Chemical Thermodynamics

Chem 211: Lecture 6

Applications of 1st law of Thermodynamics

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Outline

- Heat capacity
- c_P/c_V Relationship for ideal gases
- Adiabatic index
- Effect of T on heat of reaction
- Kirschoff's Law
- Adiabatic expansion
- Joule experiment
- Joule-Thomson effect
- Inversion Temperature

Heat Capacity, C

- is the amount of heat necessary to raise the temperature of a certain substance (or system) one degree (Extensive property).

$$C = \frac{dq}{dT}$$

Heat Capacity at constant P (C_P)

is the amount of heat necessary to raise the temperature of a certain substance (or system) one degree at a constant pressure.

$$C_P = \frac{dq_P}{dT}$$

$$dq_P = dH = dU + PdV$$

$$C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P = \left(\frac{dU}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

Heat Capacity at constant V (C_V)

is the amount of heat necessary to raise the temperature of a certain substance (or system) one degree at a constant volume.

$$C_V = \frac{dq_V}{dT}$$

$$dq_V = dU$$

$$C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

Molar Heat Capacity, *c*

is the amount of heat necessary to raise the temperature of one mole of a certain substance (or system) one degree (intensive property)

$$c = \frac{dq}{ndT}$$

n: no. of moles

Molar heat capacity at constant P (c_P)

is the amount of heat necessary to raise the temperature of one mole of a certain substance (or system) one degree at constant pressure.

Molar heat capacity at constant V (c_V)

is the amount of heat necessary to raise the temperature of one mole of a certain substance (or system) one degree at constant volume.

Specific heat capacity (S)

is the amount of heat necessary to raise the temperature of one gram of a certain substance (or system) one degree (intensive property)

$$S = \frac{dq}{mdT}$$

m: mass (g)

Exercise

- A 2.50 kg piece of copper metal is heated from 25°C to 225°C. How much heat, in kJ, is absorbed by the copper? The specific heat of copper is 0.384 J/g °C.

Answer

$$s = \frac{dq}{mdT} = \frac{q}{m\Delta T}$$

$$q = ms\Delta T = (2.5\ kg)\left(\frac{0.384\ J}{g^{o}\mathrm{C}}\right)(200^{o}C)$$

$$= 192\ kJ$$

c_P/c_V Relationship for ideal gases

$$H = U + PV$$

$$dH = dU + PdV$$

$$\frac{dH}{dT} = \frac{dU}{dT} + \frac{PdV}{dT}$$

For one mole of an ideal gas, n=1

$$PV = RT$$

$$\frac{PdV}{dT} = R$$

$$\frac{dH}{dT} = \frac{dU}{dT} + R$$

$$c_P = c_V + R$$

kJ mol^{-1} K^{-1}

According to kinetic molecular theory of gases

The thermal energy of a mono-atomic gas consists solely of translational energy of motion of the atoms in the space and equal to 3RT/2.

$$U = \frac{3}{2}RT$$

$$\left(\frac{dU}{dT}\right)_V = c_V = \frac{3}{2}R$$

$$c_P = c_V + R$$

$$c_P = c_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

Adiabatic index, γ

- In thermal physics and thermodynamics, the heat capacity ratio or adiabatic index or ratio of specific heats or Poisson constant, is the ratio of the heat capacity at constant pressure (c_P) to heat capacity at constant volume (c_V).

$$\gamma = \frac{c_P}{c_V}$$

$$\gamma = \frac{c_P}{c_V} = \frac{c_V + R}{c_V} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

For poly-atomic gases ⇒ $U > \frac{3}{2}RT$

due to contributions from rotational and vibrational motions

Therefore,

$$\gamma = \frac{c_P}{c_V} < 1.67$$

Generally,

$$\gamma = \frac{c_P}{c_V} = \frac{c_V + R}{c_V} = 1 + \frac{R}{c_V}$$

$c_v \uparrow \rightarrow \gamma \downarrow$

Effect of T on heat of reaction

- The heat of reaction (physical or chemical change) depends on T.
- For any system, on going from a state A to state B,

$$\Delta H = H_B - H_A$$

Take a differentiation with respect to T at constant P

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_B}{dT}\right)_P - \left(\frac{dH_A}{dT}\right)_P = c_{P,B} - c_{P,A} = \Delta c_P$$

Kirschoff's equation

$$d\Delta H = \Delta c_P dT$$

$$d\Delta H = \Delta c_P dT$$

$$\int_{\Delta H_1}^{\Delta H_2} d\Delta H = \int_{T_1}^{T_2} \Delta c_P dT$$

ΔH_1 and ΔH_2 : heats of reaction at T_1 and T_2, respectively.

- Assuming ΔC_P is independent of T in the assigned domain (between T_1 and T_2) therefore,

$$\Delta H_2 - \Delta H_1 = q_P = \Delta c_P (T_2 - T_1)$$

Exercise

- The heat of formation of liquid water at 25°C is –285.7 kJ/mol. The mean molar heat capacities of $H_2(g)$, $O_2(g)$, and $H_2O(l)$ are 28.8, 29.1, and 75.3 $Jmol^{-1}K^{-1}$. Calculate the heat of formation of water at 100 °C.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_{298K} = -285.7\ kJ/mol$$

Answer

$$\Delta c_P = c_{P,H_2O} - c_{P,H_2} - \frac{1}{2}c_{P,O_2}$$

$$= 75.3 - 28.8 - \frac{1}{2}(29.1) =$$

$$31.95\ Jmol^{-1}K^{-1} = 0.032\ kJ\ mol^{-1}K^{-1}\ at\ 25^oC$$

$$\int_{\Delta H_1}^{\Delta H_2} d\Delta H = \int_{T_1}^{T_2} \Delta c_P dT$$

$$\Delta H_2 - \Delta H_1 = q_P = \Delta c_P (T_2 - T_1)$$

$$\Delta H_{373K} - \Delta H_{298K} = 0.032(373 - 298)$$

$$\Delta H_{373K} - (-285.7\ kJ/mol) = 2.4$$

$$\Delta H_{373K} = -283.3\ kJ/mol$$

Hypothetical $\Delta H_{reaction}$ at 0K

- The integrated **Kirschoff's** equation can be used to calculate the hypothetical heat of reaction at the absolute zero.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta c_P \, dT$$

c_p is T's dependent

$$\Delta c_P = a + bT + cT^2 + \text{.....etc}$$

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} (a + bT + cT^2 + \ldots.)\, dT$$

$$\Delta H_2 = \Delta H_1 + \left(aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \ldots. \right)$$

Exercise

- The heat of formation of ammonia at 25°C is –92.4 kJ/mol. The molar heat capacities of N_2(g), H_2(g), and ammonia at constant pressure are function of temperatures and given by the following equations in $J\ mol^{-1}K^{-1}$. Calculate the heat of formation of ammonia at 125 °C.

$$c_{P,N_2(g)} = 27.2 + 4.2(10^{-3}T)$$

$$c_{P,H_2(g)} = 27.2 + 3.8(10^{-3}T)$$

$$c_{P,NH_3(g)} = 33.6 + 2.9(10^{-3}T) + 2.1(10^{-5}T^2)$$

Answer

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H_{298K} = -92.4\ kJ/mol$$

$$\text{for 2 moles } NH_3 = 2(-92.4) = 184.8kJ$$

$$\Delta c_P = 2c_{P,NH_3} - c_{P,N_2} - 3c_{P,H_2}$$

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H_{298K} = -92.4\ kJ/mol$$

$$\Delta c_P = 2\left(33.6 + 2.9(10^{-3}T)\ + 2.1(10^{-5}T^2)\right)$$
$$- \left(27.2 + 4.2(10^{-3}T)\right) - 3\left(27.2 + 3.8(10^{-3}T)\right)$$
$$= \ -41.6 + 9.8(10^{-3}T)\ + 4.2(10^{-5}T^2)\ J\ mol^{-1}K^{-1}$$

$$\int_{\Delta H_{1,298K}}^{\Delta H_{2,398K}} d\Delta H = \Delta H_{2,398K} - \Delta H_{1,298K} = \int_{298K}^{398K} \Delta c_P dT$$

$$\Delta H_{2,398K} - \Delta H_{1,298K} = \int_{298K}^{398K} \Delta c_P \, dT$$

$$= \int_{298K}^{398K} \left(-41.6 - 9.8(10^{-3}T) + 4.2(10^{-5}T^2)\right) dT$$

$$= -41.6(T_2 - T_1) - \frac{9.8 \times 10^{-3}(T_2^2 - T_1^2)}{2} + \frac{4.2 \times 10^{-5}(T_2^3 - T_1^3)}{3}$$

$$= -41.6(398 - 298) - \frac{9.8 \times 10^{-3}\left((398)^2 - (298)^2\right)}{2} + \frac{4.2 \times 10^{-5}\left((398)^3 - (298)^3\right)}{3}$$

$$\Delta H_{2,398K} - (-92400\, J/mol) = -4160 - 341 + 512$$

$$\Delta H_{2,398K} = 96389 J/mol = 96.389 \;\; kJ/mol$$

Homework

- Use the data provided in the last example to calculate the heat of formation of ammonia at 0K?

Rationalization of Kirschoff's Law

- It outlines the variation of a reaction's enthalpy with temperature.
- In general, enthalpy of any substance **increases** with temperature, which means both the products and the reactants' enthalpies increase.
- The overall enthalpy of the reaction will **change** if the increase in the enthalpy of products and reactants is different.

Δc_P is independent of T

$$\Delta H_2 = \Delta H_1 + \Delta c_P (T_2 - T_1)$$

Δc_P is +ve and $T_2 > T_1$, therefore, $\Delta H_2 > \Delta H_1$

Δc_P is T dependent

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta c_P \, dT$$

- The change in enthalpy is a function of the difference in temperature and heat capacities.
- It is proportional to the product of temperature change and change in heat capacities of products and reactants

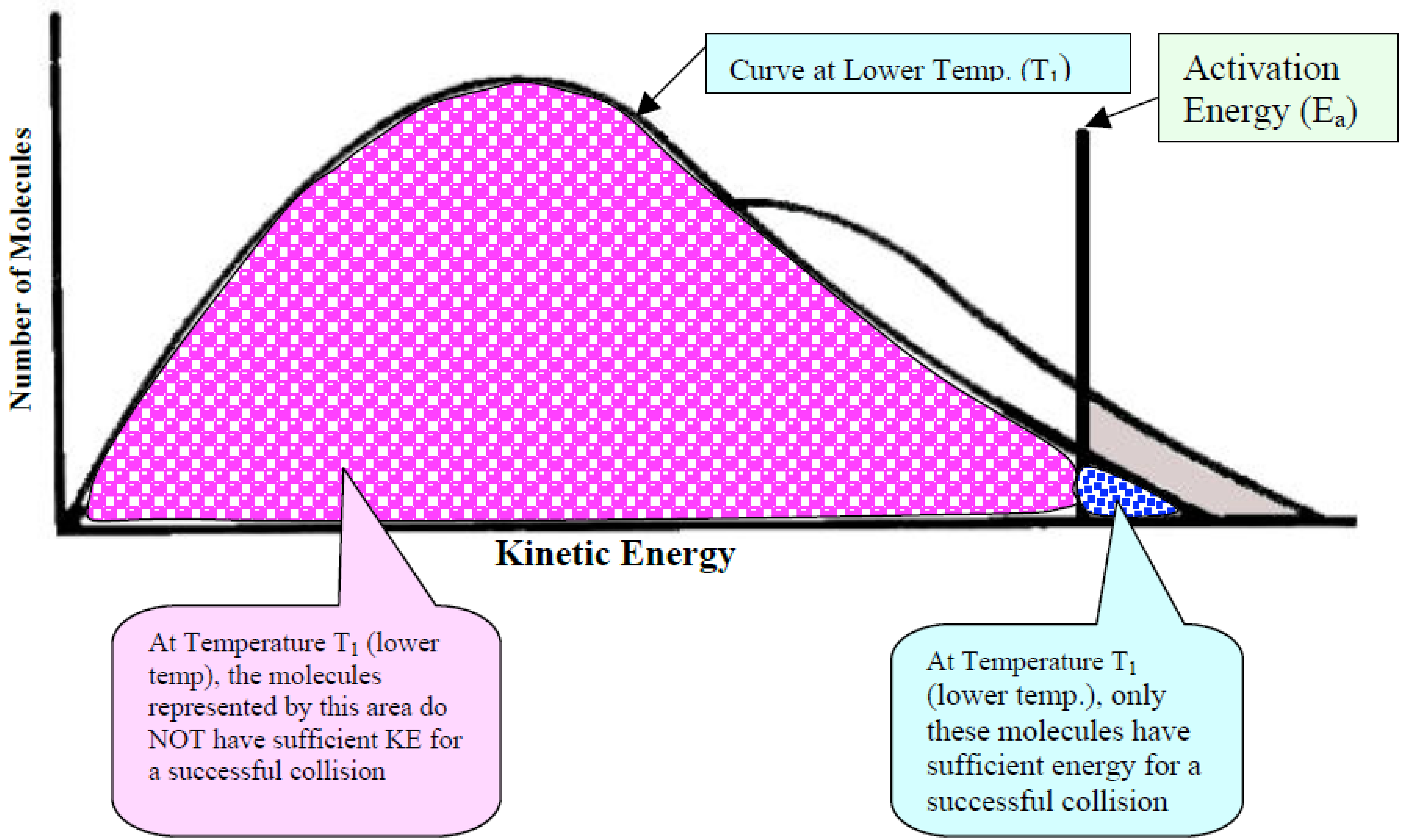
Consider a reaction

$$aA \rightarrow bB, \quad \Delta H_1$$

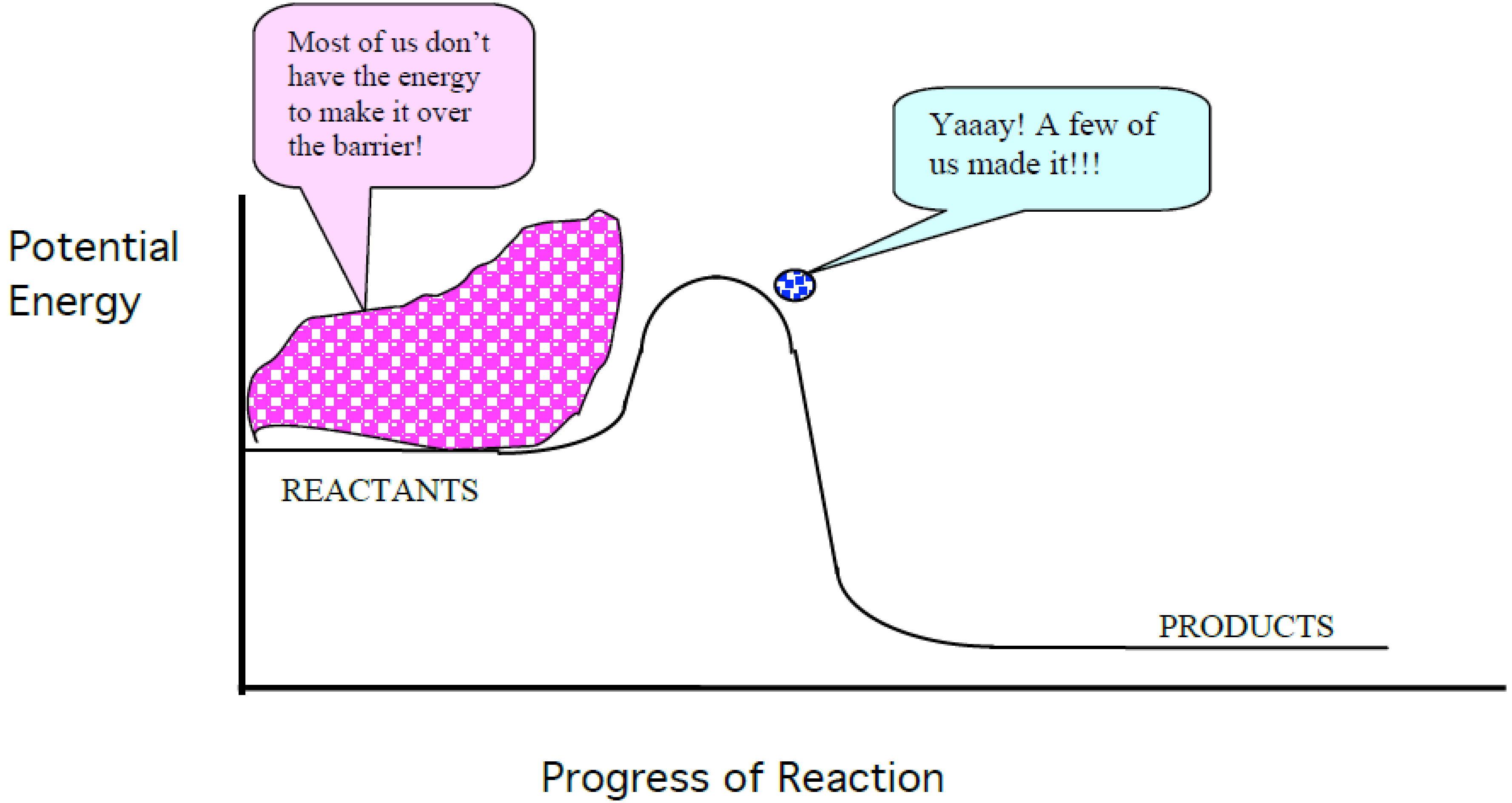
- proceeds at a given T_1, which is necessary to overcome the activation energy (E_a) the reactants need to reach the transition state (state corresponding to the highest potential energy (PE) along this reaction coordinate) or sometimes called activated complex, AC.
- E_a (minimum energy required for a successful collision that produces AC by converting the KE into PE, bonds formation).
- E_a depends on nature of reactants (numbers & strengths of bonds in reactants) but do NOT depend on the change in T & concentration.

- AC is a very short-lived, unstable combination of reactant atoms that exists before products are formed. It has different PE from that of reactants.
- This change in PE is likely provided from the KE of the system which depends on T.
- Once the PE of the reactants reaches this TS, the products will readily be formed.
- If T_1 is not sufficient to move the reactants into this TS, the products will not form.
- The temperature determines how many (or what fraction of the) molecules will have energy > E_a (to make it over the barrier & have a successful collision)

KE distributions at low T_1

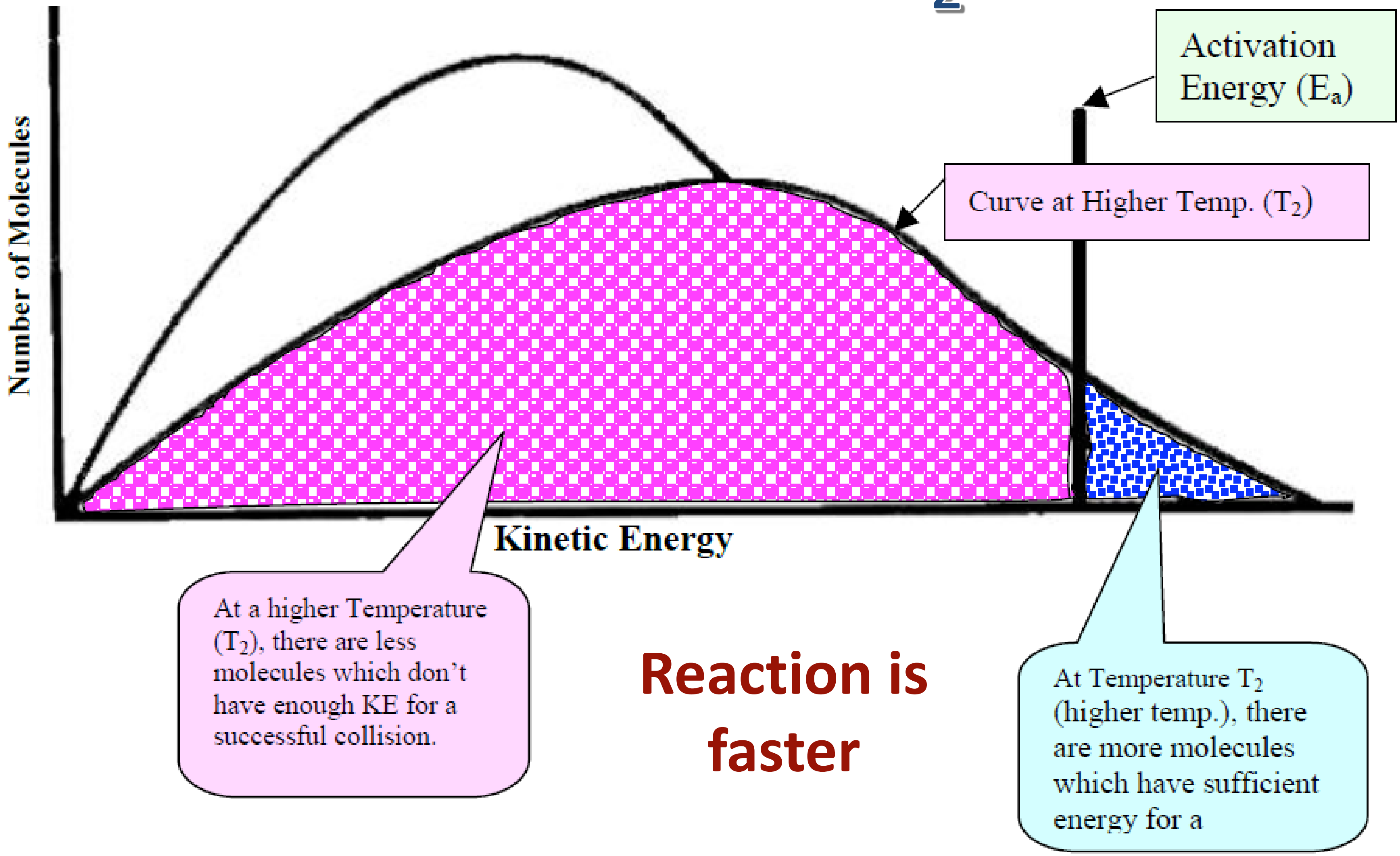


KE distributions at low T_1



Only a small fraction of the molecules had enough energy to overcome the Activation Energy barrier.

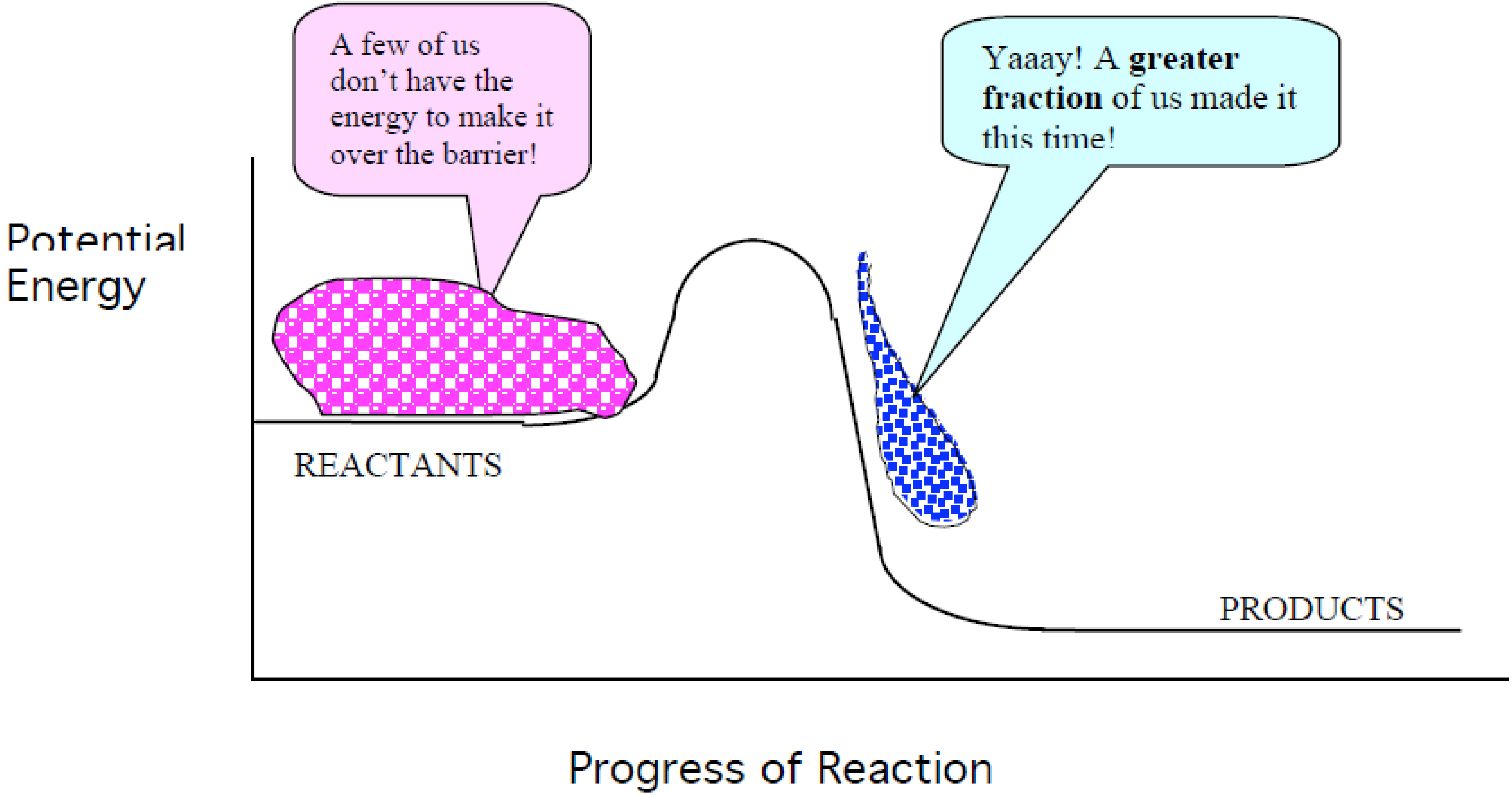
KE distributions at low T_2



Reaction is faster

At high T, a greater fraction of the molecules have sufficient energy to "make it over" the Activation Energy barrier.

KE distributions at low T_2



A larger fraction of the molecules had enough energy to overcome the Activation Energy barrier.

If you provided a reaction with energy higher than what is required (running at $T_2>T_1$)

- PEs of reactants and products are supposed to be unchanged (do not depend on T but vary with composition or position).
- KE & consequently U and H of reactants increase.
- Reaching TS and moving from TS into products will likely be faster because increasing T will increase the particles' collisions.
- PE diagram is not supposed to change with T.
- The internal energy and enthalpy level diagrams will change based on the impact of increasing T on both of reactants and products.

- The influence of T on KE, U, and H of reactants and products is not necessarily to be the same.

- At constant P, the change of $\Delta_r H$ ($\Delta_r H_2$- $\Delta_r H_1$) with increasing T from T_1 to T_2 depends on $(T_2 - T_1)$ and $\Delta_r c_P$.

$$\Delta_r c_P = \sum_{\text{products}} v\Delta c_P - \sum_{\text{reactants}} v\Delta c_P$$

where v = stoichiometric coefficient of species

Isothermal/adiabatic expansion

- Typically, any expansion is accompanied by cooling; (losing energy and lowering in system's T)
- If the system permits heat transfer with surrounding, the system may absorb Q from surrounding to keep its temperature unchanged (isothermal) and $\Delta U=0$.
- Otherwise, as adiabatic processes, the expansion should result in a lowering of the system T.

$$\Delta U_{isothermal} = Q + W = 0$$

$$\Delta U_{adiabatic} = 0 + W = W$$

Adiabatic expansion, $Q = 0$

$$\Delta U = W = -PdV$$

$$dU = dW = -\int_{V_1}^{V_2} PdV$$

For ideal gases, $P = f(V)$, $n = 1$

$$dU = dW = -\int_{V_1}^{V_2} \frac{RTdV}{V}$$

$$c_V = \left(\frac{dU}{dT}\right)_V$$

$$\int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} c_V dT = -\int_{V_1}^{V_2} \frac{RTdV}{V}$$

- Adiabatic: T is not constant.
- Assume c_v is independent of T

$$c_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$c_V \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

However, $c_P = c_V + R$ **Or** $R = c_P - c_V$

Substitute

$$c_V \ln\frac{T_2}{T_1} = -(c_P - c_V)\ \ln\frac{V_2}{V_1}$$

$$\ln\frac{T_2}{T_1} = -\left(\frac{c_P - c_V}{c_V}\right)\ln\frac{V_2}{V_1}$$

Know $\gamma = \frac{c_P}{c_V}$

$$\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2}$$

Note the (V_2 / V_1) flipping

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

Or

$$T_1 V_1{}^{(\gamma-1)} = T_2 V_2{}^{(\gamma-1)}$$

Considering

$$\gamma = \frac{c_P}{c_V} = \frac{c_V + R}{c_V} = 1 + \frac{R}{c_V}$$

$$T_1 V_1{}^{\left(\frac{R}{c_V}\right)} = T_2 V_2{}^{\left(\frac{R}{c_V}\right)}$$

Or

$$T_1{}^{\left(\frac{c_V}{R}\right)} V_1 = T_2{}^{\left(\frac{c_V}{R}\right)} V_2$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

For ideal gases

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

$$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\frac{P_2}{P_1} = \frac{V_1}{V_2}\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

Or

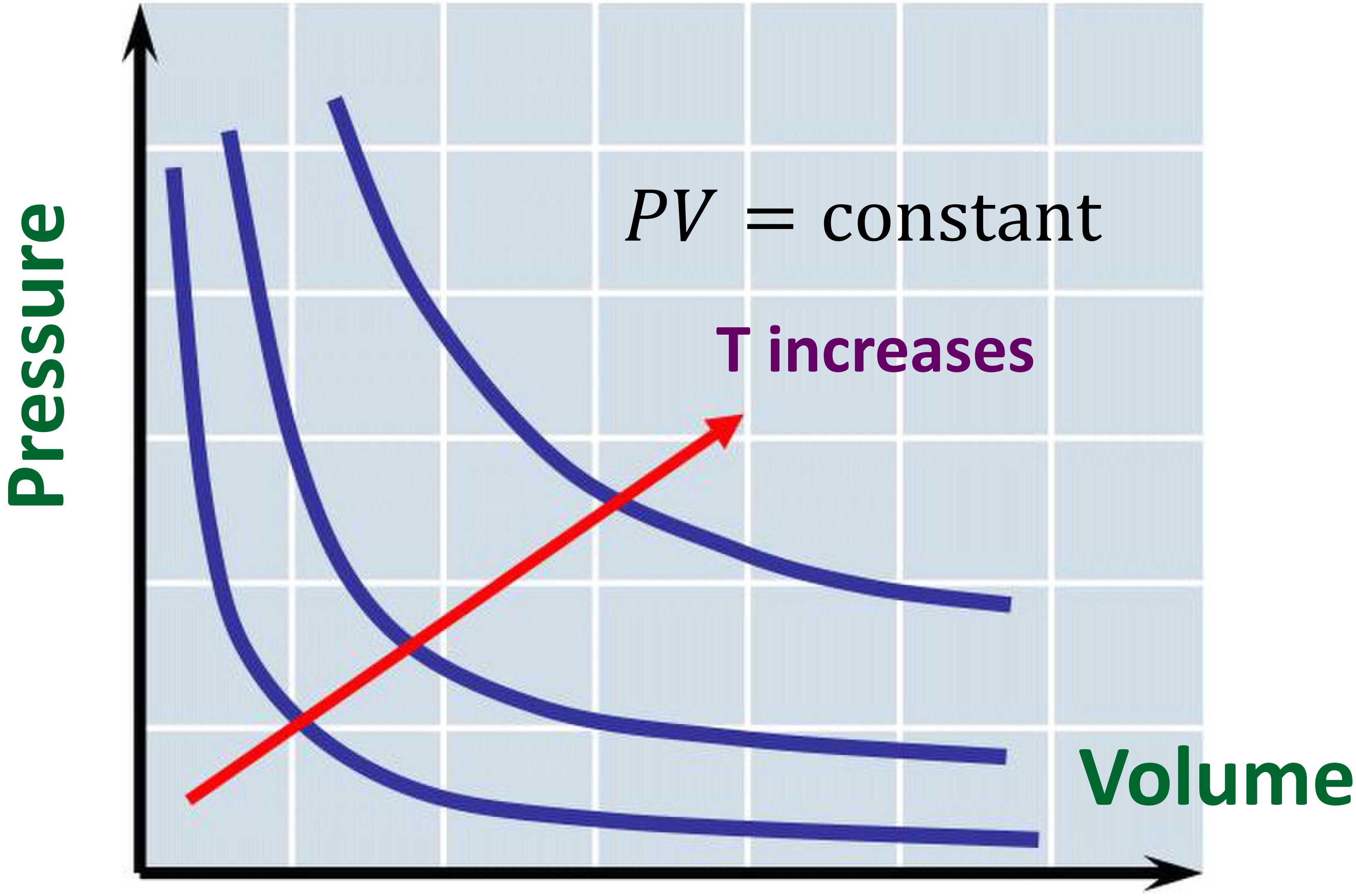
$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

For adiabatic expansion

Compare with isothermal expansion (Boyl's Law)

$$P_1V_1 = P_2V_2$$

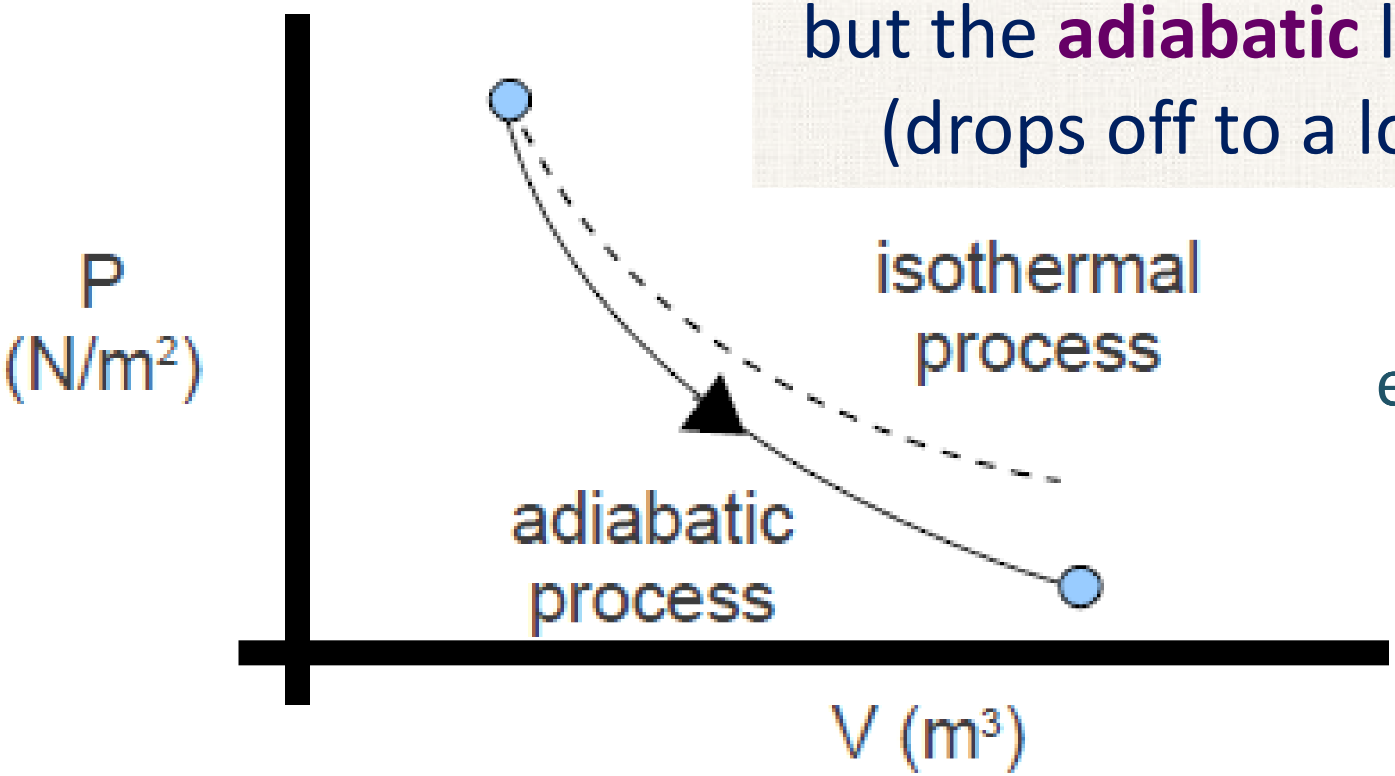
Boyle's Law



- As T decreases, the isotherm is shifted downward because of lowering the internal energy.

Isothermal/adiabatic expansion

Their PV diagrams look similar, but the **adiabatic** line is **steeper** (drops off to a lower point)



Adiabatic expansion drops to a lower isotherm

- In the adiabatic process where a gas expands, the work done by the gas causes the internal energy to decrease, so the temperature must decrease as well.

Comment

- On the PV diagrams, the adiabatic change is steeper than the isothermal change?

Answer

- Because the pressure decreases (from P_1 to P_2) more (inspect it graphically) in adiabatic processes than in isothermal processes.

- This is also clear from the derived equation for adiabatic expansion where $\gamma > 1$ in comparison to $\gamma = 1$ in case of isothermal expansion

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

Ex.

- Calculate the work done during an adiabatic reversible expansion of 0.85 mole of an ideal mono-atomic gas (c_v = 12.36 J mol^{-1} K^{-1}) from a pressure of 15 atm to 1 atm at 300 K?

Answer

Assume c_v is independent of T, and for ideal gases

$$V_1 = \frac{nRT}{P_1} = \frac{(0.85\ mol)(0.82\ L\ atm\ K^{-1} mol^{-1})(300\ K)}{15\ atm} = 1.39\ L$$

For mono-atomic gas

$$\gamma = \frac{c_P}{c_V} = \frac{5}{3} = 1.67$$

For adiabatic expansion of an ideal gas

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}}$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} = (1.39\ L)\left(\frac{15}{1}\right)^{\frac{1}{1.69}} = 7.1\ L$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(1\ atm)(7.1\ L)}{(0.85\ mol)(0.82\ L\ atm\ K^{-1}mol^{-1})} = 101.2\ K$$

Alternatively, To calculate T_2

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

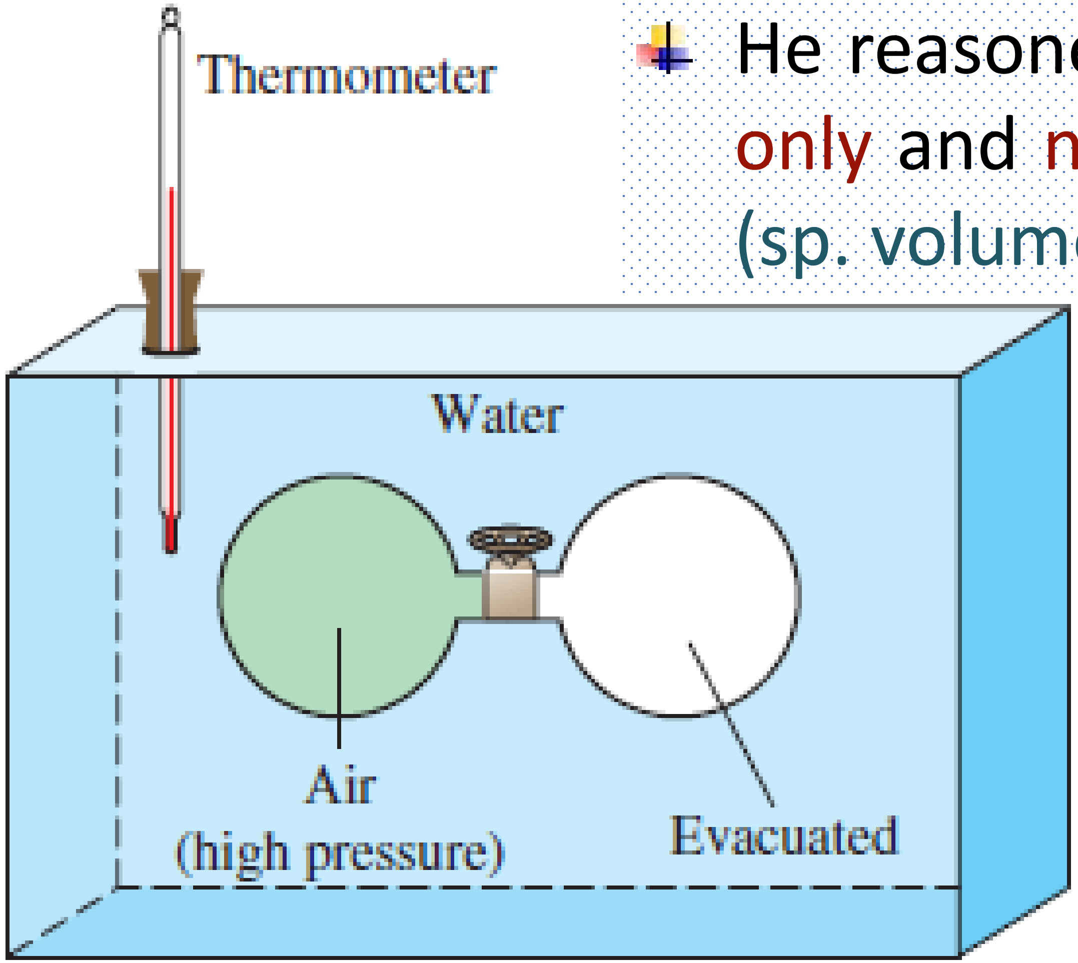
$$W = \Delta U = nc_V(T_2 - T_1) =$$
$$(0.85\ mol)(12.36\ J\ \text{mol}^{-1}K^{-1})(101.2 - 300\ K) = -2120\ J$$

- If you compared this W with that of isothermal reversible expansion of ideal gases, you would notice: $W_{adiabatic} < W_{isothermal}$

$$W_{rev} = -\int_1^2 PdV = -\int_1^2 \frac{nRT}{V} dV = -P_1V_1 \ln\frac{V_2}{V_1}$$
$$\left(-(15\ atm)(1.39L)(2.303)\log\left(\frac{7.1}{1.39}\right)\right)\left(\frac{101.396\ J}{L\ atm}\right) = -3448.28\ J$$

Joule experiment $U = U(T)$

- demonstrated for an ideal gas, U depends only on T.
- He submerged two tanks (one containing air at a high P and the other was evacuated) connected with a pipe and a valve in a water bath.
- When thermal equilibrium was attained, he opened the valve to let air pass from one tank to the other until the pressures equalized.
- He observed no change in T of water bath and assumed that no heat was transferred to or from surrounding air (adiabatic isolated process).
- Since there was also no work done (free expansion), he concluded that U of the air did not change even though $\boldsymbol{v}$ and $\boldsymbol{P}$ changed.



- He reasoned, U is a function of T only and not a function of P or v (sp. volume)

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

Intermolecular forces are ignored, and no energy is required to pull gas molecules apart

(Joule later showed that for gases that deviate significantly from ideal gas behavior, the internal energy is not a function of temperature alone.)

Generally,

$$U = U(T, P, v)$$

- $\boldsymbol{U}$ of a real gas is a function of P, v, and T.
- The equation of state (ideal or real gas laws) indicates the possibility of estimating the third variable if two of them were known.
- is possible to write $\boldsymbol{U}$ in terms of just 2 independent intensive variables: v and T, P and T, or P and v.
- Expressing $\boldsymbol{U}$ as a function of v and T fits the purpose.

At constant P

$$U = f(v, T)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv = 0$$

Interpretation,

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv = 0$$

- In a closed system of constant composition, any infinitesimal change in the internal energy is proportional to the infinitesimal changes of volume and temperature.

- The coefficients of proportionality being the two partial derivatives.

Adiabatic expansion of a gas against vacuum

$$Q = W = dU = 0$$

but

$$\left(\frac{\partial U}{\partial T}\right)_v = c_v$$

$$0 = c_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv$$

$$\left(\frac{\partial U}{\partial v}\right)_T = -c_V \left(\frac{dT}{dv}\right)_U$$

Let us say, $\left(\frac{\partial U}{\partial v}\right)_T = \pi_T$

π_T: **internal pressure**

- π_T measures of the variation of U of a substance with its volume at a constant temperature.
- As it has the same dimensions as pressure, we will call it the internal pressure.
- This indicates that a change in U of the system as a results of a volume change should be accompanied by a temperature change.
- Lowering U necessitates a lowering in T, in case of expansion, as a part of U is consumed to overcome intermolecular forces between gas particles (Real gas perspective) to permit expansion. Reverse is true for compression.

- The temperature change accompanying a gas expansion is given by

$$\left(\frac{dT}{dv}\right)_U = \frac{-1}{c_v}\left(\frac{\partial U}{\partial v}\right)_T = \frac{-\left(\frac{\partial U}{\partial v}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_v}$$

For real gas

- A temperature change accompanying a gas expansion should be on the expense of the internal energy (This is true for real gases).
- For ideal gases, intermolecular forces are neglected, and Joule's conclusion is valid.

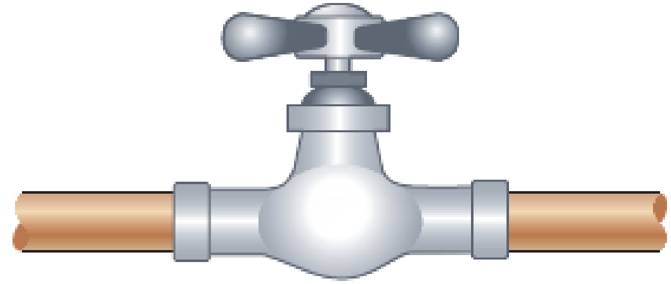
$$\left(\frac{\partial U}{\partial v}\right)_T = 0 = \left(\frac{dT}{dv}\right)_U$$

- An ideal gas can, therefore, be defined as the gas whose energy at constant temperature is independent of its volume

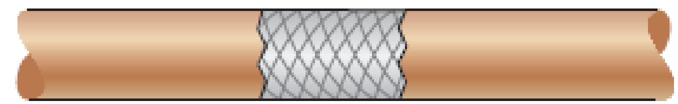
$$\left(\frac{dT}{dv}\right)_U$$ is called the **Joule coefficient**

Throttling valves

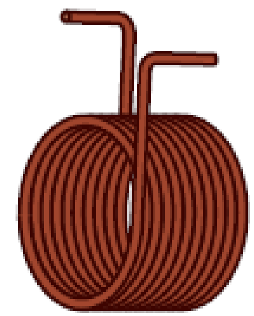
- are flow-restricting devices that cause a significant pressure drop in fluids, e.g., ordinary adjustable valves, capillary tubes, & porous plugs.
- They produce a pressure drop without involving any work.



(a) An adjustable valve



(b) A porous plug



(c) A capillary tube

- The pressure drop in the fluid is often accompanied by a large drop in temperature, and for that reason throttling devices are commonly used in **refrigeration** and **air-conditioning** applications.

- The magnitude of the temperature drop (or, sometimes, the temperature rise) during a throttling process is governed by a property called the **Joule-Thomson coefficient**.
- Throttling valves are usually small devices, and the flow through them may be assumed to be **adiabatic** ($Q \approx 0$) since there is neither sufficient time nor large enough area for any effective heat transfer to take place.
- Also, there is **no work done** ($W = 0$), and the change in potential energy, if any, is very small ($\Delta pe \approx 0$).
- Even though the exit velocity is often considerably higher than the inlet velocity, in many cases, the increase in kinetic energy is insignificant ($\Delta ke \approx 0$).

Energy Conservation in Throttling valves

- For this single-stream steady-flow device, energy conservation reduces to $H_2 \approx H_1$, i.e., H values at the inlet and exit of a throttling valve are the same.
- For throttling devices with large exposed surface areas such as capillary tubes, heat transfer may be significant.

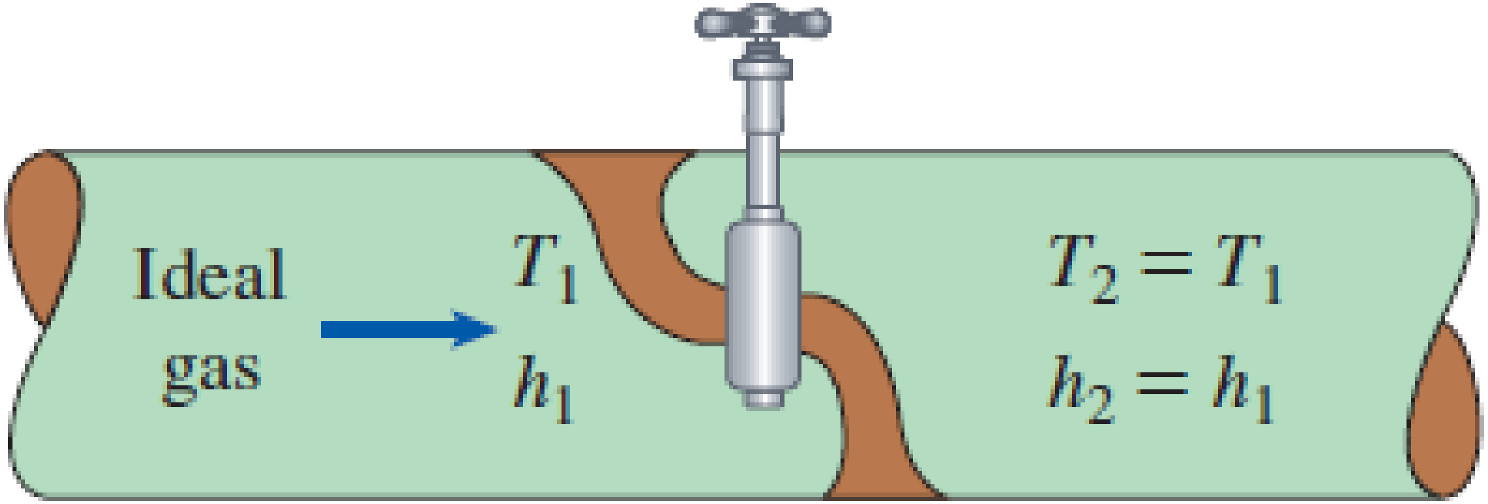
$$H_1 = H_2$$

$$U_1 + P_1 v_1 = U_2 + P_2 v_2$$

- The outcome of a throttling process depends on which of the two quantities increases in the process.
- If the flow energy ($Pv = \frac{P}{\rho}$) increases during the process ($P_2 v_2 > P_1 v_1$), internal energy must decrease, which is usually accompanied by a drop in T.

- If the product Pv decreases, the internal energy and the temperature of a fluid will increase during a throttling process.
- In the case of an ideal gas, H = H(T), and thus the temperature must remain constant during a throttling process.

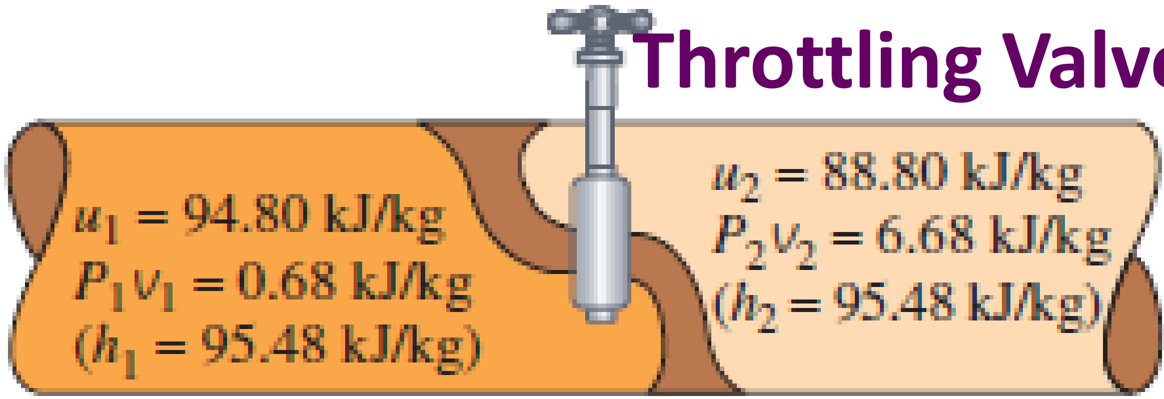
Throttling Valve



Ex.

- Refrigerant-134a enters the capillary tube of a refrigerator as saturated liquid at 0.8 MPa and is throttled to a pressure of 0.12 MPa. Determine the **quality** of the refrigerant at the final state and the temperature drop during this process?

Answer



Saturated refrigerant-134a—Pressure table

		Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
Press., P kPa	Sat. temp., T_{sat} °C	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
120	−22.32	0.0007323	0.16216	22.38	195.15	217.53	22.47	214.52	236.99	0.09269	0.85520	0.94789
800	31.31	0.0008457	0.025645	94.80	152.02	246.82	95.48	171.86	267.34	0.35408	0.56445	0.91853

- Flow through a capillary tube is a **throttling** process; thus, the enthalpy of the refrigerant remains constant.

At inlet: **(sat. liquid or fluid)**

$P_1 = 0.8$ MPa
$T_1 = T_{sat\ @\ 0.8\ MPa} = 31.31^oC$
$h_1 = h_{f\ @\ 0.8\ MPa} = 95.48$ kJ/kg

At exit: **(sat. liquid or fluid)**

$P_2 = 0.12$ MPa
$T_{sat} = -22.32\ ^oC$
$h_f = 22.47$ kJ/kg
$h_g = 236.99$ kJ/kg

- $h_2 = h_1 = 95.48$ kJ/kg, a value between $h_f < h_2 < h_g$
- Thus, the refrigerant exists as a **saturated mixture** at the exit state.

- The quality, χ_2, at this state is

$$\chi_2 = \frac{h_2 - h_f}{h_{fg}} = \frac{95.48 - 22.47}{236.99 - 22.47} = 0.340$$

- Since the exit state is a saturated mixture at 0.12 MPa, the exit temperature must be the saturation temperature at this pressure, which is –22.32°C.
- Then the temperature change for this process becomes

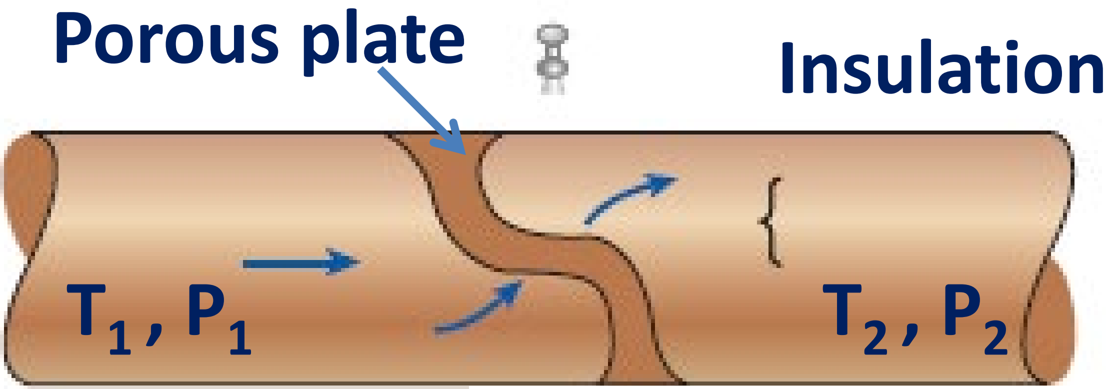
$$\Delta T = T_2 - T_1 = (-22.32 - 31.31)^o C = -53.63^o C$$

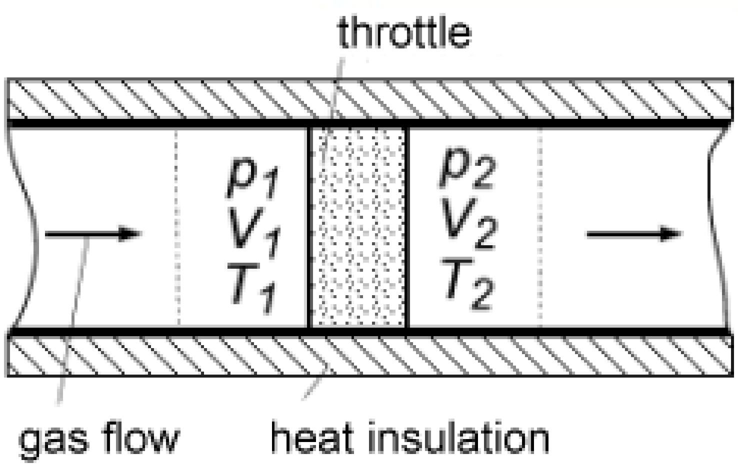
Note that

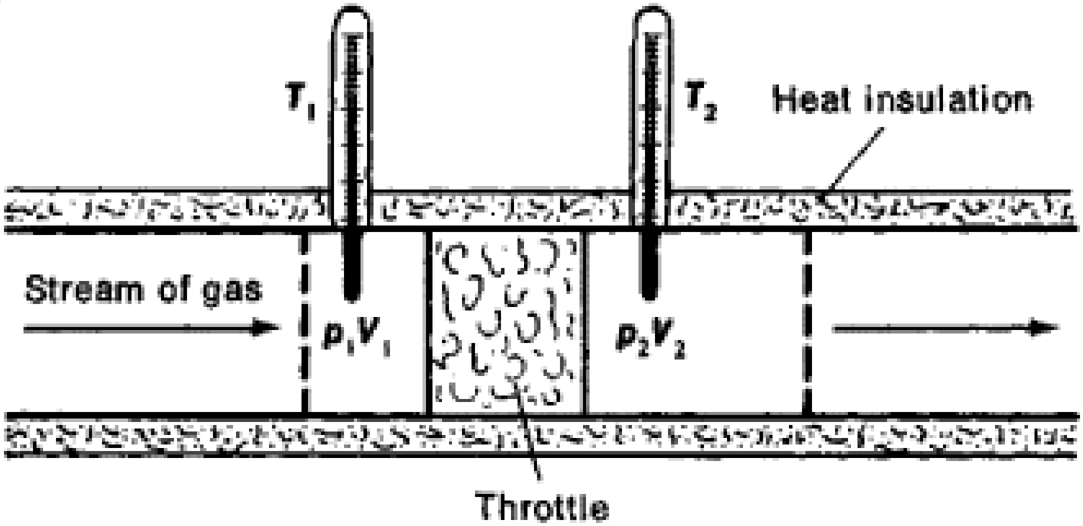
- T of the refrigerant drops by 53.63°C.
- 34.0 percent of the refrigerant vaporizes during this throttling process and the energy needed to vaporize this refrigerant is absorbed from refrigerant itself.

Joule-Thomson effect

- When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases.







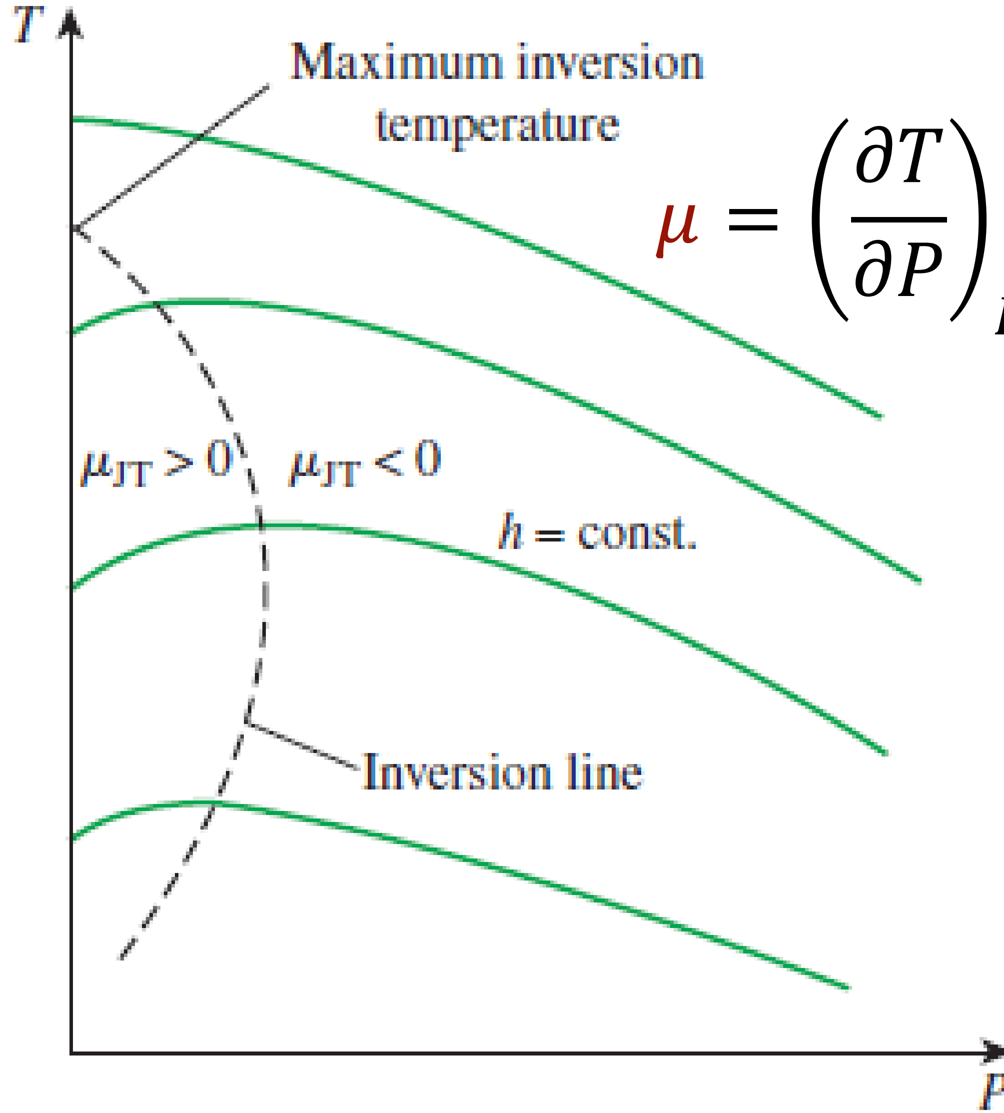
- The enthalpy of the fluid remains approximately **constant** during such a throttling process.
- A fluid may experience a large drop in its temperature as a result of throttling. This is not always the case.
- The temperature of the fluid may remain unchanged, or it may even increase during a throttling process.

The temperature behavior of a fluid during a throttling (H = constant) process is described by the Joule-Thomson coefficient, defined as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \begin{cases} < 0, & \text{T increases} \\ = 0, & \text{T remains constant} \\ > 0, & \text{T decreases} \end{cases}$$

- The Joule-Thomson coefficient represents the slope of H = constant lines on a T-P diagram.
- A fluid at a fixed temperature and pressure T_1 and P_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and P_2) are measured.
- The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and P_2.
- Plotting the temperatures against the pressures gives us an h = constant line on a T-P diagram.
- Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a T-P diagram for a substance with several h = constant lines.

- Some constant-enthalpy lines pass through a point of zero slope or zero μ.
- The line that passes through these points is called the inversion line.
- The temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.



$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

Constant-enthalpy lines of a substance on a T-P diagram.

- The T at the intersection of the P = 0 line (ordinate) and the upper part of the inversion line is called the maximum inversion temperature.
- Notice that the slopes of the h = constant lines are negative ($\mu < 0$) at states to the right of the inversion line and positive ($\mu > 0$) to the left of the inversion line.
- A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left.
- Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line.
- However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.

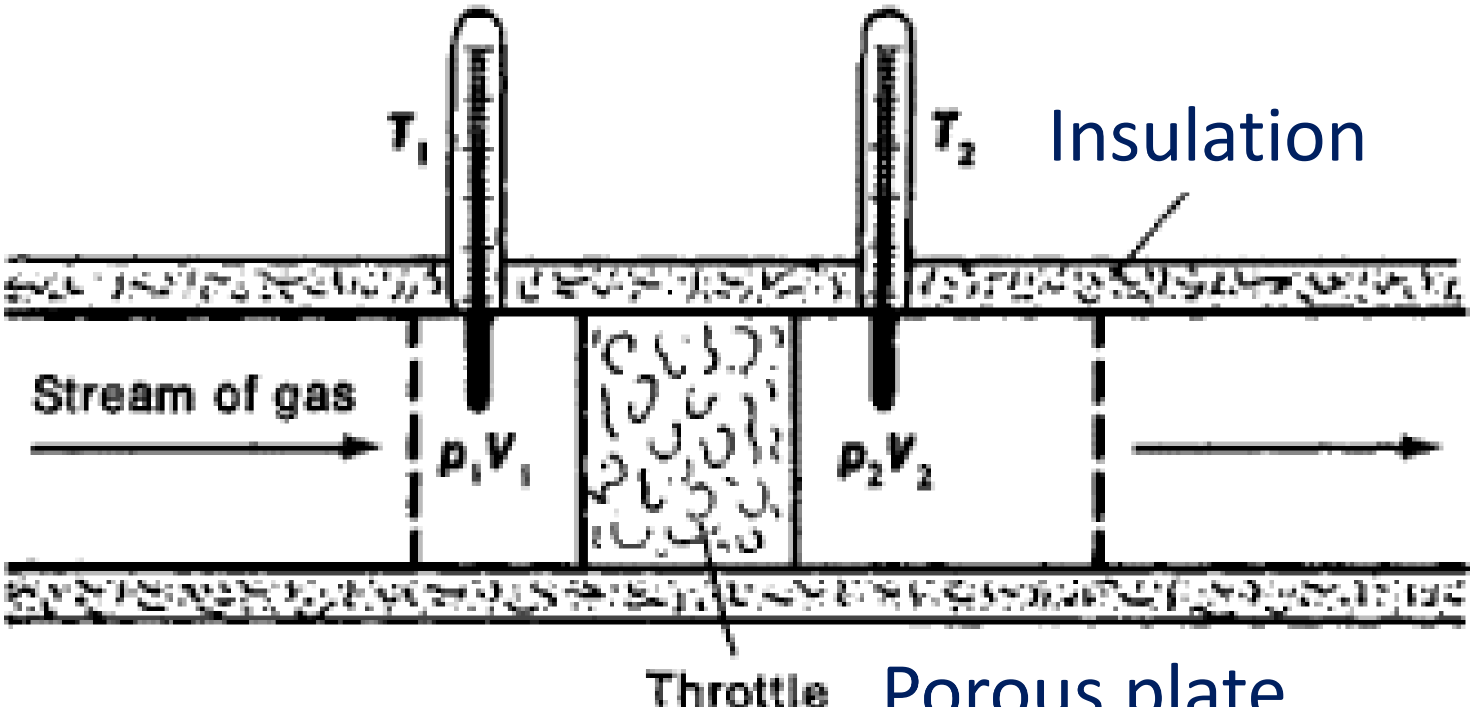
- It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature.

- This presents a problem for substances whose maximum inversion temperature is well below room temperature.

- For hydrogen, for example, the maximum inversion temperature is $-68^{o}C$. Thus, it must be cooled below this temperature if any further cooling is to be achieved by throttling. Hydrogen shows exceptionally a heating effect. Comment?

Mathematically

- By applying a pressure on the left side (piston) so slowly that no change in P_1 occurs but a volume of gas V_1 passes slowly through the porous plug to expand in the right compartment to V_2



- The work done on the system at the left piston is P_1V_1 and the work done by the system at the right piston is P_2V_2.
- The net work done on the system is given by

$$W = (P_1V_1 - P_2V_2) = -(P_2V_2 - P_1V_1)$$

- For adiabatic expansion, $Q = 0$ and $\Delta U = W$.

$$U_2 - U_1 = -P_2V_2 + P_1V_1$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

$$\Delta H = 0$$

Adiabatic processes occurs under constant enthalpy

- Joule & Thomson observed that all real gases (except H_2) undergo cooling during adiabatic expansion.

- ΔT depends on the initial conditions (T, P of the gas, which identify the system enthalpy that will remain constant during expansion).
- The Joule-Thomson coefficient (μ) is give by:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

Consider an adiabatic expansion of a real gas

$$H = H(T, P)$$

$$dH = 0$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$\left(\frac{\partial H}{\partial T}\right)_P = c_P$$

$$c_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$\left(\frac{dT}{dP}\right)_H = -\frac{1}{c_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$\mu = -\frac{1}{c_P}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{c_P}\left(\frac{\partial (U + Pv)}{\partial P}\right)_T$$

$$\mu = -\frac{1}{c_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{c_P}\left(\frac{\partial Pv}{\partial P}\right)_T$$

$\left(\frac{\partial U}{\partial P}\right)_T$ is always −Ve

- Because for real gases, work is done against the intermolecular attraction during expansion
- In adiabatic expansion P decreases and T decreases. In order to keep T constant, the system should receive work from surrounding to increase U

$$\mu = -\frac{1}{C_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_P}\left(\frac{\partial Pv}{\partial P}\right)_T$$

- Therefore, the first term of the above equation leads to cooling effect.

$$\left(\frac{\partial Pv}{\partial P}\right)_T \begin{cases} < 0, \text{ at low P} \longrightarrow \text{cooling /+Ve } \mu \\ > 0, \text{ at High P} \longrightarrow \text{Heating/–Ve } \mu \end{cases}$$

Inversion Temperature

The temperature at which the cooling effect of the first term is equal the heating effect of the second term and thus $\mu=0$.

- At this temperature, the gas will not undergo a temperature change on expansion.
- Above the inversion temperature, the gas undergoes a heating effect upon expansion.
- Below the inversion temperature, the gas undergoes a cooling effect upon expansion.