible)

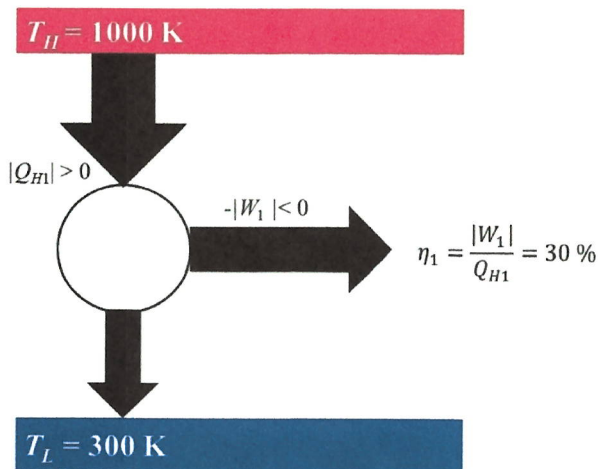
$$\eta_{rev} = \frac{\text{Best Work}}{\text{Heat in}} \quad ; \quad \eta_{engine} = \frac{\text{Work}}{\text{Heat in}}$$
$$= 1 - \frac{T_L}{T_H} \quad = 1 - \frac{|Q_L|}{Q_H}$$

and Law effectiveness  $\eta_{and} = \frac{\eta_{engine}}{\eta_{rev}} \leq 1$

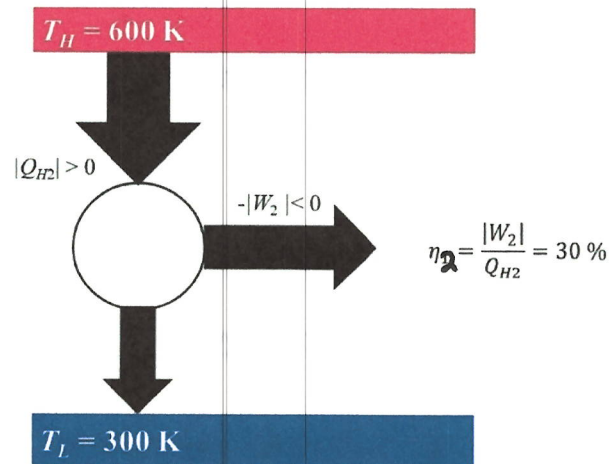
An environment change (+ve) reduces internal energy that can be used for work.

Thermodynamics – Handout 9

Example 15.1



Engine 1, with efficiency 30 %, takes in heat from 1000 K and rejects to environment (300 K).



Engine 2, also with efficiency 30 %, takes in heat from 600 K and rejects to environment (300 K)

If engines were Carnot cycles — *efficiency with temperature*

$$\eta_{\text{rev1}} = 1 - \left( \frac{300}{1000} \right) = 70 \% \quad ; \quad \eta_{\text{rev2}} = 1 - \left( \frac{300}{600} \right) = 50 \%$$

*Reversible engines have different efficiency  
Engine 1 has a greater work potential*

The second law efficiencies are then

$$\eta_{\text{2nd1}} = \frac{30}{70} = 0.43 \quad ; \quad \eta_{\text{2nd2}} = \frac{30}{50} = 0.60.$$

*↑  
Performing badly*

## 16. Availability + Available Energy

What is the most work we can theoretically obtain?  
Process takes system to a 'dead state' - in thermal equilibrium with the environment.

Availability  $A = U + p_0 V - T_0 S$

Work against the environment:  $p_0 V$

environment entropy change:  $T_0 S$

$$dA = dU + p_0 dV - T_0 dS$$

$$= (U_F - U_I) + p_0 (V_F - V_I) - T_0 (S_F - S_I)$$

A system taking infinitesimal amount of heat from surroundings,  $\delta Q$

$$dS_{\text{surround}} = -\frac{\delta Q}{T_0} \quad [\text{Heat left surroundings}]$$

$$\Delta S_u = dS_{\text{system}} + dS_{\text{surround}} = dS_{\text{system}} - \frac{\delta Q}{T_0} \geq 0$$

Must have energy conservation ( $dU = \delta Q + \delta W$ )

Work  $\delta W = \delta W_{\text{system}} - p_0 dV$

Useful work:  $\delta W_{\text{system}}$

Work against environment:  $p_0 dV$

$$\begin{aligned} \delta W_{\text{system}} &= dU - \delta Q + p_0 dV \\ &\geq dU - T_0 dS_{\text{system}} + p_0 dV \end{aligned}$$

$$\delta W_{\text{system}} \geq dA$$

Availability change provides energy for work



A mechanically isolated system  $\delta W_{\text{system}} = 0$

$$\therefore dA = A_{\text{final}} - A_{\text{initial}} \leq \delta W_{\text{system}} = 0$$

Availability of energy decreases (spontaneously). All processes force  $A$  to a minimum.

Once  $A$  is a minimum at equilibrium, no more work can be obtained.

- Thermally isolated at fixed volume.

$$dA = dU + p_0 dV - T_0 dS$$

$$dU = 0, dV = 0$$

$$dA = -T_0 dS. \quad \text{Maximise entropy for equilibrium}$$

- Constant temp + fixed volume

$$dA = dU - T_0 dS$$

$$dF = d(U - T_0 S) \quad \text{at constant } T$$
$$= dU - T_0 dS$$

$$dA = dF \leq 0$$

Minimise  $F$  for equilibrium

- Constant pressure + temp, Minimise  $G$  for equilibrium.

$dG, dF$  are  $> 0$ , process not spontaneous + must supply energy to make it happen.