

Simple thermodynamic systems

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1. Different statements of the second law

We have seen that Clausius defined the second law as **the entropy of an isolated system cannot decrease during a natural process**. From this one can immediately see that Clausius's original form, namely that *heat cannot by itself pass from a colder to a hotter body* immediately follows. For if there was a machine that transforms an amount dQ of heat from system A (with temperature T_1) to system B (with $T_2 > T_1$), then the entropy change would be

$$\Delta S = dQ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) < 0, \quad (1)$$

which violates the principle of entropy increase.

Lord Kelvin had another definition of the second law: **a process whose only effect is the complete conversion of heat into work, cannot occur**. Let us show that Kelvin's and Clausius's definitions are in fact equivalent.

Suppose we have some machine M that extracts heat Q from a heat bath, and converts it completely into work, $W = Q$. The work is done on a body, B (e.g., by lifting it). Since the only net effect of the process is conversion of heat into work, the machine, M must operate in such a way so that at the end of the process it returns to its original state (namely, its operation must be cyclic). Since it returns to its original state, its entropy doesn't change in the process. Similarly, the machine is doing a work on the body B thereby changing some of its external parameters (e.g., lifting it up in the air), but does not change its internal properties such as its entropy. Thus, the total change in entropy is just the change in entropy of the heat bath,

$$\Delta S_{HB} = -\frac{Q}{T} < 0 \quad (2)$$

which violates Clausius's definition of the second law. Thus, Clausius's and Kelvin's definitions are, in fact, equivalent. In reality, only a fraction of the heat extracted from a heat bath can be converted into work. A machine (or device) that converts heat into work is called **heat engine**.

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2. Heat engines

We have seen that there is no such thing as a perfect heat engine, which converts 100% of the heat taken from a heat bath into work: such a machine violates the second law of thermodynamics. However, we can think of (and build) machines which convert part of the heat taken from a heat bath into work: these could work provided the total entropy in the process increases. Thus, such a machine (demonstrated in Figure 1) would in general operate in the following steps:

1. Extract some heat Q_1 from a heat bath at temperature T_1 .
2. Use this heat to do some work, W .
3. Dump the remaining heat Q_2 into another heat bath at lower temperature, $T_2 (< T_1)$. Thus, $Q_2 = Q_1 - W$.

The net entropy change during the cycle is

$$\Delta S = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2}, \quad (3)$$

which must of course be $\Delta S \geq 0$, or

$$Q_2 \geq Q_1 \frac{T_2}{T_1}. \quad (4)$$

Since $W = Q_1 - Q_2$, then the larger Q_2 is, the less work W can be done by the cycle. Thus, generally, we would like to lower Q_2 as much as possible.

We define the **efficiency of a heat engine** by

$$\eta \equiv \frac{W}{Q_1}, \quad (5)$$

which is the ratio of the work done by the system to the amount of heat taken from the heat bath. Of course, ideally we would want $\eta = 1$ - all heat taken is converted to work. As we discussed above, the second law tells us that this is impossible. Using equation 4 we find:

$$\begin{aligned} Q_2 &\geq Q_1 \frac{T_2}{T_1} \\ Q_1 - W &\geq Q_1 \frac{T_2}{T_1} \\ 1 - \eta &\geq \frac{T_2}{T_1} \\ \eta &\leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1} \end{aligned} \quad (6)$$

Obviously, the *maximum theoretical efficiency* occurs when the process is reversible, and the inequality becomes equality. An 'ideal' process with maximum efficiency is known as **Carnot cycle**. Thus, a Carnot cycle has 4 different stages:

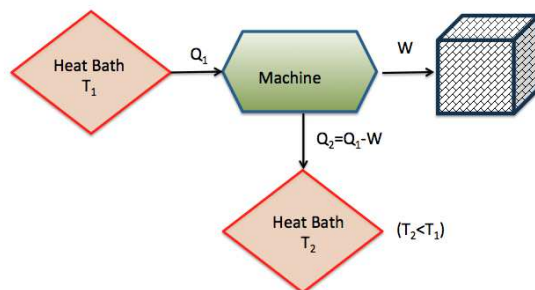


Fig. 1.— A sketch of a heat engine. Heat Q_1 is taken from heat bath at temperature T_1 , and used to do work W on a body. The remaining heat, $Q_2 = Q_1 - W$ is deposited in a second heat bath at temperature $T_2 < T_1$.

1. Extract heat Q_1 from the hotter heat bath at temperature T_1 : this is done at constant temperature, and thus this process is *isothermal*.
2. The working substance of the device is cooled reversibly and adiabatically from T_1 to T_2 : this process is done at constant entropy, and is thus an *isentropic* expansion.
3. Dump an amount of heat Q_2 into the cooler heat bath at T_2 (again, by an isothermal process).
4. The working substance is heated adiabatically and reversibly from T_1 to T_2 by compression; thus, it ends up at the same state as it was at the beginning of the cycle.

Carnot cycle can be carried using various working substances, such as gases, liquids or steam. It is demonstrated in Figure 2.

It is possible to operate a heat engine *backward*, namely to use external work to extract heat from a cooler heat bath and dump it into a hotter heat bath. In this case, the heat engine is called **refrigerator**. In everyday used refrigerators, the work is electrical work. The efficiency of the process can be found in a similar way to that of heat engine, and is

$$\eta = \frac{\text{heat extracted}}{\text{Work required}} = \frac{Q_2}{W} \leq \frac{T_2}{T_1 - T_2}. \quad (7)$$

(Q_2 is the heat extracted from the cooler heat bath). Clearly, the efficiency is maximal when the temperature difference between heat baths is small.

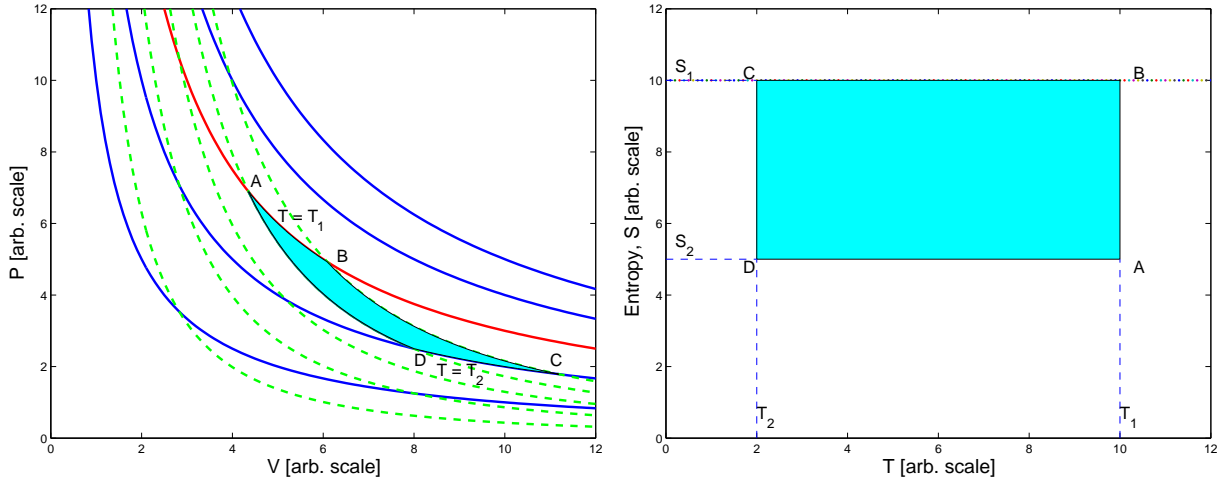


Fig. 2.— A Carnot cycle. Left- in a pV diagram. Right - in temperature - entropy space. The shaded region is equal to the work done.

2.1. Otto cycle

Another important example of heat engine is the **Otto cycle**, which is in everyday use in petrol engines. This cycle contains the following stages:

1. A mixture of air and petrol is compressed adiabatically and reversibly from volume V_2 to volume V_1 .
2. The compression leads to an explosion of the mixture: the explosion sharply increases the pressure and the temperature, while the volume (V_1) is held fixed (amount of heat Q_1 is added).
3. The hot gas pushes the piston back, doing a mechanical work: this expansion from V_1 back to V_2 can be considered reversible and adiabatic.
4. The outlet valve is opened, and the hot exhaust gases rush into the atmosphere; this can be considered as cooling at constant volume V_2 (extracting heat Q_2).

This cycle is seen in Figure 3.

Let us calculate the maximum efficiency of the cycle. The amount of heat absorbed by the gas in step (2):

$$Q_1 = C_V(T_C - T_B) \tag{8}$$

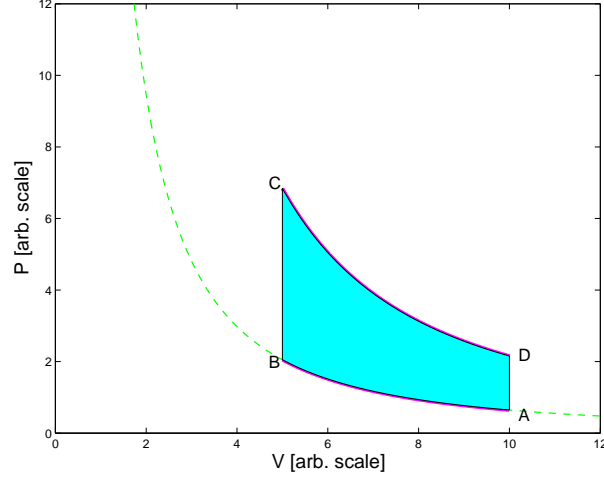


Fig. 3.— Otto cycle in a pV diagram. The shaded region is equal to the work done.

The amount of heat given from the gas to the environment in step (4):

$$Q_2 = C_V(T_D - T_A) \quad (9)$$

The work done:

$$W = Q_1 - Q_2 = C_V(T_C - T_B - T_D + T_A) \quad (10)$$

and the efficiency:

$$\eta = \frac{W}{Q_1} = \frac{T_C - T_B - T_D + T_A}{T_C - T_B} = 1 - \frac{T_D - T_A}{T_C - T_B}. \quad (11)$$

If the gas is considered as *ideal*, this can be simplified by noting that during the adiabatic compression and expansion (steps (1) and (3)), one have

$$\begin{aligned} p_C V_C^\gamma &= p_D V_D^\gamma & ; & & T_C V_C^{\gamma-1} &= T_D V_D^{\gamma-1}; \\ p_B V_B^\gamma &= p_A V_A^\gamma & ; & & T_B V_B^{\gamma-1} &= T_A V_A^{\gamma-1}; \end{aligned} \quad (12)$$

We also know that $V_B = V_C = V_1$, and $V_A = V_D = V_2$, and thus

$$\begin{aligned} T_C V_1^{\gamma-1} &= T_D V_2^{\gamma-1} \\ T_B V_1^{\gamma-1} &= T_A V_2^{\gamma-1}, \end{aligned} \quad (13)$$

which lead to

$$\frac{T_C}{T_B} = \frac{T_D}{T_A}. \quad (14)$$

Using the result of Equation 14, we can write the efficiency in Equation 11 as

$$\eta = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \frac{T_D \left(1 - \frac{T_D}{T_A}\right)}{T_C \left(1 - \frac{T_B}{T_C}\right)} = 1 - \frac{T_D}{T_C} = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}. \quad (15)$$

3. More on heat capacities

Using the second law we can obtain the thermodynamic relation between the heat capacities, expressed in terms of measurable quantities. In real life, C_p is easy to measure, but hard to calculate; while C_V is harder to measure, but easier to calculate.

If we take T and V to be independent variables, we can write the first law of thermodynamics in the form

$$\begin{aligned} dQ &= dE + pdV \\ &= \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT + pdV \\ &= C_V dT + \left[p + \left(\frac{\partial E}{\partial V}\right)_T\right] dV \end{aligned} \quad (16)$$

where $C_V = (\partial Q/\partial T)_V = (\partial E/\partial T)_V$ is the heat capacity per unit volume; pdV is the work done against external force, and the last term, $(\partial E/\partial V)_T dV$ is the change in internal energy caused by changing the mean spacing between the molecules. For **ideal gas**, the internal energy depends only on the temperature, and so the last term vanishes; but life is not always ideal.

Similarly,

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_V + \left[p + \left(\frac{\partial E}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p. \quad (17)$$

In order to proceed, let us have a closer look into the square brackets. Starting from the fundamental thermodynamic relation,

$$dE = TdS - pdV \quad \rightarrow \quad dS = \frac{1}{T}dE + \frac{p}{T}dV, \quad (18)$$

and recalling that V and T are independent variables, one finds

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{1}{T} \left[\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \right] + \frac{p}{T}dV \quad (19)$$

Equate coefficients of dT and dV , one finds:

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V; \\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right]. \end{aligned} \quad (20)$$

Using again the trick of cross-differentiation, $\partial^2 S/(\partial V \partial T) = \partial^2 S/(\partial T \partial V)$, one finds

$$\frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V \right]_T = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right] \right\}_V \quad (21)$$

Since the mixed second order derivatives of E are the same, we get

$$T \left(\frac{\partial p}{\partial T} \right)_V = p + \left(\frac{\partial E}{\partial V} \right)_T \quad (22)$$

Use this result in Equation 17, one finds

$$C_p = C_V + \left[p + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P = C_V + T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (23)$$

Equation 23 allows us to write the difference $C_p - C_V$ in terms of quantities which are relatively easily measured (unlike terms which contain derivatives of the internal energy). If we apply this equation to a perfect gas ($pV = nRT$) then we find

$$C_p - C_V = nR, \quad (24)$$

which is of course in agreement with the thermodynamic relation derived earlier this course.

In the general case, we can proceed by noting that at constant pressure we can use the relation $dp = (\partial p/\partial T)_V dT + (\partial p/\partial V)_T dV = 0$, from which

$$\left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P. \quad (25)$$

Introducing the expansion coefficient,

$$\beta_0 \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (26)$$

and the isothermal compressibility,

$$K_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (27)$$

which are easily measured quantities, we get from Equation 23

$$C_p - C_V = \frac{TV\beta_0^2}{K_T}. \quad (28)$$

All quantities on the right hand side of Equation 28 are easily measured, which enable a quick relation of C_p and C_V . Since K_T is always positive, $C_p \geq C_V$. Both heat capacities are equal if $\beta_0 = 0$, as is, e.g., in water at 4° Celsius.

4. The Joule effect (or Joule expansion)

We have considered several times the free (adiabatic) expansion of gas into a vacuum, that occurs, e.g., when the membrane that separates the gas from the vacuum breaks; the entire (gas + vacuum) system is assumed isolated from the rest of the world. The first to study this process in details was James Joule, and the process is known after him, Joule expansion (or Joule effect). Here, we would want to generalize the treatment to real (non-ideal) gases.

While for ideal gases the internal energy is a function of temperature only, $E = E(T)$, for real gases $E = E(T, V)$. When the gas expands, its energy is conserved; since its volume changes, we therefore expect to see a (small) change in its temperature. Let us quantify this. Start with $dE = 0$, to write

$$\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = 0, \quad (29)$$

which implies

$$\left(\frac{\partial E}{\partial T}\right)_V dT = - \left(\frac{\partial E}{\partial V}\right)_T dV \quad (30)$$

The first thing to note is that both $(\partial E/\partial T)_V$ and $(\partial E/\partial V)_T$ are positive; the first is obvious, while the second originates from an increase in the potential energy of particles with increase in their average separation. Since in an expansion $dV > 0$, Equation 30 implies that $dT < 0$, namely the temperature decreases in free expansion.

A quantitative measure of this expansion is given by the **Joule coefficient**,

$$\alpha_J \equiv \left(\frac{\partial T}{\partial V}\right)_E = - \frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\partial E}{\partial T}\right)_V}. \quad (31)$$

From the discussion following Equation 16, we know that the denominator is $(\partial E/\partial T)_V = C_V$. For the numerator, we repeat the arguments and calculations as in Equations 18 — 22 to write

$$dE = TdS - pdV \quad \rightarrow \quad dS = \frac{1}{T}dE + \frac{p}{T}dV, \quad (32)$$

and recalling that V and T are independent variables,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{1}{T} \left[\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \right] + \frac{p}{T}dV \quad (33)$$

Equate coefficients of dT and dV , one finds:

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V; \\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right]. \end{aligned} \quad (34)$$

Using again the trick of cross-differentiation, $\partial^2 S/(\partial V \partial T) = \partial^2 S/(\partial T \partial V)$,

$$\frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V \right]_T = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[\left(\frac{\partial E}{\partial V} \right)_T + p \right] \right\}_V \quad (35)$$

Since the mixed second order derivatives of E are the same, we get

$$T \left(\frac{\partial p}{\partial T} \right)_V = p + \left(\frac{\partial E}{\partial V} \right)_T \quad (36)$$

Overall, we can write the Joule coefficient in Equation 31 as

$$\alpha_J = -\frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] \quad (37)$$

Example. The equation of state of real gases can be written as

$$pV \simeq RT \left(1 + \frac{B}{V} \right) \quad (38)$$

(per mole). Thus,

$$\alpha_J = -\frac{1}{C_V} \frac{RT^2}{V^2} \frac{dB}{dT}. \quad (39)$$

For Argon gas, at S.T.P. (standard temperature and pressure; $T = 273^\circ \text{ K}$, $p = 1 \text{ Atm}$), $C_V = (3/2)R$ and $dB/dT = 0.25 \text{ cm}^{-3} \text{ K}^{-1} \text{ mol}^{-1}$. Thus, $\alpha_J \approx -2.5 \times 10^{-5} \text{ K cm}^{-2} \text{ mole}$. When the gas expands, its temperature changes. The temperature change is found using Equation 31:

$$\Delta T = T_2 - T_1 = \int_{V_1}^{V_2} \left(\frac{\partial T}{\partial V} \right)_E dV. \quad (40)$$

For constant α_J , doubling the volume ($V_2 - V_1 = 22.4 \times 10^3 \text{ cm}^3 \text{ mole}^{-1}$), $\Delta T = -0.6 \text{ deg}$.

5. The Joule-Thomson effect

By the **Joule-Thomson effect** we refer to a change in the temperature of a gas which occurs during adiabatic expansion of gas through a throttle from high pressure p_1 to lower pressure p_2 . We will now calculate this change in temperature. Similar to the Joule effect, this is an irreversible process.

Assume that before the expansion, the gas occupies volume V_1 , after the expansion - V_2 . We can think of the system as having two pistons, one at each side of the throttle, that keeps the pressures p_1 and p_2 constants (see Figure 4).

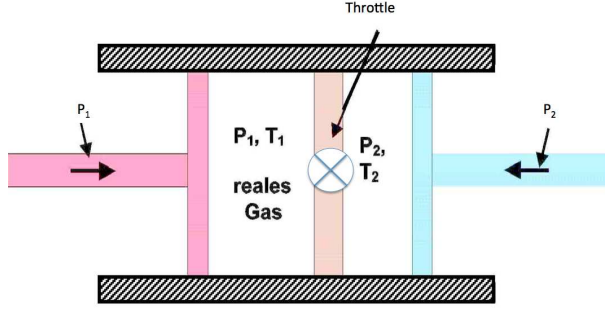


Fig. 4.— The Joule-Thomson expansion through a throttle. The two pistons ensure constant pressures on the two sides of the throttle.

The work done on the gas by the pistons is

$$W = - \int_{V_1}^0 p_1 dV - \int_0^{V_2} p_2 dV = -p_1(0 - V_1) - p_2(V_2 - 0) = p_1 V_1 - p_2 V_2 \quad (41)$$

The device is thermally isolated. Thus, from the first law $\Delta E = Q + W = W$, or

$$\begin{aligned} E_2 - E_1 &= p_1 V_1 - p_2 V_2 \\ E_2 + p_2 V_2 &= E_1 + p_1 V_1. \end{aligned} \quad (42)$$

Recall the definition of the Enthalpy, $H \equiv E + pV$; Equation 42 is simply $H_1 = H_2$. Thus, the Joule-Thomson process conserves the enthalpy - it is an **isenthalpic** process.

We can now repeat similar calculations to those used in calculating the temperature in the Joule effect (Equations 30 - 36), but with H replacing E and p replacing V . We use $dH(T, p) = 0$; The temperature T and the pressure p change during the process, and so

$$\left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp = 0. \quad (43)$$

In analogue to Equation 31 we can define the **Joule-Thomson coefficient**,

$$\alpha_{JT} \equiv \left(\frac{\partial T}{\partial p} \right)_H = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p}. \quad (44)$$

Similar to the discussion on the Joule effect, our goal now is to express α_{JT} using measurable quantities. The denominator in Equation 44 is

$$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial Q}{\partial T} \right)_p = C_p, \quad (45)$$

from which

$$\alpha_{JT} = -\frac{1}{C_p} \left[\left(\frac{\partial E}{\partial p} \right)_T + \left(\frac{\partial(pV)}{\partial p} \right)_T \right]. \quad (46)$$

We can write the numerator using the fundamental relation:

$$\begin{aligned} dE &= TdS - pdV \\ dS &= \frac{1}{T}dE + \frac{p}{T}dV \\ &= \frac{1}{T}dH - \frac{V}{T}dp. \end{aligned} \quad (47)$$

Let us substitute in:

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial p} \right)_T dp + \left(\frac{\partial S}{\partial T} \right)_p dT \\ dH &= \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT. \end{aligned} \quad (48)$$

Equating coefficients of dT , dp , one gets (analogue to Equation 34),

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \right)_p &= \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_p; \\ \left(\frac{\partial S}{\partial p} \right)_T &= \frac{1}{T} \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right]. \end{aligned} \quad (49)$$

cross-differentiate ($\partial^2 S/(\partial p \partial T) = \partial^2 S/(\partial T \partial p)$) and simplify, one gets

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p, \quad (50)$$

from which we obtain

$$\alpha_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]. \quad (51)$$

For an ideal gas, $\alpha_{JT} = 0$; thus, the temperature of the gas doesn't change. However, even for non-ideal gas, $\alpha_{JT} = 0$ provided that

$$T \left(\frac{\partial V}{\partial T} \right)_p = V \quad (52)$$

Equation 52 defines a curve in the $T - p$ plane (see Figure 5): this curve is known as **inversion curve**. Also plotted in the figure are **isenthalps**, curves of constant enthalpy. Inside the inversion curve, T increases with p along isenthalp, and thus $\alpha_{JT} = (\partial T/\partial p)_H > 0$: the gas cools in expansion. Outside the inversion curve, $\alpha_{JT} < 0$, and so the gas *warms up* in expansion. Above a certain temperature, T_i , known as the **inversion temperature**, the gas is always outside the inversion curve, and thus it is always warmed in Joule-Thomson expansion. For most gases, T_i is above room temperature.

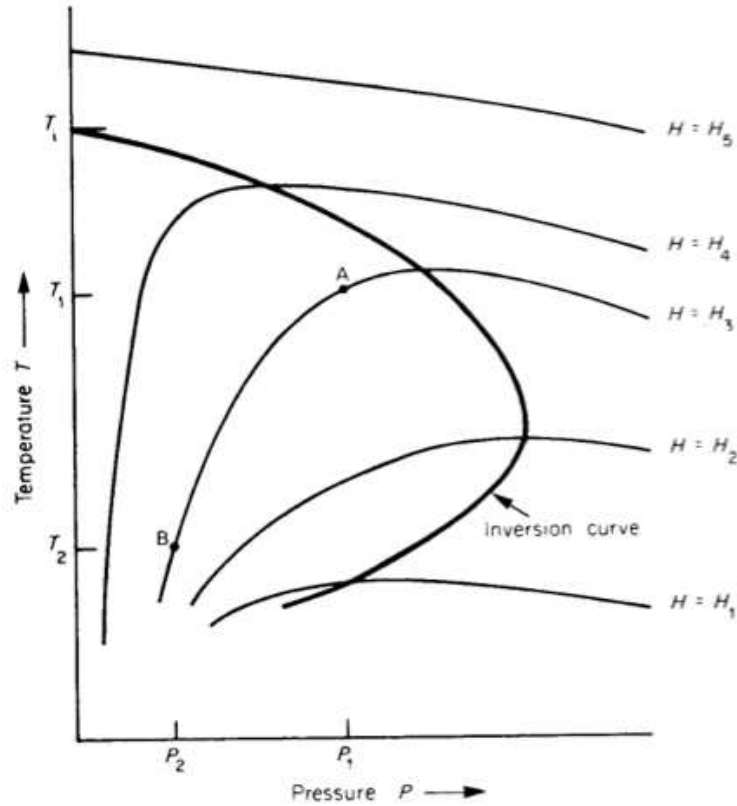


Fig. 5.— Inversion curve in the T - p plane is shown in bold. The solid lines are isenthalps (=curves of constant enthalpy, $H(p, T) = Const$). Inside the inversion curve, T increases with p along isenthalp, while outside it decreases.

Calculation of temperature change during Joule-Thomson expansion is done using

$$\Delta T = T_2 - T_1 = \int_{p_1}^{p_2} \left(\frac{\partial T}{\partial p} \right)_H dp \quad (53)$$

This is difficult to evaluate analytically, since non-ideal gases often do not have a simple relation between T and p . But this equation can easily be solved numerically.

6. Adiabatic cooling

We know from the third law, that when the temperature of a system approaches zero, so does the entropy. Thus, a cooling process is a process in which the entropy decreases.

In a reversible process, the entropy doesn't change, $\Delta S = 0$. Thus, adiabatic cooling

process depends on the the fact that the entropy of a system depends not only on the temperature, but on other parameters as well (e.g., the volume, magnetic field, etc.). We shell label these parameters by α . During a reversible adiabatic process (in a thermally isolated system),

$$S = S(T, \alpha) = \text{Const.} \tag{54}$$

Thus, the process must change the parameter α to compensate for the decrease in temperature, so that over all the entropy will remain constant.

Example - 1. Adiabatic expansion of the gas is a good example of adiabatic cooling. For α we take the pressure. This is a 2-step process:

1. Isothermal compression of gas from p_1 to p_2 : during this process, the gas is in contact with a heat bath of temperature T_1 (line $A - B$ in Figure 6).
2. Heat bath is removed, and the gas is now thermally isolated. It is now allows to expand reversibly and adiabatically back to the lower pressure p_1 (line $B - C$ in Figure 6).

At the end of the process, the gas have the same pressure as initially, but have a lower temperature. This is the basis of **Clausius process** for liquefying gases. (see Figure 6).

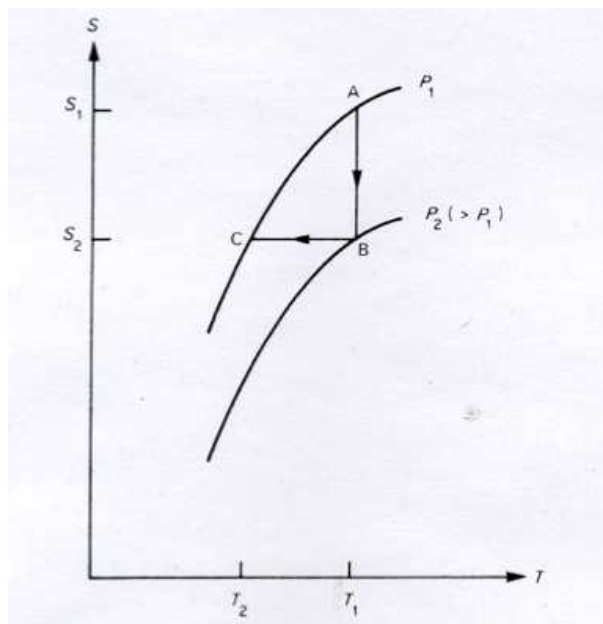


Fig. 6.— Entropy-temperature diagram for cooling of a gas by adiabatic expansion

Example - 2. Adiabatic demagnetization is another powerful method of achieving low temperatures. It is based on the examples discussed earlier about a paramagnetic solid in a magnetic field. The entropy (=amount of disorder) depends on the temperature and on the magnetic field. Thus, if we reversibly decrease the magnetic field, the magnetic moment becomes more disordered - hence the temperature must decrease if S is to be constant.

We can estimate the magnitude of this effect on a paramagnetic solid of N spin 1/2 molecules (we already discussed this system in class):

$$S = \frac{1}{T}(E - F) = \frac{N}{T}(E_1 - F_1) = \frac{N}{T} \left(-\frac{\partial \ln Z_1}{\partial \beta} + k_B T \ln Z_1 \right) \quad (55)$$

Recall that the partition function for a single particle was found to be

$$Z_1 = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2 \cosh \frac{\mu B}{k_B T}, \quad (56)$$

from which we find

$$S = Nk_B \left[\ln \left(2 \cosh \frac{\mu B}{k_B T} \right) - \frac{\mu B}{k_B T} \tanh \frac{\mu B}{k_B T} \right], \quad (57)$$

which is a function of B/T ; hence during step 2 (adiabatic reversible de-magnetization), this ratio remains constant, and the final temperature is

$$\frac{B_f}{T_f} = \frac{B_i}{T_i} \quad \rightarrow \quad T_f = \frac{B_f}{B_i} T_i. \quad (58)$$

For $T_i \approx 1^\circ \text{ K}$, a change in the magnetic field by a factor of ~ 100 , can cool paramagnets down to $\sim 10^\circ \text{ mK}$. This is demonstrated in Figure 7.

And final question: Can this process give us absolute zero ?

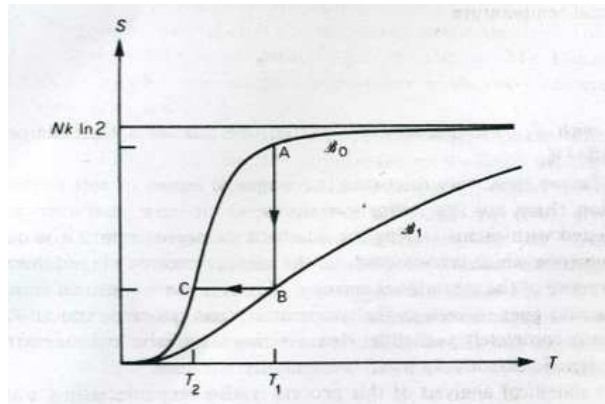


Fig. 7.— Entropy-temperature diagram for a paramagnetic salt, for different applied magnetic fields