CRYOGENIC ENGINEERING

Prof. Milind D. Atrey

Department of Mechanical Engineering,
IIT Bombay

Lecture No - 9

Earlier Lecture

- Basics of Refrigeration/Liquefaction, coefficient of performance and importance of Carnot COP.
- Throttling, heat exchanger, compression/expansion systems. Definition of a refrigerator, liquefier and a combination of these two systems.
- J – T expansion is an isenthalpic process and initial temperature of the gas should be less than **T_{INV}** to have a cooling effect.
- For an ideal gas $\left(\frac{\partial T}{\partial p}\right)_h = 0$. Hence, $\mu_{JT} = 0$.

Outline of the Lecture

Topic : Gas Liquefaction and Refrigeration Systems (contd)

- J – T expansion of a real gas
- Adiabatic expansion
- Comparison of J – T and Adiabatic expansions
- Ideal Thermodynamic Cycle

Introduction

- We know that work input is needed to generate and maintain low temperatures.
- As T_L decreases, Carnot COP decreases stating that more work input is required to maintain very low temperatures.
- Hence, a knowledge of performance of various refrigeration/liquefaction cycles is necessary to design the system with maximum COP.

Joule – Thompson Coefficient

- Enthalpy (h) is the sum of the internal energy (u) and pv work.

$$h = u + pv$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_p \left(\frac{\partial h}{\partial p}\right)_T$$

- Substitution of Enthalpy (h) in above expression of J – T coefficient, we get

$$\mu_{JT} = -\frac{1}{c_p}\left[\left(\frac{\partial u}{\partial p}\right)_T + \left(\frac{\partial (pv)}{\partial p}\right)_T\right]$$

- In order that the J – T expansion results in cooling, the bracket should be negative.

Joule – Thompson Coefficient

$$\mu_{JT} = -\frac{1}{c_p}\left[\boxed{\left(\frac{\partial u}{\partial p}\right)_T} + \left(\frac{\partial (pv)}{\partial p}\right)_T\right]$$

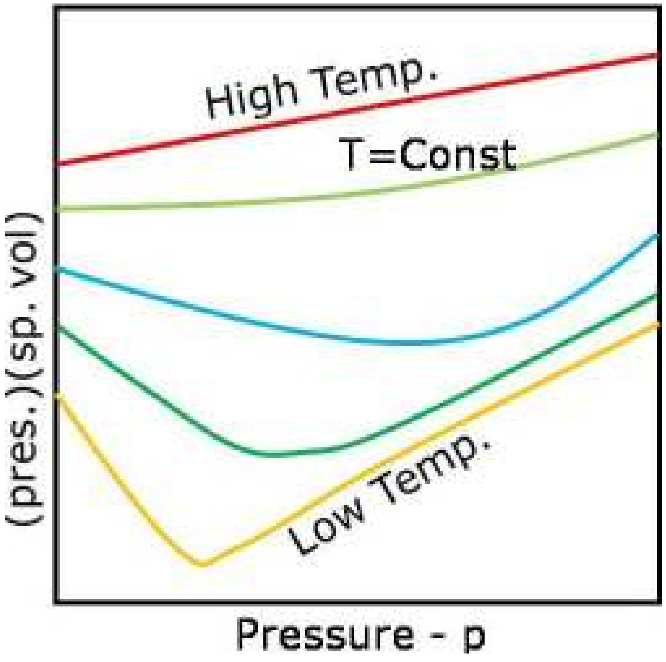
- The first term represents the departure from Joule’s law.

- At low pressures, the molecules are pulled apart. This results in increase in the potential energy. As a result, the kinetic energy decreases to keep the total energy constant and hence the temperature.

- Therefore, the first term is always negative for a real gas.

Joule – Thompson Coefficient

$$\mu_{JT} = -\frac{1}{c_p}\left[\left(\frac{\partial u}{\partial p}\right)_T + \boxed{\left(\frac{\partial (pv)}{\partial p}\right)_T}\right]$$

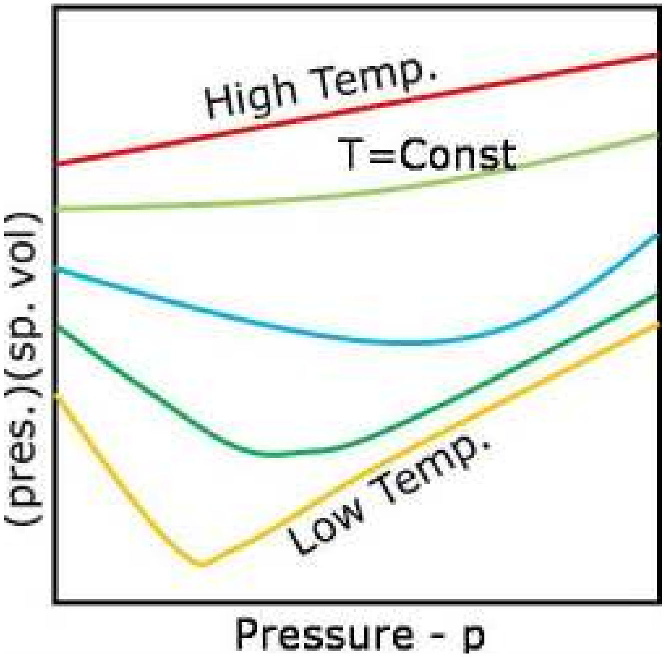


- The second term can either be positive, negative or zero. It represents the departure from the Boyle's law.

- At high pressures, the molecules are squeezed together and hence, are less compressible than the Boyle's law prediction.

Joule – Thompson Coefficient

$$\mu_{JT} = -\frac{1}{c_p}\left[\boxed{\left(\frac{\partial u}{\partial p}\right)_T} + \boxed{\left(\frac{\partial (pv)}{\partial p}\right)_T}\right]$$



- The second term is negative at low pressures and low temperatures, where the gases are more compressible than the Boyle’s law.
- For a real gas, J – T coefficient depends upon the relative magnitude of both the terms.

Equation of State

- van der Waals equation of state for a real gas is as given below.

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

- where, **a** and **b** are constants, which gives the measure of intermolecular forces and size of the particles respectively. For an ideal gas both **a** and **b** are 0.

- Rearranging the terms, we get

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

Equation of State

- Upon differentiating the following equation at constant pressure (only T and v are variables), we get

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

$$0=\frac{R}{(v-b)}\left(\frac{\partial T}{\partial v}\right)_p-\frac{RT}{(v-b)^2}+\frac{2a}{v^3}$$

- Rearranging the terms, we have

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{\dfrac{R}{(v-b)}}{\dfrac{RT}{(v-b)^2}-\dfrac{2a}{v^3}}$$

Equation of State

- Substituting $\left(\frac{\partial v}{\partial T}\right)_p$ in the J – T Coefficient equation, we have

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{\dfrac{R}{(v-b)}}{\dfrac{RT}{(v-b)^2} - \dfrac{2a}{v^3}}$$

$$\mu_{JT} = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

- For real gas, we get

$$\mu_{JT} = \frac{\dfrac{2a}{RT}\left(1-\dfrac{b}{v}\right)^2 - b}{c_p\left[\left(1-\dfrac{2a}{vRT}\right)\left(1-\dfrac{b}{v}\right)^2\right]}$$

- For large specific volumes

$$v >>> a, b$$

$$\therefore \mu_{JT} = \frac{1}{c_p}\left(\frac{2a}{RT} - b\right)$$

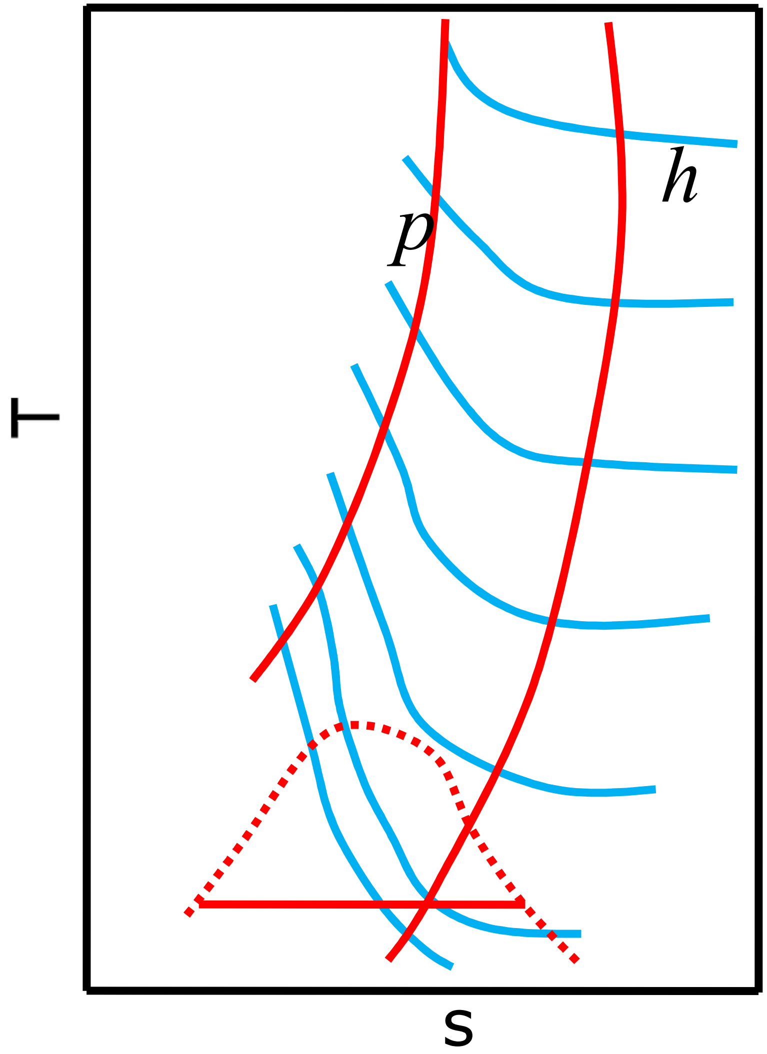
Joule – Thompson Coefficient

- For a real gas with large specific volumes

$$\mu_{JT} = \frac{1}{c_p}\left(\frac{2a}{RT} - b\right)$$

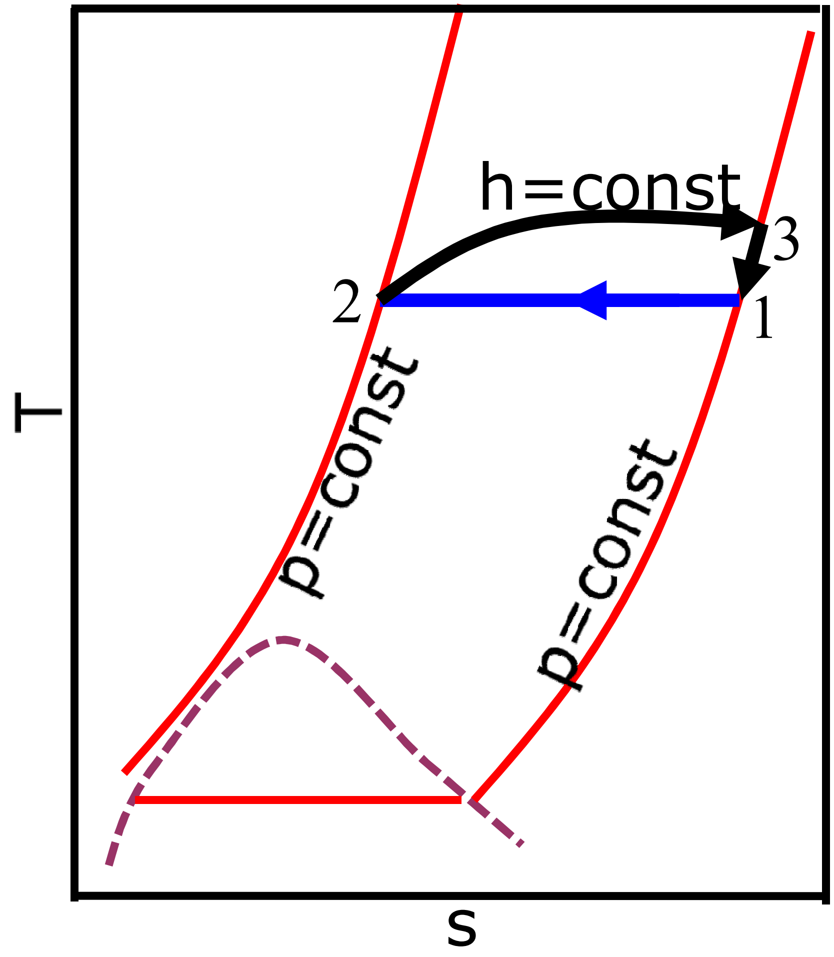
μ_{JT}	**Cond.**	**T**
>0	$\left(\frac{2a}{RT} - b\right) > 0$	$T < \frac{2a}{Rb}$
<0	$\left(\frac{2a}{RT} - b\right) < 0$	$T > \frac{2a}{Rb}$
=0	$\left(\frac{2a}{RT} - b\right) = 0$	$T = \frac{2a}{Rb}$
	$a = b = 0$	**Ideal**

Isenthalpic lines on T – s Chart



- Typical isenthalpic lines are as shown in T – s diagram.
- The drop in temperature obtained after isenthalpic expansion at lower temperatures is very high.
- This is because the gases are imperfect at very low temperatures.

Maximum Inversion Temp.



- The figure shows the J – T expansion on a T – s diagram.
- When the fluid expands from state 2 to state 3, the temperature rises.
- This occurs because the initial temperature at state 2 is above the inversion temperature.

Maximum Inversion Temp.

Gas	T_{inv} (K)
Helium	45
Hydrogen	205
Neon	250
Nitrogen	621
Air	603
Argon	794
Oxygen	761
Methane	939

- For the gases like He, Hydrogen and Neon, in order to experience J – T effect, they have to be precooled below $\mathbf{T_{INV}}$.
- While the other gases show J – T cooling when expanded at room temperature.

Isentropic Expansion

- Enthalpy (h) and Entropy (s) are the two thermodynamic state properties of matter which are functions of pressure and temperature.

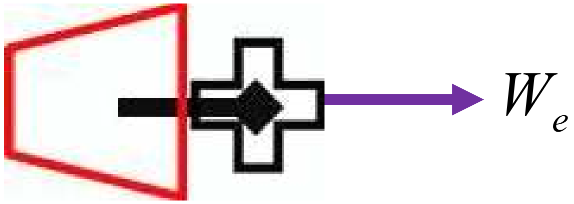
- When the gases are expanded at constant enthalpy, as in a J – T expansion, it is called as an Isenthalpic expansion.

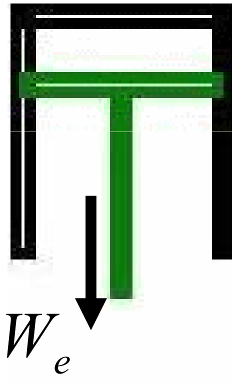
- On the similar lines, when the high pressure gases are expanded at constant entropy, it is called as an Isentropic expansion or a Reversible Adiabatic expansion.

Isentropic Expansion

- The commonly used expansion devices are turbo expanders and reciprocating expanders.

- This is a work producing process as shown in the schematics.





- The ratio $\left(\frac{\partial T}{\partial p}\right)_s$ is called as an Isentropic Expansion Coefficient.

Isentropic Expansion

- The enthalpy (s) is a function of both pressure (p) and temperature (T).

$$s = f\,(p, T)$$

- Using the calculus, the following can be derived.

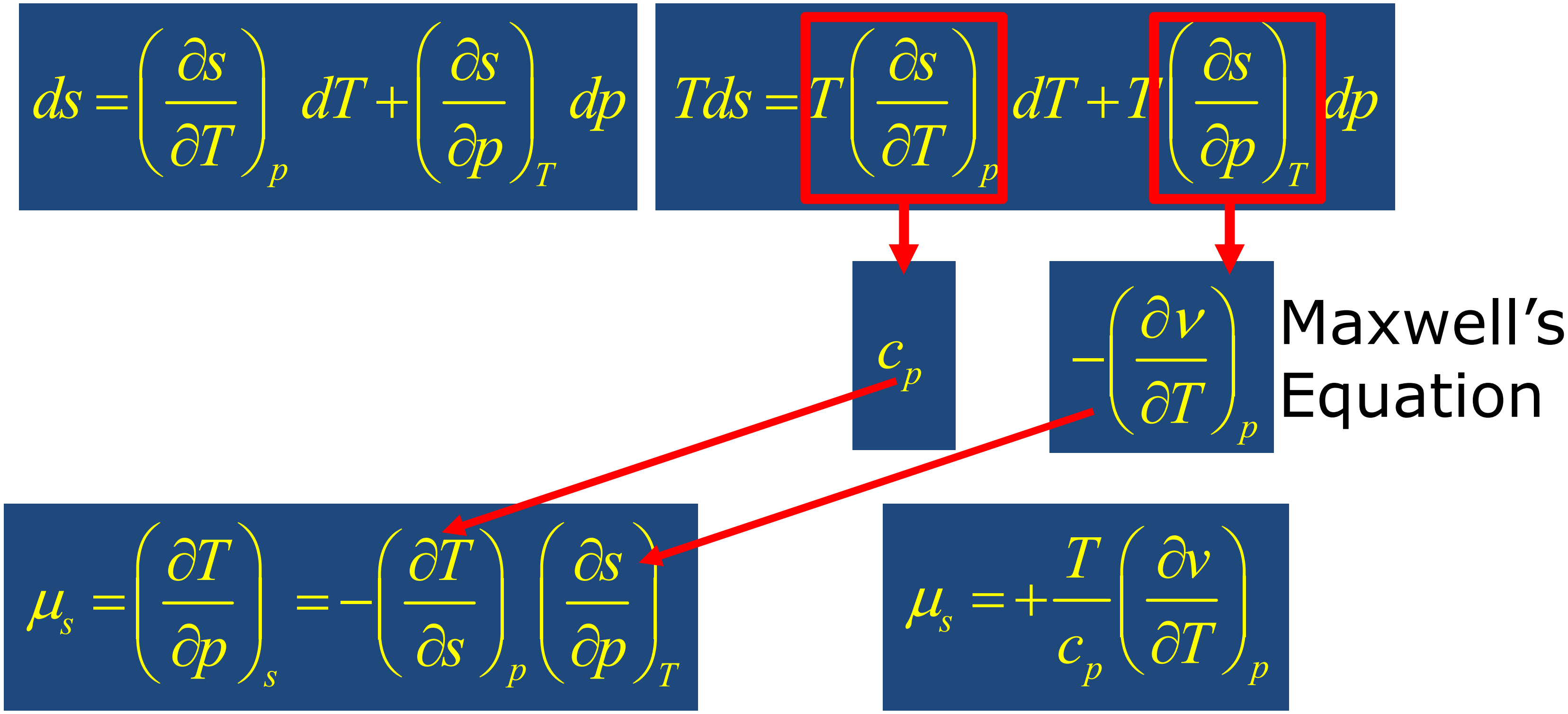
$$\left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial T}{\partial s}\right)_p = -1$$

- Rearranging the terms, we have

$$\mu_s = \left(\frac{\partial T}{\partial p}\right)_s = -\left(\frac{\partial T}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T$$

Isentropic Expansion

- For the same variables, entropy (s), temperature (T) and pressure (p), using the calculus, we can arrive at the following.



$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$Tds = \boxed{T\left(\frac{\partial s}{\partial T}\right)_p} dT + T\boxed{\left(\frac{\partial s}{\partial p}\right)_T} dp$$

$$c_p$$

$$-\left(\frac{\partial v}{\partial T}\right)_p$$

Maxwell's Equation

$$\mu_s = \left(\frac{\partial T}{\partial p}\right)_s = -\left(\frac{\partial T}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T$$

$$\mu_s = +\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p$$

Isentropic Expansion

- For an ideal gas, the equation of state is

$$v = \frac{RT}{p}$$

- Differentiating w.r.t **T** at constant **p**, we get

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

- On substitution, we get

$$\mu_s = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p = \frac{\cancel{T}}{c_p}\left(\frac{v}{\cancel{T}}\right) = \frac{v}{c_p}$$

- For an ideal gas $\mu_s \neq 0$, unlike the case in the J – T expansion $\mu_{JT} = 0$. It means that the ideal gas does exhibit a cooling effect, when it undergoes an isentropic expansion.

Isentropic Expansion

$$\mu_s = +\frac{T}{c_p}\boxed{\left(\frac{\partial v}{\partial T}\right)_p}$$

- The derivative term represents the variation of volume with temperature at constant pressure.
- This term is called as the volumetric coefficient and is always positive and hence the isentropic expansion coefficient.
- It is clear that the isentropic expansion results in cooling irrespective of its initial state, unlike the J – T expansion.

Equation of State

- As derived in the earlier slide, differentiating the van der Waals equation, we get

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{\dfrac{RT}{(v-b)}}{\dfrac{RT}{(v-b)^2} - \dfrac{2a}{v^3}}$$

- Substituting in μ_s, we get

$$\mu_s = \frac{v\left(1-\dfrac{b}{v}\right)}{c_p\left[\left(1-\dfrac{2a}{vRT}\right)\left(1-\dfrac{b}{v}\right)^2\right]}$$

Equation of State

- For real gas

$$\mu_s = \frac{v\left(1-\frac{b}{v}\right)}{c_p\left[\left(1-\frac{2a}{vRT}\right)\left(1-\frac{b}{v}\right)^2\right]}$$

- For large specific volumes

$$v >>> a,b$$

$$\therefore \mu_{JT} = \frac{v}{c_p}$$

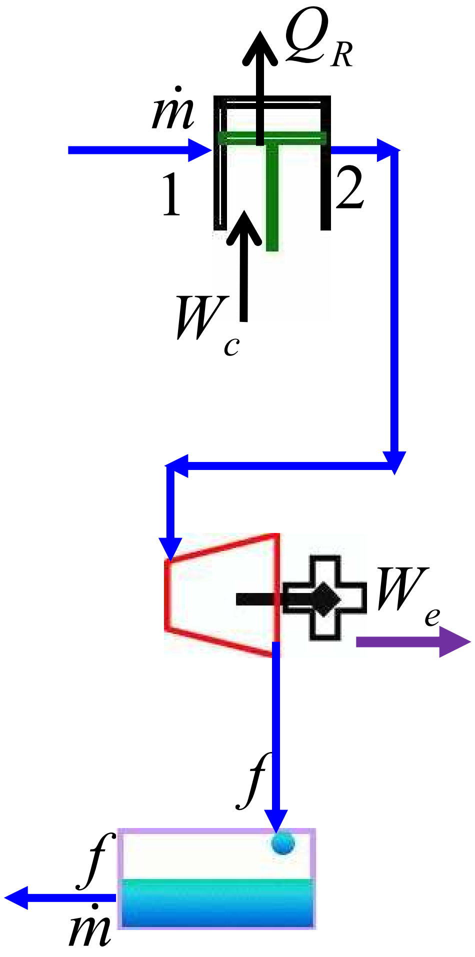
Comparative Study

J – T Expansion	Adiabatic Expansion
It has a condition of T_{INV}.	No such condition exists.
It produces no work. This is an Internal Work process.	It produces work. This is an External Work process.
The device is simple in construction.	The device involve complex mechanisms.
Normally used for a phase change of fluids.	Normally used for a single phase fluids.
The clogging of constriction is a disadvantage.	Regular maintenance and periodic checks are required.

Gas Liquefaction Systems

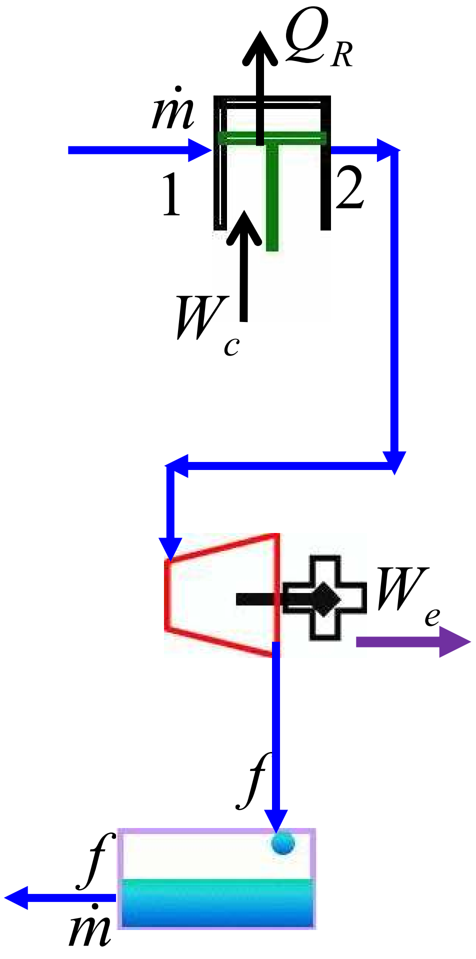
System
Thermodynamically Ideal System
Linde Hampson System
Precooled Linde Hampson System
Linde Dual Pressure System
Claude System
Kapitza System
Heylandt System
Collins System

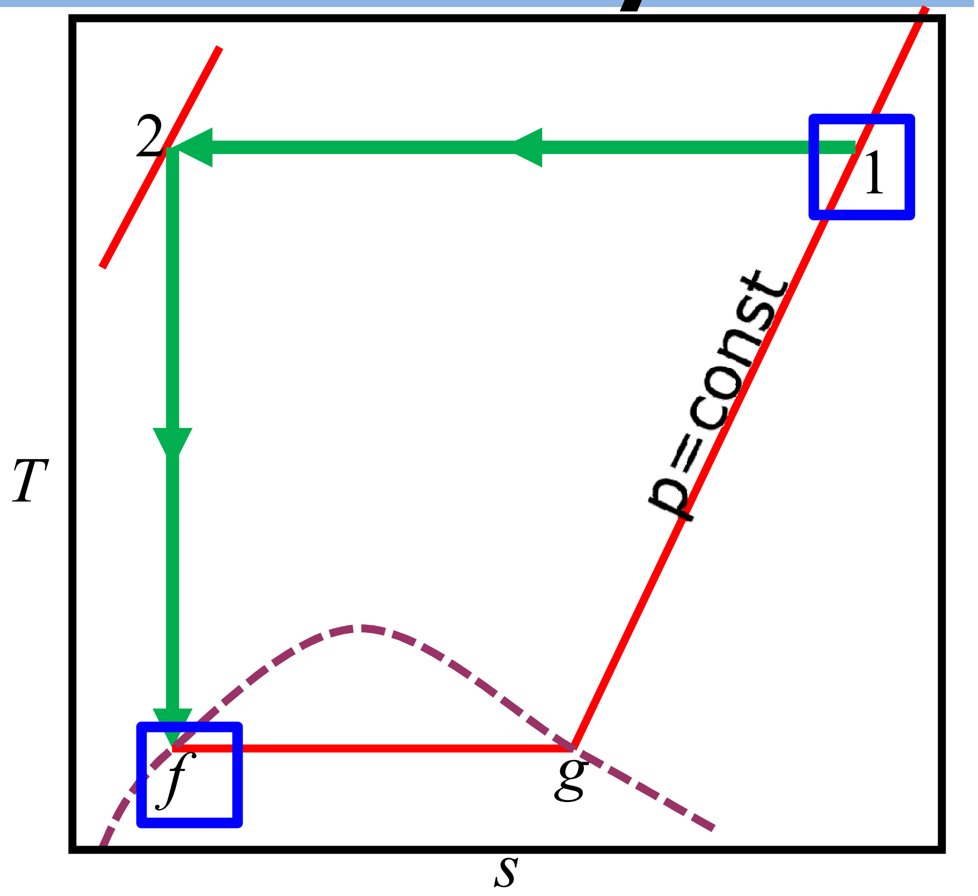
Thermodynamic Ideal System



- The salient features of this system are as follows.
- All the gas that is compressed, gets liquefied.
- All the processes are ideal in nature and there are no irreversible pressure drops.
- Process of compression and expansion are isothermal and isentropic respectively.

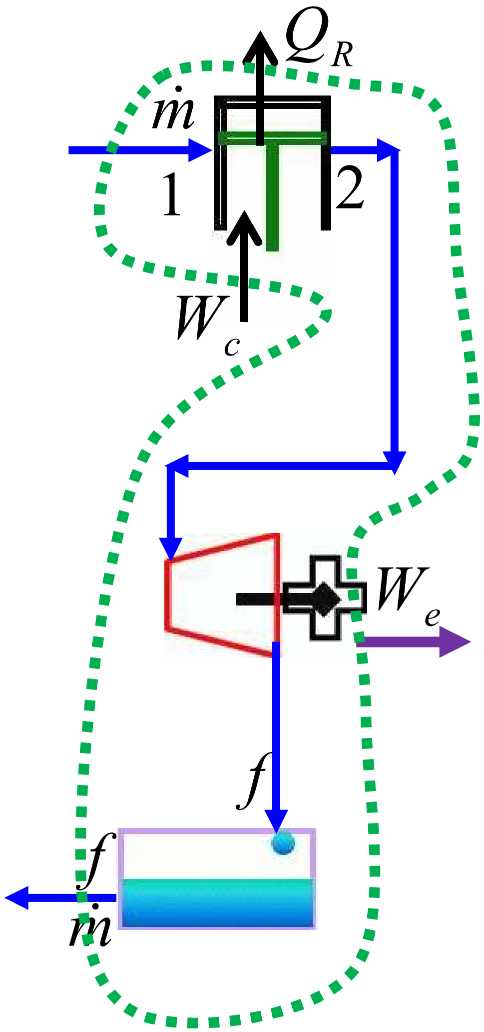
Thermodynamic Ideal System





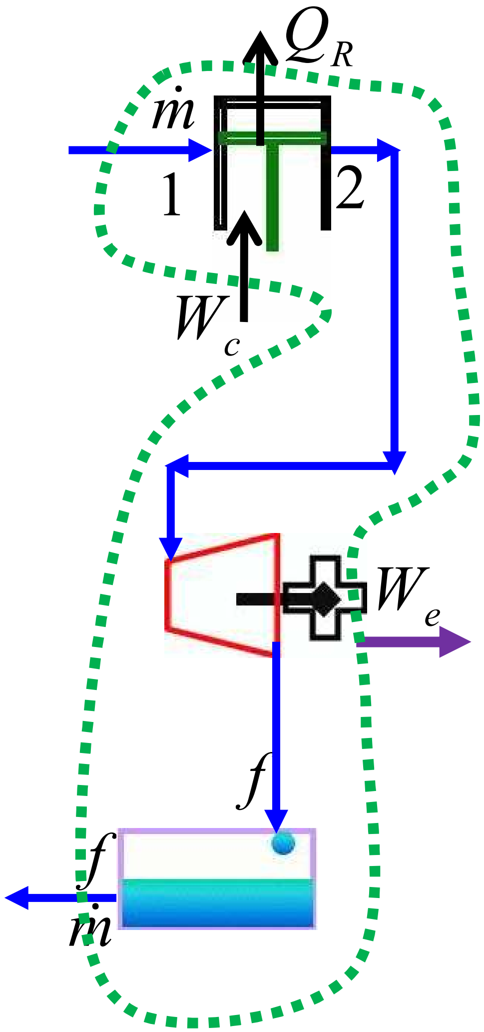
- The initial condition **1** of the gas determines the position of point **f**.

Thermodynamic Ideal System



- It is an open thermodynamic system because the working fluid flows across the system.
- Consider a control volume for this system as shown in the figure.
- 1^{st} Law of Thermodynamics is applied to analyse the system.
- The changes in the velocities and datum levels are assumed to be negligible.

Thermodynamic Ideal System



- The quantities entering and leaving the system are as given below.

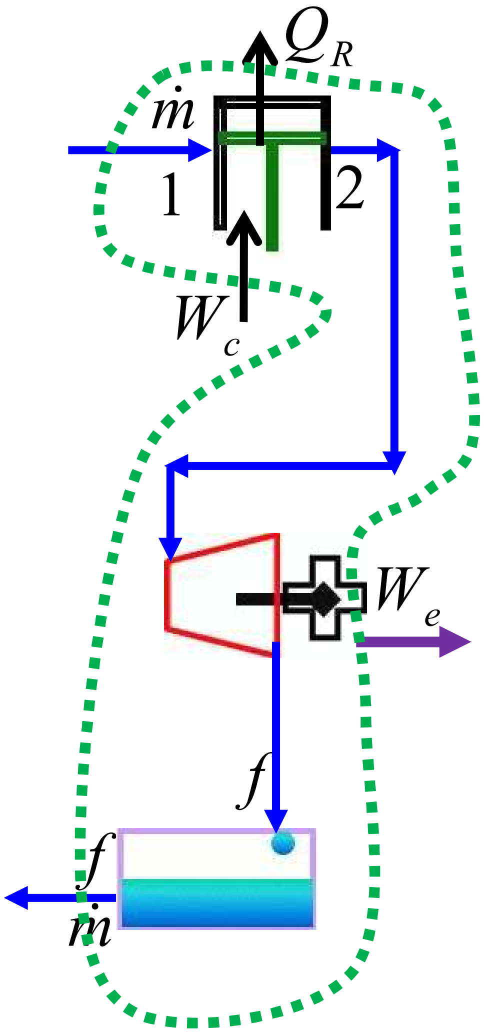
IN	OUT
m_1 @ 1	Q_R
W_c	W_e
	m_1 @ f

- Using 1st Law , we get

$$E_{in} = E_{out}$$

$$\dot{m}_1 h_1 + W_c = Q_R + W_e + \dot{m}_f h_f$$

Thermodynamic Ideal System



- The work W_e produced by the expander is negligible as compared to other terms.

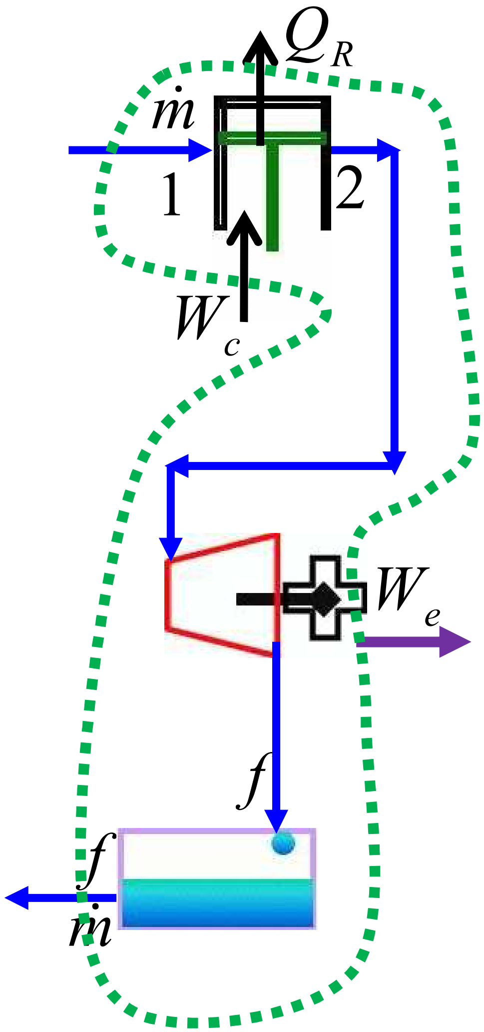
$$\dot{m}_1 h_1 + W_c = Q_R + \cancel{W_e} + \dot{m}_f h_f$$

- Rearranging the terms, we have

$$Q_R - W_c = \dot{m}_1 \left(h_1 - h_f \right)$$

- The compression process is assumed to be isothermal.

Thermodynamic Ideal System



- Hence, from the Second Law of Thermodynamics, we can write

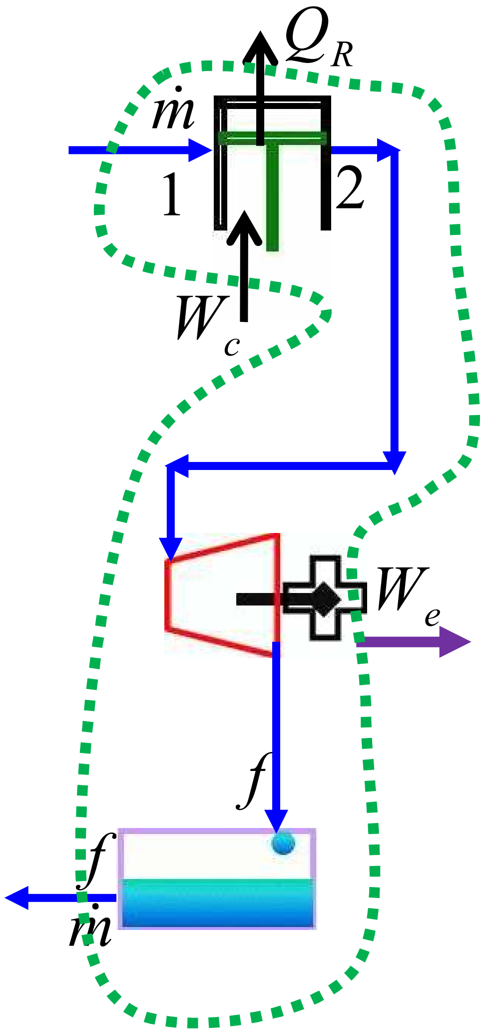
$$Q_R = \dot{m}_1 T_1 \left(s_2 - s_1\right)$$

- Also, the expansion process is an isentropic process. Therefore, $s_2 = s_f$.

- By substitution,

$$W_c = \dot{m}_1 T_1 \left(s_f - s_1\right) - \dot{m}_1 \left(h_f - h_1\right)$$

Thermodynamic Ideal System



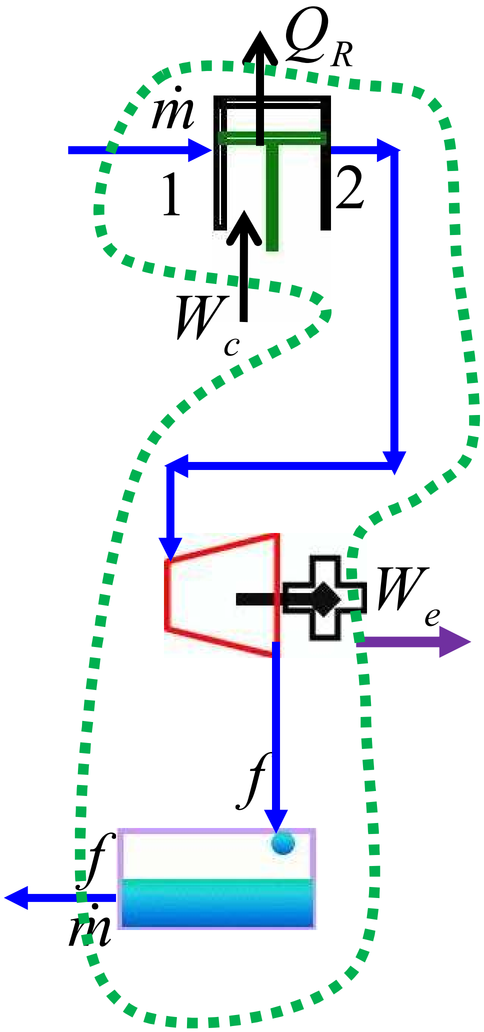
- This work of compression is done on the system. Hence, the value is expressed as a negative quantity.

$$-W_c = \dot{m}_1 T_1 \left(s_1 - s_f\right) - \dot{m}_1 \left(h_1 - h_f\right)$$

- Work required per unit mass of the **gas compressed** is given by

$$-\frac{W_c}{\dot{m}_1} = T_1 \left(s_1 - s_f\right) - \left(h_1 - h_f\right)$$

Thermodynamic Ideal System



- Since in an ideal system, mass of gas compressed is same as mass of gas liquefied, $m_1 = m_f$.
- Work required per unit mass of the **gas liquefied** is given by

$$-\frac{W_c}{\dot{m}_f} = \underline{T_1(s_1} - s_f) - (\underline{h_1} - h_f)$$

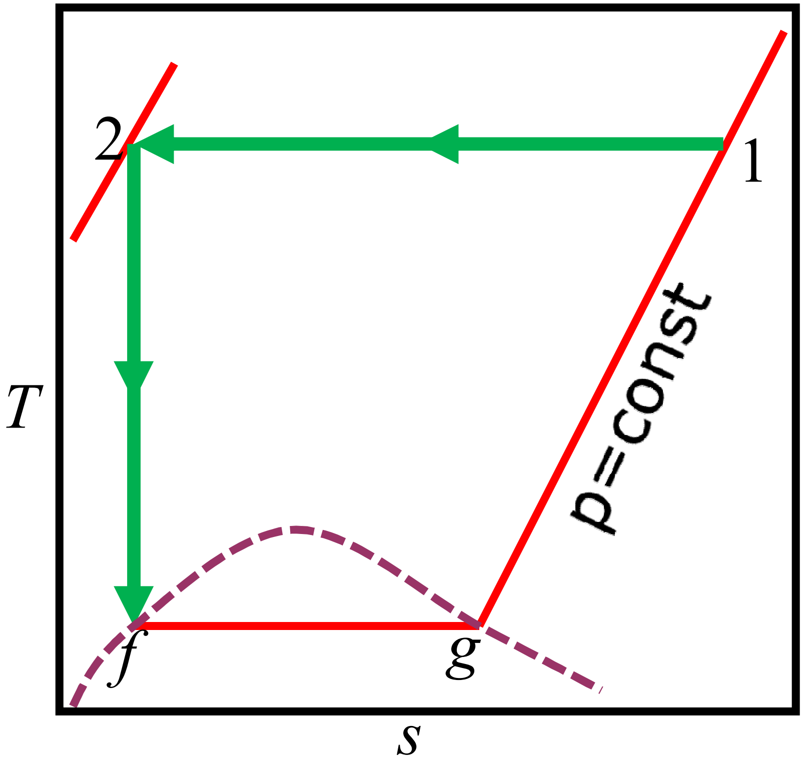
- Work required per unit mass of the gas is dependent on the initial condition of the gas.

Tutorial – 1

- Determine the ideal work requirement for liquefaction of nitrogen beginning at 1 bar pressure and 300 K.

- **Step 1**

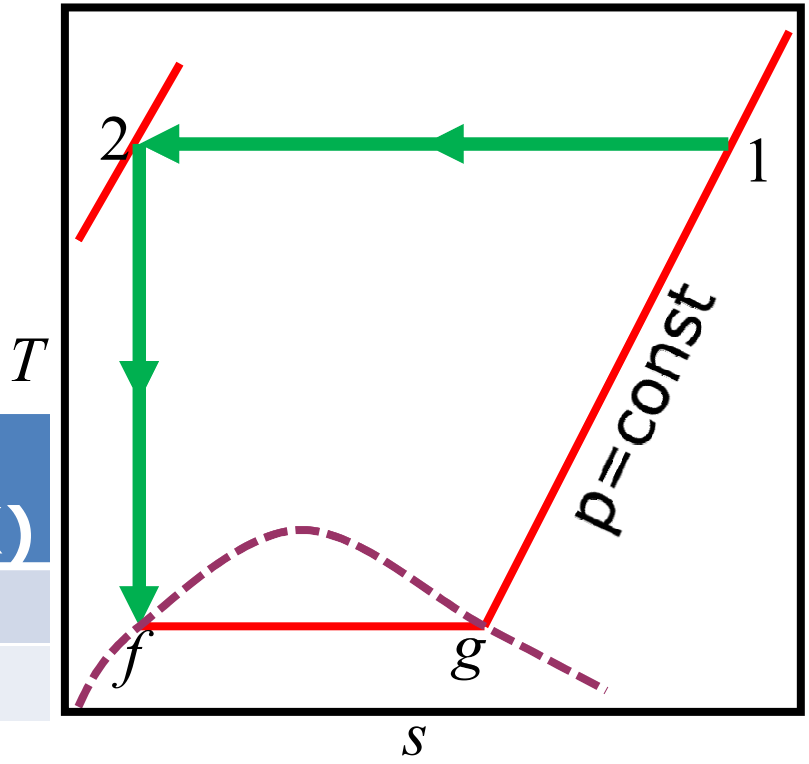
- The T – s diagram for an ideal thermodynamic cycle is as shown



Tutorial – 1

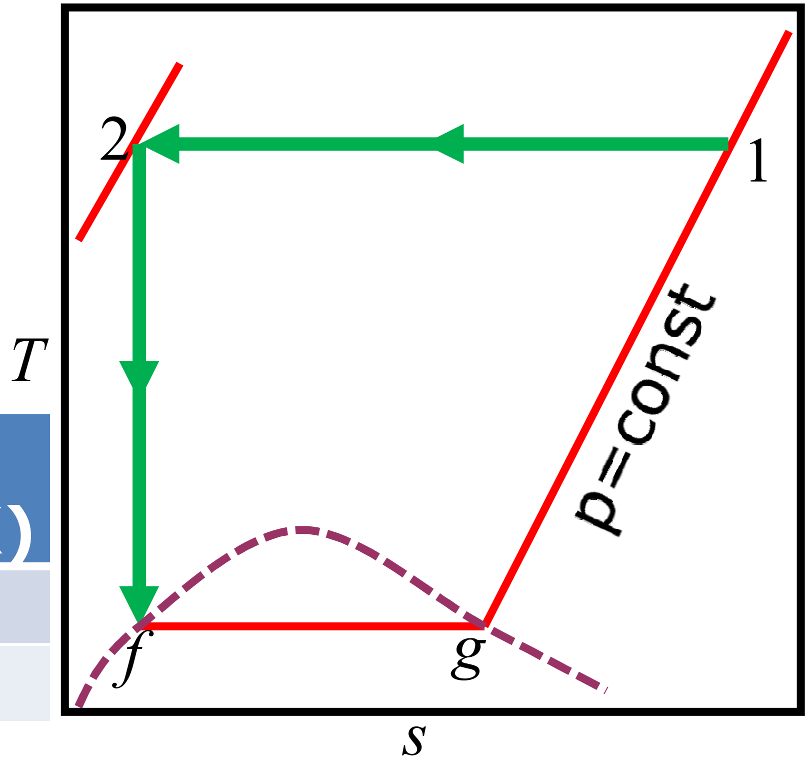
- **Step 2**
- The state properties at different points are as given below.

	p (bar)	T (K)	h (J/g)	s (J/gK)
1	1	300	462	4.42
f	1	77	29	0.42



Tutorial – 1

- **Step 3**
- Substitution into the equation.



	p (bar)	T (K)	h (J/g)	s (J/gK)
1	1	300	462	4.42
f	1	77	29	0.42

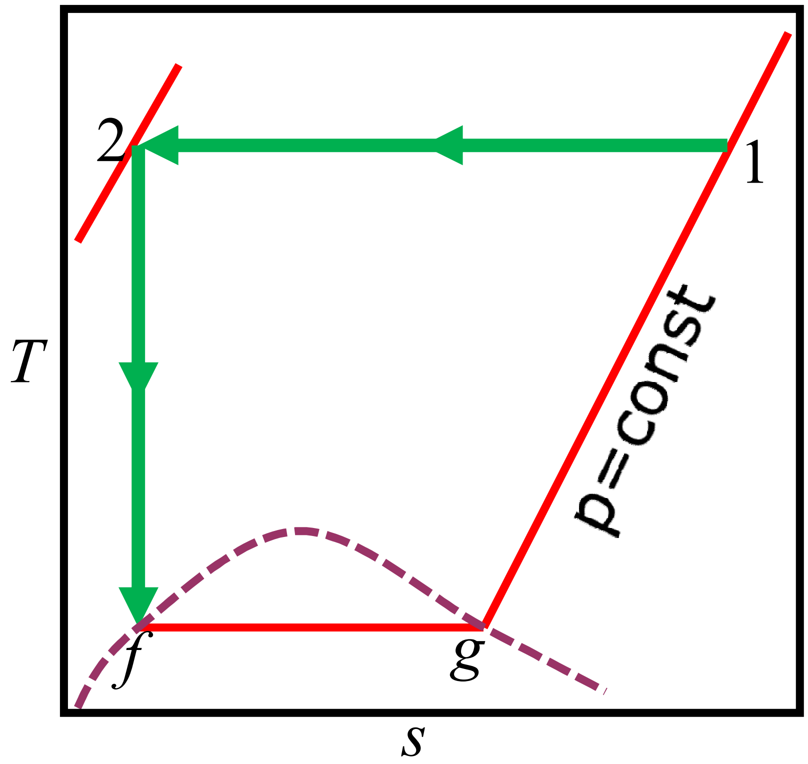
$$-\frac{\dot{W}_i}{\dot{m}_f} = T_1\left(s_1 - s_f\right) - \left(h_1 - h_f\right)$$

$$= 300(4.42 - 0.42) - (462 - 29) = 767\, J/g$$

Tutorial – 2

- Calculate the ideal work requirement for liquefaction of Helium and Hydrogen beginning at 1 bar pressure and 300 K. Compare the results.

- **Step 1**
- The T – s diagram for an ideal thermodynamic cycle is as shown



Tutorial – 2

- **Step 2**
- The state properties for hydrogen and Helium at different points are as given below.

	p (bar)	T (K)	h (J/g)	s (J/gK)
Hydrogen				
1	1	300	4190	65
f	1	20	-75	18
Helium				
1	1	300	1575	31.5
f	1	4.2	9.5	3.45

Tutorial – 2

- **Step 3**
- Substitution into the equation.

$$-\frac{\dot{W}_i}{\dot{m}_f} = T_1\left(s_1 - s_f\right) - \left(h_1 - h_f\right)$$

	p (bar)	T (K)	h (J/g)	s (J/gK)
Hydrogen				
1	1	300	4190	65
f	1	20	-75	18
Helium				
1	1	300	1575	31.5
f	1	4.2	9.5	3.4

H_2

$$= 300(65-18)-(4190+75)$$

$$= 9835\,J/g$$

He

$$= 300(31.5-3.4)-(1575-9.5)$$

$$= 6864.5\,J/g$$

Ideal Work Requirement

Gas	Normal Boiling Point (K)	Ideal Work (kJ/Kg)
Helium	4.21	6819
Hydrogen	20.27	12019
Nitrogen	77.36	768.1
Air	78.8	738.9
Argon	87.28	478.6
Oxygen	90.18	635.6
Ammonia	239.8	359.1

Assignment

1. Calculate using the charts, ideal work of liquefaction for
   - Air
   - Oxygen
   - Helium
   - Ammonia

2. Compare the values obtained with the values given in the table

Summary

- For an ideal gas $\mu_{JT} = 0$, but for a real gas, J – T coefficient depends upon the relative magnitude of departure from Joule’s Law and Boyle’s Law.

- The gases like nitrogen, air show J – T cooling when expanded at room temperature because the $\mathbf{T_{INV}}$ is more than room temperature.

- While the gases like He, Hydrogen and Neon, are to be precooled in order to experience J – T effect.

Summary

- In expansion devices like turbo-expanders and expansion engines, the expansion process is isentropic or reversible adiabatic.

- Coefficient of an isentropic expansion is given by

$$\mu_s = +\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p$$

- The isentropic expansion is always positive for both real and ideal gases. It results in cooling for any initial state, unlike the J – T expansion which is dependent on T_{INV}.

Summary

- J – T expansion is normally used where phase changes are required, where as isentropic expansion is used for single phase fluids.

- In a thermodynamic ideal system, all the gas that is compressed gets liquefied.

- The work required per unit mass of the **gas compressed** and **gas liquefied** are given by

$$-\frac{W_c}{\dot{m}_f}=T_1\left(s_1-s_f\right)-\left(h_1-h_f\right)$$

Thank You!