



Representation of equation of state using Massieu entropy function

PARAG M AHMEDABADI[✉]* and VIVEKANAND KAIN

Materials Processing and Corrosion Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

*Corresponding author. E-mail: aparag@barc.gov.in

MS received 31 March 2020; revised 29 July 2021; accepted 28 August 2021

Abstract. New entropy functions can be obtained through Legendre transformation on natural variables. Massieu functions are obtained through Legendre transformation on natural variable \mathbf{X} , where \mathbf{X} can be either P , V , S or T . In the present investigation, generalised Massieu functions are derived using other methods and it is shown that these functions can be represented as a total change in \mathbf{X} which is a consequence of relationships among energy potentials. Thus, Massieu functions also follow linear relationships like energy potentials. Variation of energy potentials with natural variables, their partial derivatives, are derived using Massieu functions. It is further shown that variation of energy potentials with natural variables can be represented either as its conjugate or a Massieu function of its conjugate. Massieu entropy function $S_\alpha^* = PV/T$ can be used to represent the equation of state. It follows that for an ideal gas, entropy S_α^* is constant and equal to R , the universal gas constant for ideal gases. Thus, the ideal gas constant is an entropy term. It is also inferred that Boltzmann's constant represents entropy S_α^* of a single element. It is proved that the change in entropy S_α^* during the mixing of distinguishable and indistinguishable ideal gases is zero.

Keywords. Legendre transformation; Massieu function; equation of state; entropy; universal gas constant; Boltzmann constant.

PACS Nos 05.70.-a; 05.70.Ce; 05.90.+m

1. Introduction

Legendre transformation of internal energy, E , leads to new thermodynamic potentials F (Helmholtz free energy), H (enthalpy) and G (Gibbs free energy). Similarly, Legendre transformation of the Lagrangian, \mathcal{L} , in classical mechanics leads to the formulation of the Hamiltonian, \mathcal{H} . In addition, Legendre transformation was also applied to entropy in the following expression:

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \quad (1)$$

This leads to the introduction of new entropy potentials collectively known as Massieu functions [1]:

$$M_1 = -\frac{F}{T}, \quad M_2 = \frac{TS - PV}{T}, \quad M_3 = -\frac{G}{T}.$$

Here, P is the pressure, V is the volume, S is the entropy and T is the temperature of the system. It was argued that for minimum values of F and G , M_1 (at constant T and V) and M_3 (at constant T and P) are maximum [2].

On the other hand, M_2 was described as a mathematical construct with no clear physical meaning [2].

This was generalised by applying Legendre transformation to independent variables P , V , S and T [3]. This leads to new thermodynamic functions known as generalised Massieu potentials [3]. Though the applications of Massieu potentials are limited, they are particularly useful in irreversible thermodynamics, statistical mechanics and in theory of thermal fluctuations [1]. A generalised form of Massieu potential was derived and was shown to be related to Tsallis' entropy S_{2-q} by Wada and Scarfone [4]. Massieu potential was also used for studying variation in free energy changes involved with the stability of proteins and hydrophobic interactions [5]. Recent studies relate Massieu functions to flat geometries in κ -deformed statistical mechanics [6] and to free entropy involved in a system of interacting particles subjected to friction and connected to heat baths [7].

In this paper, Massieu functions are derived using another method and are interpreted as the total change in thermodynamic systems under different conditions. A short-hand notation for Legendre transformation is

introduced and Massieu functions are represented using this notation. Massieu functions are represented in a manner which directly follows from different energy balance relationships. It is shown that Massieu functions can be given statistical representation using partition and grand partition functions. It is also proposed to represent equation of state using a Massieu entropy function.

2. Mathematical preliminaries

Consider a function $\phi(x, y)$ having the differential form:

$$d\phi = \left(\frac{\partial\phi}{\partial x}\right)_y dx + \left(\frac{\partial\phi}{\partial y}\right)_x dy = u dx + v dy. \tag{2}$$

Notation $\phi_{x,y}^*$ will be used for Legendre transformations of ϕ with respect x , for a fixed value of y , when ϕ is expressed as $\phi(x, y)$. Thus,

$$\phi_{x,y}^* = \phi - x \left(\frac{\partial\phi}{\partial x}\right)_y.$$

However, for brevity, the second variable y will be mentioned only under specific cases. Then, Legendre transformation of ϕ with respect to x , y and x & y are denoted as ϕ_x^* , ϕ_y^* and ϕ_{xy}^* , respectively. This notation makes the interpretation and distinction of variables obtained through Legendre transformation easier. As there are several Massieu functions, the notation also eliminates the requirement of individual nomenclature for each Massieu function.

Legendre transformation of x with respect to ϕ is given by rearranging eq. (2):

$$x_\phi^* = x - \frac{\phi}{u} = -\frac{\phi_x^*}{u} \Rightarrow \phi = u(x - x_\phi^*). \tag{3}$$

This represents the generalised form of Legendre transformation of independent variable with respect to the dependent variable. The relationship between ϕ_x^* and x_ϕ^* can be written as

$$\phi_x^* = -u x_\phi^*. \tag{4}$$

This equation implies a one-to-one correspondence between Massieu functions and energy potentials, as mentioned earlier by DeBenedetti [3].

Geometrically, Legendre transformation of the dependent variable ϕ_x^* is the intercept of a tangent on y -axis to curve $\phi(x)$ for a given y . Similarly, x_ϕ^* is the intercept of a tangent on x -axis to curve $x(\phi)$ for a given y . Legendre transformation x_ϕ^* given in eq. (4) cannot be defined for $u = 0$. This corresponds to a point where the slope of the tangent is zero and tangent to the curve is parallel to x -axis.

The differential form of x_ϕ^* can be easily derived:

$$dx_\phi^* = \frac{\phi}{u^2} du - \frac{v}{u} dy. \tag{5}$$

Thus, x_ϕ^* is a function of u and y , that is, it is represented as $x_\phi^*(u, y)$. From eq. (5) we get

$$\left(\frac{\partial x_\phi^*}{\partial y}\right)_u = -\frac{v}{u}, \quad \left(\frac{\partial x_\phi^*}{\partial u}\right)_y = \frac{\phi}{u^2}. \tag{6}$$

From the equality of mixed partial derivatives, eq. (6) gives the following relationship:

$$\left(\frac{\partial\phi}{\partial y}\right)_u = v - u \left(\frac{\partial v}{\partial u}\right)_y = v_{u,y}^*. \tag{7}$$

It is interesting to observe that expression $(\partial\phi/\partial y)_u = v - u(\partial v/\partial u)_y$ can be expressed as Legendre transformation of v with respect to u when v is expressed as $v(u, y)$.

From eq. (5) we get

$$\left(\frac{\partial u}{\partial y}\right)_{x_\phi^*} = \frac{uv}{\phi}.$$

Similarly, from eq. (2), the Legendre transformation of y with respect to ϕ can be obtained and the corresponding partial derivatives can be written. Comparing partial derivatives of x_ϕ^* and y_ϕ^* , we shall get the Maxwell-like relationship:

$$\left(\frac{\partial u}{\partial y}\right)_{x_\phi^*} = \left(\frac{\partial v}{\partial x}\right)_{y_\phi^*} = \frac{uv}{\phi}. \tag{8}$$

So far, Legendre transformation of independent variables with respect to the dependent variables are presented. It can also be applied to other independent variables to get Legendre transformation such as x_y^* and y_x^* . This gives the following Massieu functions:

$$x_y^* = \frac{ux + vy}{u}, \quad y_x^* = \frac{ux + vy}{v}. \tag{9}$$

Analysis presented here pertains to a differential form with two conjugate pairs of variables. This can be easily extended to three or more conjugate pairs. For $d\phi = u dx + v dy + w dz$ with three conjugate pairs (u, x) , (v, y) and (w, z) , it is straightforward to derive new potentials of the forms $\pm ux \pm vy \pm wz$, $\pm ux \pm vy$ or $\pm ux$. Through Legendre transformation on independent variables, we can get new functions of the forms $\pm ux/v$, $(\pm ux \pm vy)/v$ and $(\pm ux \pm vy \pm wz)/v$.

Mathematical analysis given in the present investigation is a generalised treatment and can be applied to any physical phenomenon. The conjugate pairs (u, x) and (v, y) will be different for different applications. For

example, Lagrangian in classical mechanics is given by

$$d\mathcal{L} = \left(\frac{\partial \mathcal{L}}{\partial \dot{q}}\right)_{\dot{q}} d\dot{q} + \left(\frac{\partial \mathcal{L}}{\partial q}\right)_{\dot{q}} dq, \quad \left(\frac{\partial \mathcal{L}}{\partial \dot{q}}\right)_{\dot{q}} = p,$$

where the terms have their usual meaning [8]. Hamiltonian \mathcal{H} is derived by Legendre transformation of \mathcal{L} with respect to \dot{q} (that is, $\mathcal{H} = \mathcal{L}_{\dot{q}}^*$) and is given by $\mathcal{H} = p\dot{q} - \mathcal{L}$. Then, Legendre transformation of \dot{q} with respect to \mathcal{L} and of p with respect to \mathcal{H} are given by

$$\dot{q}_{\mathcal{L}}^* = \frac{\mathcal{H}}{p}, \quad p_{\mathcal{H}}^* = \frac{\mathcal{L}}{\dot{q}} \Rightarrow \mathcal{H} = p\dot{q}_{\mathcal{L}}^*, \quad \mathcal{L} = \dot{q}p_{\mathcal{H}}^*.$$

3. Derivation of Massieu functions

Legendre transformation of internal energy $E (= \phi)$ are $\phi_x^* = F$, $\phi_y^* = H$ and $\phi_{xy}^* = G$. By comparing eq. (1) with eq. (2), we get $\phi = E$, $u = T$, $x = S$, $v = -P$, $y = V$. The differential form of these energy potentials are given by

$$\begin{aligned} dE &= TdS - PdV, & dF &= -SdT - PdV \\ dH &= TdS + VdP, & dG &= -SdT + VdP. \end{aligned} \quad (10)$$

Maxwell relationships are as follows:

$$\begin{aligned} -\left(\frac{\partial T}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial S}\right)_V, & \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P, & -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P. \end{aligned} \quad (11)$$

Massieu functions can be easily written using equations derived in the previous section. Table 1 summarises Massieu functions derived along with their partial derivatives. Observe that in column (4), the partial derivatives have the same energy potentials on both sides. Massieu functions are intercepts on x -axis of tangents to energy potentials curves and, their values are specific to a particular system. It is obvious from eq. (3) that Massieu functions cannot be defined when thermodynamic variable \mathbf{X} is zero. Hereafter, thermodynamic variables P, V, S, T will be referred to as \mathbf{X} , that is, $\mathbf{X} \in \{P, V, S, T\}$.

Legendre transformation of one \mathbf{X} with respect to another \mathbf{X} can be obtained using eq. (9). For example, entropy Massieu functions are S_V^* and S_P^* have the following relationships:

$$\mathbb{W} = T(S - S_V^*), \quad \mathbb{W} = -T(S - S_P^*). \quad (12)$$

Here, $\mathbb{W} = PV$ is related to mechanical work, referred to as w -potential and $\mathbb{Q} = TS$ is related to heat and referred to as q -potential. Let $U_\beta = TS + PV = \mathbb{Q} + \mathbb{W} = H - F$ and $U_\alpha = TS - PV = \mathbb{Q} - \mathbb{W} =$

$E - G$. Then, Massieu functions given in eq. (12) can be expressed as

$$U_\alpha = TS_V^*$$

and

$$U_\beta = TS_P^*.$$

If Legendre transformation is applied to U_α and U_β , we can obtain new energy potentials $-TS + PV$ and $-TS - PV$. Collectively, we get four potentials, $U_i = \pm TS \pm PV$ or $\pm U_\alpha$ and $\pm U_\beta$. Other energy potentials that can be obtained are $\pm TS$ and $\pm PV$. It is interesting to see that when U_i is expressed as a function of natural variables, Legendre transformation on U_i generates new energy potentials that are negative energy potentials E, F, G and H .

The variational form of U_α is

$$dU_\alpha = d\mathbb{Q} - d\mathbb{W} = TdS + SdT - d\mathbb{W}.$$

From this, we can express entropy S as:

$$dS = \frac{1}{T}dU_\alpha - \frac{S}{T}dT + \frac{1}{T}d\mathbb{W}.$$

If we denote Legendre transformation of entropy S with respect to U_α as S_α^* , then

$$S_\alpha^* = \frac{PV}{T}. \quad (13)$$

Legendre transformation for other variables can be easily derived.

$$P_\alpha^* = \frac{ST}{V}, \quad V_\alpha^* = \frac{ST}{P}, \quad T_\alpha^* = \frac{PV}{S} \quad (14)$$

and from the expression of U_β we get

$$\begin{aligned} S_\beta^* &= -\frac{PV}{T}, & T_\beta^* &= -\frac{PV}{S} \\ V_\beta^* &= -\frac{ST}{P}, & P_\beta^* &= -\frac{ST}{V}. \end{aligned} \quad (15)$$

Thus, Massieu functions derived from variational forms of U_α and U_β are equal in magnitude and opposite in sign. Thermodynamic parameters T and P that are equal in magnitude and opposite in sign were earlier reported by Dunkel and Hilbert for a quantum particle in an infinite box [9]. However, the difference is two values with opposite signs which were obtained for different models of entropy, viz. Gibbs and Boltzmann. It is worth mentioning here that irrespective of the model chosen for representing entropy, the corresponding values of S_α^* and S_β^* remain the same. Since a negative value of temperature for the Boltzmann entropy model corresponds to a negative value of pressure, $S_\alpha^* = PV/T$ remains positive. Similarly, S_α^* corresponding to Gibbs' entropy model also remains positive. This is true in

Table 1. Definitions of Massieu functions, their variational forms and partial derivatives.

(1)	(2)	(3)	(4)	(5)
$-\frac{E}{T} = S_E^* - S$	$-\frac{F}{T} = S_E^*$	$dS_E^* = \frac{E}{T^2}dT + \frac{P}{T}dV$	$\left(\frac{\partial S_E^*}{\partial T}\right)_V = \frac{E}{T^2}$	$\left(\frac{\partial S_E^*}{\partial V}\right)_T = \frac{P}{T}$
$\frac{E}{P} = V_E^* - V$	$\frac{H}{P} = V_E^*$	$dV_E^* = -\frac{E}{P^2}dP + \frac{T}{P}dS$	$\left(\frac{\partial V_E^*}{\partial P}\right)_S = -\frac{E}{P^2}$	$\left(\frac{\partial V_E^*}{\partial S}\right)_P = \frac{T}{P}$
$\frac{F}{S} = T_F^* - T$	$\frac{E}{S} = T_F^*$	$dT_F^* = -\frac{F}{S^2}dS - \frac{P}{S}dV$	$\left(\frac{\partial T_F^*}{\partial S}\right)_V = -\frac{F}{S^2}$	$\left(\frac{\partial T_F^*}{\partial V}\right)_S = -\frac{P}{S}$
$\frac{F}{P} = V_F^* - V$	$\frac{G}{P} = V_F^*$	$dV_F^* = -\frac{F}{P^2}dP - \frac{S}{P}dT$	$\left(\frac{\partial V_F^*}{\partial P}\right)_T = -\frac{F}{P^2}$	$\left(\frac{\partial V_F^*}{\partial T}\right)_P = -\frac{S}{P}$
$-\frac{H}{T} = S_H^* - S$	$-\frac{G}{T} = S_H^*$	$dS_H^* = \frac{H}{T^2}dT - \frac{V}{T}dP$	$\left(\frac{\partial S_H^*}{\partial T}\right)_P = \frac{H}{T^2}$	$\left(\frac{\partial S_H^*}{\partial P}\right)_T = -\frac{V}{T}$
$-\frac{H}{V} = P_H^* - P$	$-\frac{E}{V} = P_H^*$	$dP_H^* = \frac{H}{V^2}dV - \frac{T}{V}dS$	$\left(\frac{\partial P_H^*}{\partial V}\right)_S = \frac{H}{V^2}$	$\left(\frac{\partial P_H^*}{\partial S}\right)_V = -\frac{T}{V}$
$\frac{G}{S} = T_G^* - T$	$\frac{H}{S} = T_G^*$	$dT_G^* = -\frac{G}{S^2}dS + \frac{V}{S}dP$	$\left(\frac{\partial T_G^*}{\partial S}\right)_P = -\frac{G}{S^2}$	$\left(\frac{\partial T_G^*}{\partial P}\right)_S = \frac{V}{S}$
$-\frac{G}{V} = P_G^* - P$	$-\frac{F}{V} = P_G^*$	$dP_G^* = \frac{G}{V^2}dV + \frac{S}{V}dT$	$\left(\frac{\partial P_G^*}{\partial V}\right)_T = \frac{G}{V^2}$	$\left(\frac{\partial P_G^*}{\partial T}\right)_V = \frac{S}{V}$

the case of S_β^* too; different entropy models give the same value for S_β^* . As $dS \geq 0$, from eq. (1) we have $(\partial S/\partial V)_E \geq P/T \geq 0$; this necessarily means that when $T < 0$ we must have $P < 0$ [10].

4. Alternative derivations of Massieu functions

Massieu functions can also be derived using a different approach. Different thermodynamic energy potentials are prevalent under different conditions. For example, Helmholtz free energy F is prevalent for a system undergoing isothermal and isochoric transformations. In such cases, the entropy of the combined system – system and heat bath (or surroundings) – always increases. It is trivial to show that the total entropy change represents a Massieu entropy function. Let the heat bath be at constant temperature T' and ΔQ be the amount of heat transferred from the bath to the system. The total change in entropy, ΔS^* , of the combined system (system + bath) is given by $\Delta S^* = \Delta S + \Delta S'$. Entropy $\Delta S'$ is related to the amount of heat transfer as $\Delta S' = -\Delta Q/T'$. As no mechanical work is done, $\Delta Q = \Delta E \Rightarrow \Delta S' = -\Delta E/T'$. Under equilibrium, the system and the heat bath are at the same temperature $T = T'$. Then, ΔS^* is given by [11]

$$\Delta S^* = \Delta S - \frac{\Delta E}{T} = -\frac{\Delta F}{T} = \Delta S_E^*. \quad (16)$$

It may be noted that the expression for ΔP_G^* can be derived from eq. (16).

$$T \Delta S_E^* = T \Delta S - \Delta E = V \Delta P - \Delta G.$$

Now, $F = -TS_E^* = -VP_G^*$. Then, for constant V and T , we have $T \Delta S_E^* = V \Delta P_G^*$. Substituting this in the above equation, we get

$$V \Delta P_G^* = V \Delta P - \Delta G \Rightarrow \Delta P_G^* = \Delta P + \Delta P',$$

where $\Delta P' = -\Delta G/V$ represents the change in pressure in the heat bath and ΔP is the change in pressure of the system. Thus, the Massieu pressure function P_G^* represents the total change in pressure of the systems undergoing changes at constant volume and temperature.

It may be emphasised that the expressions for change in parameters can be deduced from the first column of table 1. Thus, from $G = S(T_G^* - T)$, we can infer that the change in temperature of the heat bath during transformation at constant S and P is given by $\Delta T' = \Delta G/S = \Delta T_G^* - \Delta T$.

The expressions given in column (1) of table 1 follows from relationships between thermodynamic energy potentials. For example, $F = E - TS$, that is, $F/T = E/T - S$. Then, defining F/T and E/T as different forms of entropy, we get $S_E^* = S + S'$. This can also be applied to Massieu functions given in eq. (12). For example, for $S_V^* = (TS - PV)/T$, we have

$$S_V^* = S - \frac{PV}{T} = S - \frac{\mathbb{W}}{T}.$$

Massieu functions S_P^* is given by $S_P^* = (TS + PV)/T$ and can be written as

$$S_P^* = S + \frac{PV}{T} = S + \frac{\mathbb{W}}{T}.$$

In the above two equations, the opposite sign of \mathbb{W} indicates the opposite directions of the change. Hence, the change in entropy of the combined system for S_P^* is $\mathbb{W}/T = S_\alpha^*$ and for S_V^* it is $-\mathbb{W}/T = S_\beta^*$. It may also be noted that the expression for S_V^* can also be derived for a system such that internal energy of the system under consideration remains constant during the process. In such cases, $\Delta E = \Delta Q - \Delta W = 0$. Hence,

$\Delta Q = P \Delta V$. Therefore,

$$\Delta S^* = \Delta S - \frac{\Delta Q}{T} = \frac{T \Delta S - P \Delta V}{T} = \Delta S_V^*.$$

This method of deriving Massieu functions can be generalised as

$$\mathbf{X}_\phi^* = \mathbf{X} + \mathbf{X}', \quad (17)$$

where $\mathbf{X} \in \{P, V, S, T\}$, \mathbf{X}' represents the corresponding change and \mathbf{X}_ϕ^* denotes the total change, that is, the corresponding Massieu function. Here, \mathbf{X}' is expressed as the ratio of the energy potential ϕ , $\phi \in \{E, F, G, H, U_\alpha, U_\beta, Q, W\}$ and the conjugate variable of \mathbf{X} . Here, ϕ always represents the potential (w or q) corresponding to the conjugate pair other than that contains \mathbf{X} . Similarly, energy potentials obtained through Legendre transformation on E are linearly related to each other if we consider PV and TS as thermodynamic potentials corresponding to the amount of work and heat exchange, respectively. For example, $F = E - TS$.

Massieu entropy function S_α^* can be split into two terms as

$$S_\alpha^* = S - \frac{U_\beta}{T}.$$

Entropy S_α^* can also be represented in another way by considering thermodynamic systems that are capable of exchanging particles. So we can apply eq. (17). For such systems, the differential form of E is given by

$$dE = TdS - PdV + \mu dN,$$

where μ is the chemical potential of the system and N is the number of particles. Legendre transformation on E with respect to all variables will give grand potential $\Phi_G = E - TS - \mu N$. So, when we consider a combined system capable of exchanging heat and particles, the total entropy change in such a system $\Delta S^* = \Delta S + \Delta S'$ is given by (at constant T):

$$\begin{aligned} \Delta S^* &= \frac{T \Delta S - \Delta E + \mu \Delta N}{T} = -\frac{\Delta \Phi_B}{T} \\ &= \frac{\Delta(PV)}{T} = \Delta S_\alpha^*. \end{aligned}$$

We have used the relationship $\Phi_B = -PV$ assuming homogeneous system. As $\Delta S^* \geq 0$, we have $\Delta S_\alpha^* \geq 0$.

Variations in Massieu functions can be related to the corresponding change in energy potentials, as described now.

Helmholtz free energy, F : It is clear that ΔS_E^* and ΔP_G^* are proportional to ΔF (see table 1). For a finite change in such systems, we have $\Delta F \leq 0$. It implies that $\Delta S_E^*, \Delta P_G^* \geq 0$. For $\Delta S_E^* \geq 0$, we have

$$\Delta S_E^* \equiv \Delta S - \frac{\Delta E}{T} \geq 0 \Rightarrow \Delta S \geq \frac{\Delta E}{T}.$$

For $\Delta E \rightarrow 0$, infinitesimal change in energy, we have

$$T \geq \left(\frac{\partial S}{\partial E} \right)^{-1}.$$

The equality holds for the equilibrium, that is, $T \equiv (\partial S / \partial E)^{-1}$, as followed from eq. (1).

Gibbs free energy, G : Changes in Massieu functions, ΔS_H^* and ΔV_F^* , are proportional to ΔG . For equilibrium, $\Delta G = 0$. Therefore, $\Delta V_F^* = 0$ and $\Delta S_H^* = 0$. A spontaneous change is given by $\Delta G < 0$. Then, we have $\Delta S_H^* > 0$ and $\Delta V_F^* < 0$.

Enthalpy, H : Changes ΔV_E^* and ΔT_G^* are proportional to the change in enthalpy, ΔH . For $\Delta H = 0$, we have $\Delta V_E^* = 0$ and $\Delta T_G^* = 0$. Further, for exothermic processes $\Delta H < 0$. Hence, $\Delta V_E^* < 0$ and $\Delta T_G^* < 0$. Similarly, for endothermic processes $\Delta H > 0$ and hence, $\Delta V_E^* > 0$ and $\Delta T_G^* > 0$.

Internal energy, E : Changes in T_F^* and P_H^* are proportional to E . For an ideal gas, internal energy depends only on its temperature. Hence, for isothermal processes, $\Delta P_H^* = 0$ and $\Delta T_F^* = 0$. Further, for processes that involve increase in temperature of an ideal gas, we have $\Delta P_H^* < 0$ and $\Delta T_F^* > 0$ and vice-versa.

5. Thermodynamic variables as functions of partial derivatives

Thermodynamic variables can be represented as functions of partial derivatives. For example, from eq. (10), we have

$$P = T \left(\frac{\partial S}{\partial V} \right)_E.$$

Massieu functions follow similar relationships according to eq. (6). For example, we have

$$P = T \left(\frac{\partial S_E^*}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V_E^*} \right)_P.$$

This can be extended to other variables. In addition, we have $F = -T S_E^*$ and $G = -T S_H^*$. Then, it is clear that

$$T = - \left(\frac{\partial S_E^*}{\partial F} \right)_T = - \left(\frac{\partial S_H^*}{\partial G} \right)_T.$$

This is analogous to the expression obtained when entropy S is represented as $S(E, V)$ and $S(H, P)$ in eq. (10):

$$T = \left(\frac{\partial S}{\partial E} \right)_V = \left(\frac{\partial S}{\partial H} \right)_P.$$

In a similar fashion, we write relationships for other variables as summarised in table 2. These relationships

Table 2. Symmetrical relationships between thermodynamic variables and Massieu functions.

$T =$	$\left(\frac{\partial S}{\partial E}\right)_V^{-1}$	$\left(\frac{\partial S}{\partial H}\right)_P^{-1}$	$-\left(\frac{\partial S_E^*}{\partial F}\right)_T^{-1}$	$-\left(\frac{\partial S_H^*}{\partial G}\right)_T^{-1}$	$\left(\frac{\partial S_\alpha^*}{\partial W}\right)_T^{-1}$	$-\left(\frac{\partial S_\beta^*}{\partial W}\right)_T^{-1}$
$P =$	$-\left(\frac{\partial V}{\partial F}\right)_P^{-1}$	$-\left(\frac{\partial V}{\partial E}\right)_S^{-1}$	$\left(\frac{\partial V_F^*}{\partial G}\right)_P^{-1}$	$\left(\frac{\partial V_E^*}{\partial H}\right)_P^{-1}$	$-\left(\frac{\partial V_\alpha^*}{\partial Q}\right)_P^{-1}$	$\left(\frac{\partial V_\beta^*}{\partial Q}\right)_P^{-1}$
$V =$	$\left(\frac{\partial P}{\partial H}\right)_S^{-1}$	$\left(\frac{\partial P}{\partial G}\right)_T^{-1}$	$-\left(\frac{\partial P_H^*}{\partial E}\right)_V^{-1}$	$-\left(\frac{\partial P_G^*}{\partial F}\right)_V^{-1}$	$-\left(\frac{\partial P_\alpha^*}{\partial Q}\right)_V^{-1}$	$\left(\frac{\partial P_\beta^*}{\partial Q}\right)_V^{-1}$
$S =$	$-\left(\frac{\partial T}{\partial G}\right)_P^{-1}$	$-\left(\frac{\partial T}{\partial F}\right)_V^{-1}$	$\left(\frac{\partial T_G^*}{\partial H}\right)_S^{-1}$	$\left(\frac{\partial T_E^*}{\partial E}\right)_S^{-1}$	$\left(\frac{\partial T_\alpha^*}{\partial W}\right)_S^{-1}$	$-\left(\frac{\partial T_\beta^*}{\partial W}\right)_S^{-1}$
$P =$	$T \left(\frac{\partial S}{\partial V}\right)_E$	$T \left(\frac{\partial S}{\partial V^*}\right)_P$	$T \left(\frac{\partial S_E^*}{\partial V}\right)_T$	$-S \left(\frac{\partial T}{\partial V}\right)_F$	$-S \left(\frac{\partial T}{\partial V^*}\right)_P$	$-S \left(\frac{\partial T_E^*}{\partial V}\right)_S$
$V =$	$S \left(\frac{\partial T}{\partial P}\right)_G$	$S \left(\frac{\partial T}{\partial P^*}\right)_V$	$S \left(\frac{\partial T_G^*}{\partial P}\right)_S$	$-T \left(\frac{\partial P}{\partial S}\right)_H$	$-T \left(\frac{\partial S}{\partial P^*}\right)_V$	$-T \left(\frac{\partial S_H^*}{\partial P}\right)_S$
$T =$	$-V \left(\frac{\partial P}{\partial S}\right)_H$	$-V \left(\frac{\partial P}{\partial S^*}\right)_T$	$-V \left(\frac{\partial P_H^*}{\partial S}\right)_V$	$P \left(\frac{\partial V}{\partial S}\right)_E$	$P \left(\frac{\partial V}{\partial S^*}\right)_T$	$P \left(\frac{\partial V_E^*}{\partial S}\right)_P$
$S =$	$-P \left(\frac{\partial V}{\partial T}\right)_F$	$-P \left(\frac{\partial V}{\partial T^*}\right)_S$	$-P \left(\frac{\partial V_F^*}{\partial T}\right)_P$	$V \left(\frac{\partial P}{\partial T}\right)_G$	$V \left(\frac{\partial P}{\partial T^*}\right)_S$	$V \left(\frac{\partial P_G^*}{\partial T}\right)_V$

indicate that variations of Massieu functions are identical to that of thermodynamic variables. The first four rows of table 2 show that Massieu functions provide remaining two partial derivatives of energy potential ϕ for variable \mathbf{X} . That is, we can express each \mathbf{X} as partial derivative of its conjugate variable with respect to each of the four energy potentials given by ϕ .

6. Characteristics of Massieu functions

Massieu functions enable representation of energy potentials as either q -potential or w -potential (table 1). By equating expressions of each thermodynamic potential in column (1) of table 1, we get similar relationships for potentials U_α and U_β :

$$U_\alpha = TS + PV = TS_E^* + PV_E^* = ST_G^* + VP_G^*$$

$$U_\beta = TS - PV = TS_H^* - VP_H^* = ST_F^* - PV_F^*.$$

It can be seen that U_α and U_β represent ‘mixed’ potentials that contain both w - and q -potentials. These expressions are indicative of energy balance as in the case of energy potentials. It is interesting to observe that such expressions involving Massieu functions associated with different potentials are all zero. This can be readily deduced by expressions of the given energy potential in column (2) of table 1.

$$TS_E^* - VP_G^* = ST_G^* - PV_E^*$$

$$= ST_F^* + VP_H^* = PV_F^* + TS_H^* = 0.$$

Using the definitions of Massieu functions, it is easy to show that Massieu functions of one kind are linearly related. This is analogous to thermodynamic energy

potentials that are also linearly related if TS and PV are treated as energy potentials. From table 1 we get

$$P_G^* - P_H^* = \frac{TS}{V} = P_\alpha^*, \quad V_E^* - V_F^* = \frac{TS}{P} = V_\alpha^*,$$

$$T_G^* - T_F^* = \frac{PV}{S} = T_\alpha^*, \quad S_E^* - S_H^* = \frac{PV}{T} = S_\alpha^*. \quad (18)$$

From eq. (12), we get the following linear relationships:

$$S_V^* = S - S_\alpha^*, \quad S_P^* = S + S_\alpha^*, \quad S_P^* + S_V^* = 2S.$$

From the above two equations we get more linear relationships:

$$S = S_V^* + S_E^* - S_H^* = S_P^* + S_H^* - S_E^*.$$

Equations (14) and (15) will give:

$$P_\alpha^* + P_\beta^* = V_\alpha^* + V_\beta^* = T_\alpha^* + T_\beta^* = S_\alpha^* + S_\beta^* = 0.$$

It is also trivial to derive following:

$$\frac{T_P^*}{S_V^*} = \frac{T_V^*}{S_P^*} = \frac{T_\alpha^*}{S_\alpha^*} = \frac{T_\beta^*}{S_\beta^*} = \frac{T}{S}.$$

Similar ratio exists for Massieu functions for conjugate pair (P, V) . Thus, the ratios of variables in conjugate pair are equal for Massieu functions as well as thermodynamic variables. Also,

$$\chi = \frac{W}{Q} = \frac{PV}{ST} = \frac{P_H^* V_F^*}{S_H^* T_F^*} = \frac{P_G^* V_E^*}{S_E^* T_G^*}$$

$$\frac{1}{\chi^3} = \left(\frac{Q}{W}\right)^3 = \left(\frac{TS}{PV}\right)^3 = \frac{P_\alpha^* V_\alpha^*}{S_\alpha^* T_\alpha^*} = \frac{P_\beta^* V_\beta^*}{S_\beta^* T_\beta^*}$$

$$-\frac{1}{\chi} = -\frac{Q}{W} = -\frac{ST}{PV} = \frac{P_S^* V_T^*}{S_P^* T_P^*} = \frac{P_T^* V_S^*}{S_V^* T_V^*}.$$

Massieu functions provide another method to derive thermodynamic relationships, e.g., partial derivatives of energy potentials with respect to variable \mathbf{X} can be written using the generalised expression given in eq. (7). These relationships are

$$\begin{aligned} \left(\frac{\partial E}{\partial V}\right)_T &= -P + T\left(\frac{\partial P}{\partial T}\right)_V, \\ \left(\frac{\partial E}{\partial S}\right)_P &= T - P\left(\frac{\partial T}{\partial P}\right)_S, \\ \left(\frac{\partial F}{\partial V}\right)_S &= -P + S\left(\frac{\partial P}{\partial S}\right)_V, \\ \left(\frac{\partial F}{\partial T}\right)_P &= -S + P\left(\frac{\partial S}{\partial P}\right)_T, \\ \left(\frac{\partial H}{\partial P}\right)_T &= V - T\left(\frac{\partial V}{\partial T}\right)_P, \\ \left(\frac{\partial H}{\partial S}\right)_V &= T - V\left(\frac{\partial T}{\partial V}\right)_S, \\ \left(\frac{\partial G}{\partial P}\right)_S &= V - S\left(\frac{\partial V}{\partial S}\right)_P, \\ \left(\frac{\partial G}{\partial T}\right)_V &= -S + V\left(\frac{\partial S}{\partial V}\right)_T. \end{aligned}$$

These relationships can be derived using other methods too [12]. A closer look indicates that the right-hand side of these expressions can be expressed as Massieu functions. For example, $(\partial E/\partial S)_P = T - P(\partial T/\partial P)_S$ is a Massieu function of T with respect to P when T is expressed as $T(P, S)$, where S is kept constant. This Massieu function can be written as $T_{P,S}^*$. The mention of the second variable in Massieu functions listed in table 1 is omitted for brevity. Therefore, the variations of energy potentials with \mathbf{X} (partial derivative with respect to \mathbf{X}) is either \mathbf{X}_c , its conjugate variable, or a Massieu function of its conjugate, that is, \mathbf{X}_c^* . Thus, variations of E with respect to S under different conditions are $(\partial E/\partial S)_V = T$ and $(\partial E/\partial S)_P = T_{P,S}^* = T_P^*$. This can help one to write variational form of energy potentials in terms of different natural variables. For example, when E is expressed as $E(S, P)$, it gives

$$dE = \left(\frac{\partial E}{\partial P}\right)_S dP + \left(\frac{\partial E}{\partial S}\right)_P dS = T_P^* dP + T dS.$$

Partial derivatives of Massieu functions given in column (4) of table 1 can be written collectively as

$$\left(\frac{\partial \mathbf{X}_\phi^*}{\partial \mathbf{X}_c}\right)_Y = \pm \frac{\phi}{\mathbf{X}_c^2},$$

where the sign of the right-hand side is the same as that of \mathbf{X}_c in $d\phi$ in eq. (10). \mathbf{X}_c is the conjugate variable of \mathbf{X} and $\mathbf{Y} \in \{P, V, S, T\}$ is not conjugate of \mathbf{X} . This relation can

be used to derive Gibbs–Helmholtz equations because $\mathbf{X}_\phi^* = \pm \phi/\mathbf{X}_c$. For example, Massieu entropy function S_H^* [13],

$$\left(\frac{\partial S_H^*}{\partial T}\right)_P = \frac{H}{T^2} \Rightarrow \left[\frac{\partial}{\partial T}\left(-\frac{G}{T}\right)\right]_P = \frac{H}{T^2}.$$

This represents one of the Gibbs–Helmholtz equations from which the van't Hoff equation can be derived.

Entropy Massieu functions S_H^* and S_E^* are known as Massieu potential and Planck potential, respectively. These potentials are maximised when energy potentials are minimised [14]. Massieu potential S_H^* is related to the equilibrium constant K through the following relationship (at constant temperature):

$$\Delta G^\circ = -RT \ln K \Rightarrow \Delta S_H^* = R \ln K,$$

where R is the universal gas constant and K is the equilibrium constant. Further, Massieu entropy function S_H^* is given by (see table 1)

$$\Delta S_H^* = -\frac{\Delta H}{T} + \Delta S.$$

This is nothing but another representation of van't Hoff equation, represented in usual notation as:

$$\ln K = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}.$$

Maxwell-like relationships involving Massieu functions can be written using eq. (8) and are similar in nature to Maxwell relationships for thermodynamic variables \mathbf{X} , eq. (11).

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{S_E^*} &= -\left(\frac{\partial P}{\partial S}\right)_{V_E^*} = -\frac{PT}{E} \\ \left(\frac{\partial V}{\partial S}\right)_{P_H^*} &= \left(\frac{\partial T}{\partial P}\right)_{S_H^*} = \frac{VT}{H} \\ \left(\frac{\partial S}{\partial P}\right)_{T_G^*} &= -\left(\frac{\partial V}{\partial T}\right)_{P_G^*} = \frac{SV}{G} \\ \left(\frac{\partial S}{\partial V}\right)_{T_F^*} &= \left(\frac{\partial P}{\partial T}\right)_{V_F^*} = -\frac{PS}{F}. \end{aligned} \tag{19}$$

These Maxwell relationships are identical, except that the variable that is kept constant for taking partial derivative is a natural variable in eq. (11) whereas in eq. (19) it is a Massieu function. Thermodynamic relationships given in column (5) can be collectively written as

$$\left(\frac{\partial \mathbf{X}_\phi^*}{\partial \mathbf{Y}}\right)_{\mathbf{X}_c} = \pm \frac{\mathbf{Y}_c}{\mathbf{X}},$$

where \mathbf{Y}_c is the conjugate of \mathbf{Y} . It also gives the following relationship:

$$\left(\frac{\partial \mathbf{X}_\phi^*}{\partial \mathbf{Y}}\right)_{\mathbf{X}_c} = \left(\frac{\partial \mathbf{X}}{\partial \mathbf{Y}_\phi^*}\right)_{\mathbf{Y}_c}.$$

Comparing partial derivatives of Massieu functions of one kind in column (5) of table 1, we get

$$\begin{aligned} \left(\frac{\partial S_H^*}{\partial S_E^*}\right)_T &= P\beta_T, & \left(\frac{\partial T_F^*}{\partial T_G^*}\right)_S &= \gamma P\beta_T, \\ \left(\frac{\partial V_E^*}{\partial V_F^*}\right)_P &= -\frac{C_P}{S}, & \left(\frac{\partial P_H^*}{\partial P_G^*}\right)_V &= \frac{C_V}{S}. \end{aligned} \quad (20)$$

Here, C_P and C_V are heat capacities at constant P and V , respectively, β_T is the compressibility at constant T and γ is the adiabatic coefficient. From this equation, we get the following relationships between conjugate pairs of Massieu functions:

$$\left(\frac{\partial T_F^*}{\partial T_G^*}\right)_S = \gamma \left(\frac{\partial S_H^*}{\partial S_E^*}\right)_T, \quad \left(\frac{\partial V_E^*}{\partial V_F^*}\right)_P = -\gamma \left(\frac{\partial P_H^*}{\partial P_G^*}\right)_V.$$

Equation (20) with the relationship $S_E^* - S_H^* = S_\alpha^*$ gives

$$\left(\frac{\partial S_\alpha^*}{\partial S_E^*}\right)_T = 1 - \beta_T P, \quad \left(\frac{\partial S_\alpha^*}{\partial S_H^*}\right)_T = \frac{1}{\beta_T P} - 1.$$

7. Massieu functions and statistical mechanics

Entropy S is given by $S = k_B \ln \Omega_s$, where the choice of Ω_s depends on whether S is defined as Gibbs entropy or Boltzmann entropy. For Gibbs entropy, it represents the number of eigenstates for a given energy. For Boltzmann entropy, Ω_s denotes density of states [9]. Massieu functions can also be expressed in terms of statistical parameters. Helmholtz free energy F is related to partition function Z by the following relationship: $F = -k_B T \ln Z$ [15]. Hence, Massieu–Planck potential $S_E^* = -F/T$ is related to the partition function as

$$S_E^* = k_B \ln Z.$$

Also, for homogeneous systems, the grand potential is related to the grand canonical partition function \mathcal{Z} . Using this, we can write S_α^* as

$$\Phi_G = -PV = -k_B T \ln \mathcal{Z} \Rightarrow S_\alpha^* = k_B \ln \mathcal{Z}.$$

From eq. (18), we have $S_E^* - S_H^* = S_\alpha^*$ and using $G = -TS_H^*$ we can write

$$S_H^* = k_B \ln \frac{Z}{\mathcal{Z}}, \quad G = -k_B T \ln \frac{Z}{\mathcal{Z}}.$$

Then, enthalpy H and internal energy E can be written as

$$H = k_B T \ln \frac{\Omega_s \mathcal{Z}}{Z}, \quad E = k_B T \ln \frac{\Omega_s}{Z}.$$

The amount of change in entropy during constant T & V and T & P can be defined as $-E/T$ and $-H/T$, respectively.

$$S'_E = -\frac{E}{T} = k_B \ln \frac{Z}{\Omega_s}, \quad S'_H = -\frac{H}{T} = k_B \ln \frac{Z}{\Omega_s \mathcal{Z}}.$$

Massieu entropy functions defined in eq. (12) can be written in similar forms:

$$S_V^* = k_B \ln \frac{\Omega_s}{\mathcal{Z}}, \quad S_P^* = k_B \ln \Omega_s \mathcal{Z}.$$

Hence, Massieu functions related to pressure and volume can easily be expressed using definitions from table 1:

$$\begin{aligned} PV_F^* &= k_B T \ln \frac{\mathcal{Z}}{Z}, & P_G^* V &= k_B T \ln Z \\ PV_E^* &= k_B T \ln \frac{\Omega_s \mathcal{Z}}{Z}, & P_H^* V &= k_B T \ln \frac{Z}{\Omega_s}. \end{aligned}$$

Similarly, Massieu temperature functions can be expressed as

$$ST_G^* = k_B T \ln \frac{\Omega_s \mathcal{Z}}{Z}, \quad ST_F^* = k_B T \ln \frac{\Omega_s}{Z}.$$

Thus, we can determine Massieu functions from microscopic statistical functions.

Governing macroscopic functions for systems with constant (E, V, N) is $S = k_B \ln \Omega_s$, energy is E and for systems with constant (T, N, V) , macroscopic functions is F . Similarly, for systems with constant (T, μ, V) , it is Φ_B . To this, we can add entropy S_E^* and S_α^* as governing macroscopic functions corresponding to F and Φ_B , respectively. Thus, we have governing entropy potentials in addition to energy potentials for all conditions. These combinations, along with respective statistical function, are (Ω_s, E, S) , (Z, F, S_E^*) and $(\mathcal{Z}, \Phi_B, S_\alpha^*)$. Statistical functions Ω_s , Z and \mathcal{Z} are given by $\exp(-S/k_B)$, $\exp(-S_E^*/k_B)$ and $\exp(-S_\alpha^*/k_B)$, respectively.

Energy and entropy potentials given here in terms of statistical mechanics functions can be written in the following general forms:

$$\mathcal{E}_g = k_B T \ln \Psi_g, \quad \mathcal{S}_g = k_B \ln \Psi_g,$$

where \mathcal{E}_g and $\mathcal{S}_g = \mathcal{E}_g/T$ represent energy potential and entropy potential, respectively. Ψ_g represents different functions of statistical parameters Z , \mathcal{Z} and Ω_s .

8. Massieu functions for the ideal gas

Internal energy (for monoatomic ideal gas) and pressure of an ideal gas are given by $E = (3/2)Nk_B T$ and $P = (2/3)E/V$. Hence, for a given state, we can assign values to Massieu functions T_F^* and P_H^* (see table 1) for a given state.

Entropy of an ideal gas is given by Sackur–Tetrode equation [15]

$$\frac{S}{k_B N} \cong \lambda_s + \frac{5}{2}, \quad \lambda_s = \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right], \quad (21)$$

where V is the volume of the gas, N is the number of particles in the gas, E is the internal energy of the gas, m is the mass of a gas particle, h is the Planck’s constant. Using this definition, we can easily derive expressions for H , F and G for an ideal gas. Then, we can determine Massieu functions given in table 1:

$$P_H^* = -\frac{3}{2}P, \quad P_G^* = (\lambda_s + 1)P$$

$$V_E^* = \frac{5}{2}V, \quad V_F^* = -\lambda_s V$$

$$T_G^* = \frac{\frac{5}{2}T}{\lambda_s + \frac{5}{2}}, \quad T_F^* = \frac{\frac{3}{2}T}{\lambda_s + \frac{5}{2}}.$$

Thus, P_H^* is always negative and V_E^* is always positive. Other functions can be negative too under certain conditions. Massieu entropy functions S_H^* and S_E^* can also be derived for one mole of an ideal gas:

$$S_E^* = R(\lambda_s + 1), \quad S_H^* = R\lambda_s. \quad (22)$$

Therefore, we have $S_E^* - S_H^* = R$, which is analogous to $C_P - C_V = R$. Heat capacity and entropy have the same physical dimension. It is clear that all Massieu functions can be written in the following form:

$$\mathbf{X}_\phi^* = \Lambda_i \mathbf{X},$$

where \mathbf{X}_ϕ^* is the Legendre transformation with respect to ϕ and Λ_i are various functions of λ_s . Similarly, all the energy potentials can be expressed as functions of λ_s and E .

9. Characteristics of S_α^*

Two Massieu entropy functions defined in eqs (13) and (15) are $S_\alpha^* = PV/T$ and $S_\beta^* = -PV/T$. Massieu entropy function S_α^* is mentioned in ref. [3] as a third-order Massieu function $\phi^{(3)}$. However, no specific physical interpretation was assigned to it. It is clear that S_α^* describes the state of a thermodynamic system in a single parameter. Evaluation of S_α^* is straightforward

because it depends directly on measurable parameters P , V and T . Therefore, a single parameter S_α^* can be used to model the behaviour of solid, gas and liquid. Equation (13) can be seen as energy balance between a w -potential (PV) and a q -potential ($S_\alpha^* T$):

$$PV = S_\alpha^* T.$$

Entropy function S_α^* can be related to the compressibility factor that describes the deviation from ideal gas behaviour. The compressibility factor Z_c for the real gas is given by

$$Z_c = \frac{PV}{nRT}.$$

Using this relationship, we can write entropy S_α^* for one mole of gas as

$$S_\alpha^* = RZ_c. \quad (23)$$

Therefore, entropy S_α^* is a measure of deviation from the ideal behaviour for real gases. As $Z < 1$ describes strong interactions between gas molecules, $S_\alpha^* < R$ also describes the same. Similarly, $S_\alpha^* > R$ describes larger extended volume. It may be recalled that S_α^* is the Legendre transformation of $S(U_\alpha, P, V, T)$ with respect to U_α . In other words, S_α^* is a Legendre transformation to curve $S = S(U_\alpha)$ for a fixed set of parameters P, V, T . Further, S_α^* is related to S_E^* and S_H^* as $S_E^* - S_H^* = S_\alpha^*$. Massieu entropy function S_E^* is related to a condition where T and V are constants and, S_H^* is related to the condition where T and P are constants. This also implies that S_α^* is related to a condition in which P, V, T are constants. Hence, when P, V, T are constants, then, $S_\alpha^*(S, U_\alpha)$ represents the effect of S on the system (recall $U_\alpha = TS - PV$). When other parameters are fixed, S can only change due to internal changes in system. The internal changes in the isolated system, under such conditions, can only occur due to the interaction among the molecules present in the system. Thus, S_α^* solely depends on interactions among molecules for a given set of parameters. In gaseous molecules, molecular interactions are characterised by the compressibility factor Z_c . This confirms the connection between S_α^* and Z_c .

The change in S_α^* when system goes to state 2 from state 1 is

$$\Delta S_\alpha^{*(1 \rightarrow 2)} = S_\alpha^{*(2)} - S_\alpha^{*(1)} = \frac{P_2 V_2}{T_2} - \frac{P_1 V_1}{T_1}.$$

This equation indicates that ΔS_α^* associated with a cyclic process is zero.

For n moles of an ideal gas, we have $PV = nRT = Nk_B T$. Hence, S_α^* for an ideal gas is

$$S_\alpha^{*(id)} = nR = Nk_B. \quad (24)$$

Thus, S_α^* for an ideal gas is constant for all the thermodynamical states. Clearly, for change in entropy S_α^* associated with change in thermodynamic state is zero, that is, $\Delta S_\alpha^{*(id)} = 0$, for a fixed composition. On the other hand, entropy S associated with change in the state of an ideal gas is not zero [16].

According to eq. (24), Boltzmann's constant can be expressed as $k_B = S_\alpha^{*(id)}/N$. Hence, k_B is the entropy S_α^* of a single element exhibiting ideal gas behaviour. Ideal gas constant R represents the entropy of one mole of ideal gas. An earlier observation by Dunkel and Hilbert [9] related Boltzmann constant to the total heat capacity when entropy is taken as Gibbs' entropy and viewed as minimal heat reservoir. Further, entropy is given by $S = Nk_B \ln \Omega_s = S_\alpha^{*(id)} \ln W$; k_B is the entropy of a single element times logarithm of all possible microstates in a given system. The numerical value of $S_\alpha^{*(id)}$ is approximately equal to the Sackur–Tetrode constant S_0/R but opposite in sign. The value of S_0/R is ≈ -1.151707 at 100 kPa pressure under standard conditions [17]. The value of S_0/R has the same sign as $S_\beta^{*(id)}$.

If we represent S_α^* as a function of T and P , variational form of S_α^* can be written in terms of compressibility and coefficient of thermal expansion. The partial derivatives of S_α^* can be written as

$$\left(\frac{\partial S_\alpha^*}{\partial P}\right)_T = \frac{V}{T} + \frac{P}{T} \left(\frac{\partial V}{\partial P}\right)_T = S_\alpha^* \left[\frac{1}{P} - \beta_T\right],$$

$$\left(\frac{\partial S_\alpha^*}{\partial T}\right)_P = -\frac{PV}{T^2} + \frac{P}{T} \left(\frac{\partial V}{\partial T}\right)_P = S_\alpha^* \left[-\frac{1}{T} + \alpha_V\right].$$

Here, β_T is the isothermal compressibility and α_V is the coefficient of volumetric isothermal expansion. From these equations we can write

$$\frac{dS_\alpha^*}{S_\alpha^*} = \left[\frac{1}{P} - \beta_T\right] dT + \left[-\frac{1}{T} + \alpha_V\right] dP.$$

10. Entropy S_α^* for real gas

Thus, using entropy S_α^* , the equation of state can be interpreted as a balance between mechanical work and heat. Hence, equation of state (EOS) can be written as

$$\frac{PV}{T} = S_\alpha^*.$$

The ideal gas behaviour, as explained above, is described by the constant value of S_α^* for all the thermodynamic states. For real gas, liquids and solids, S_α^* is not constant and varies with the variation in P , V , T . Entropy S_α^* for real gases can be described using equations of states such as van der Waals equation [18]. For one mole of

van der Waals gases, S_α^* is

$$S_\alpha^{*(Waals)} = R \left[\frac{V}{V-b} - \frac{a}{RVT} \right],$$

where the terms have their usual meaning according to the commonly used form of van der Waals equation. Point of inflections on S_α^* curves can be determined by setting $(\partial S_\alpha^*/\partial V) = 0$ at constant T . This gives two values for volume at a given temperature $V = b/(1 \pm \lambda_0)$, where $\lambda_0^2 = RbT/a$. However, only one of these values, $V = b/(1 - \lambda_0)$ gives a positive value for S_α^* for which S_α^* is minimum. Further, the positive value of S_α^* exists only for $\frac{1}{2} \leq \lambda_0 < 1$ and is given by

$$(S_\alpha^*)_{\min} = R \left[\frac{2}{\lambda_0} - \frac{1}{\lambda_0^2} \right].$$

For example, for Ar gas, we have $a = 1.3360 \text{ atm} \cdot \text{l}^2/\text{mol}^2$ and $b = 0.03201 \text{ l/mol}$ [19]. This gives $\lambda_0 \approx 0.044\sqrt{T}$. Then, $\frac{1}{2} \leq \lambda_0 < 1$ approximately translates to $130 \leq T < 520 \text{ K}$. So, for $T = 400 \text{ K}$, we get volume $V \approx 1.45 \text{ l/mol}$ for the minimum value of $S_\alpha^* \approx 0.981R$. The corresponding pressure can be obtained using the van der Waals EOS.

For Redlich–Kwong EOS [20], the expression for S_α^* is

$$S_\alpha^* = R \left[\frac{V}{V-\bar{b}} - \frac{\bar{a}}{RT^{3/2}(V+\bar{b})} \right],$$

where \bar{a} and \bar{b} are constants associated with Redlich–Kwong EOS. The point(s) of inflection for this equation can similarly be found.

Expression of S_α^* for virial EOS is [21]

$$S_\alpha^{*(virial)} = R \left[1 + \frac{A}{V} + \frac{B}{V^2} + \dots \right],$$

where A , B etc. are virial coefficients. Theoretically, the second and third virial coefficients represent interaction potentials among molecules [21]. This supports the previous explanation that S_α^* is a representative of molecular interactions.

11. Entropy of mixing

Consider two identical ideal gases in two compartments separated by a diaphragm. Then, it is trivial that the change in entropy $\Delta S_\alpha^{*(m)}$ when two gases are mixed by removing diaphragm is zero, according to eq. (24). Now, if we re-insert the diaphragm again to restore the original volume of each compartment, it is obvious that the associated ΔS_α^* with this process is also zero.

For two non-identical gases with N molecules in each compartment, it can be easily shown that $\Delta S_\alpha^{*(m)}$ associated with mixing is zero. Again, if the diaphragm is re-inserted again to make the compartments with the original volumes, it can be easily shown that $\Delta S_\alpha^{*(m)} = 0$. This is despite the fact that when the diaphragm is re-inserted, the distribution of non-identical gases in compartments will not be the same as the original one due to mixing.

This implies that entropy S_α^* does not differentiate between identical and non-identical ideal gases, as is evident from the definition of S_α^* . This is intuitive because the ideal gas equation $PV = Nk_B T$ is the same for all gases. Further, as S_α^* depends only on the number of moles of an ideal gas, thermodynamic parameters P , V and T do not affect entropy change during mixing for fixed compositions. That is, the mixing process mentioned here need not be isobaric and/or isothermal.

It may be mentioned that the changes in entropy S is given by [16]

$$S = Nk_B \ln V + \text{const.} \tag{25}$$

According to this equation, changes in entropy are non-zero and equal ($= 2Nk_B \ln 2$, for constant P and T) for both identical and non-identical mixing of ideal gases [16]. On the other hand, according to the Sackur–Tetrode equation, ΔS is zero for identical gases and equal to $2Nk \ln 2$ (for constant P and T) for non-identical gases [16].

It is clear from eq. (22) that Massieu entropy functions S_E^* and S_H^* behave analogous to entropy S expressed by Sackur–Tetrode equation for mixing of identical and non-identical ideal gases. For entropy S defined by eq. (25), change in entropy during mixing of both identical and non-identical gases will be $2Nk_B \ln 2$, as explained already.

For Massieu entropy functions $S_V^* = S - S_\alpha^*$ and $S_P^* = S + S_\alpha^*$, the change in entropy during mixing will be the same as that of S because $\Delta S_\alpha^{*(m)} = 0$ as explained already. Here too, the actual values depend on the definition of S taken into consideration.

For mixing of two liquids at constant P and T , the change in S_α^* is given by

$$\Delta S_\alpha^{*(m)} = \frac{P}{T} (V_{\text{mix}} - V_1 - V_2),$$

where V_1 and V_2 are volumes of two liquids before mixing and V_{mix} is the volume of the resultant solution. For ideal solutions, $V_{\text{mix}} = V_1 + V_2$. Hence, $\Delta S_\alpha^{*(m)} = 0$. If $V_{\text{mix}} \neq V_1 + V_2$, then, $\Delta S_\alpha^{*(m)} < 0$ when molecules of two different liquids attract each other ($V_{\text{mix}} < V_1 + V_2$) and $\Delta S_\alpha^{*(m)} > 0$ when molecules of two different liquids

repel each other ($V_{\text{mix}} > V_1 + V_2$). This further implies that entropy S_α^* depends on molecular interactions.

12. Summary

Massieu functions represent Legendre transformation of independent variables (or natural variables) with respect to energy potentials ϕ and other independent variables. These functions are derived using more than one method. It is shown that a Massieu function represents the total change in systems subjected to a finite change under different conditions. For example, entropy $S_H^* = -G/T$ is usually interpreted as the total entropy change in a system and its surroundings [22]. This is directly connected to the corresponding changes in energy potentials.

Massieu functions enable the representation of energy potentials as conjugate pairs of thermodynamic natural variables and corresponding Massieu functions. This way, energy potentials can be expressed either as w -potentials (work potentials) or q -potentials (heat potentials), as described in table 1. Several thermodynamic relationships involving Massieu functions are derived. Maxwell relationships containing Massieu functions are similar to that followed by natural variables. The partial derivative of a Massieu function with respect to the corresponding conjugate natural variable (that is, of \mathbf{X}_ϕ^* with respect to \mathbf{X}_c) represents Gibbs–Helmholtz relationships. Further, partial derivatives of column (5) of table 1 represent equilibrium conditions and are identical to that showed by natural variables. Similarly, the representation of natural variables as partial derivatives is also identical for natural variables and Massieu functions. It is proved that partial derivatives of energy potentials ϕ with respect to the natural variables \mathbf{X} can be expressed either as \mathbf{X}_c or \mathbf{X}_c^* , where \mathbf{X}_c is the conjugate of \mathbf{X} and \mathbf{X}_c^* is one of its Massieu functions.

Relationships between Massieu functions and statistical functions are derived and it is demonstrated that Massieu entropy functions are governing parameters under different conditions. It is also shown that each entropy function, including Massieu entropy function, is associated with a different statistical function.

It is interesting to note that Massieu entropy functions S_E^* and S_H^* for ideal gas are related by $S_E^* - S_H^* = R$, analogous to $C_P - C_V = R$. Extending the Legendre transformation, it is also possible to derive Massieu functions with no potential energy terms in their definitions, unlike those defined in table 1. Such functions can also be represented as a total change in systems when one of the energy potentials is kept constant. Analyses of the Massieu functions lead to the introduction of two

thermodynamic energy potentials, viz. $U_\alpha = TS - PV$ and $U_\beta = TS + PV$.

When we apply Legendre transformation to natural variables in dU_α , we get new Massieu functions that represent the ratio of a conjugate pair to a non-conjugate variable. These functions can also be viewed as the total change in systems where energy transfer takes place in terms of ΔU_α and ΔU_β . For example, entropy $S_\alpha^* = PV/T$ is one such function. Also, S_α^* is a state function and is zero for a cyclic process. This function was derived earlier. However, no significant physical description was attempted.

It is shown that for homogeneous systems, S_α^* is equal to $-\Phi_G/T$, where Φ_G is the grand potential. Entropy function S_α^* is related to other entropy functions S_E^* and S_H^* as $S_E^* - S_H^* = S_\alpha^*$ and $S_E^* - S_H^* = S_\alpha^* = R$ for an ideal gas. It is also evident from the definition $S_\alpha^* = PV/T$ that for n moles of an ideal gas, we have $S_\alpha^* = nR = Nk_B$. It implies that gas constant R is the entropy S_α^* of one mole of an ideal gas. Consequently, Boltzmann constant k_B is entropy S_α^* of a single element of an ideal gas. Dunkel and Hilbert had shown that k_B is related to the total heat capacity C [9]. Therefore, it can be inferred that the heat capacity is related to entropy S_α^* . This is also implied from the relation $S_\alpha^* = R = C_P - C_V$.

Entropy S_α^* of mixing of indistinguishable and distinguishable ideal gases is zero. This is expected as molecular interactions are not taken into account while deriving the ideal gas equation. Therefore, $S_\alpha^* = PV/T = nR$ remains constant for all the thermodynamic states of the ideal gases. This also means that for an ideal gas, entropy S_α^* is independent of the size of the system and depends only on the amount of ideal gas.

The EOS can be expressed as $PV/T = S_\alpha^*$ and, this expression can be interpreted as energy balance as $PV = S_\alpha^* T$. For real gas, S_α^* is related to compressibility factor Z_c as $S_\alpha^* = RZ_c$. Thus, it can be inferred that S_α^* depends on interaction among molecules. EOS such as van der Waals can be expressed in terms of S_α^* and minimum value of the same can be derived. The possibility of the existence of minimum value of S_α^* dependence on parameter λ_0 is defined as $\lambda_0^2 = RbT/a$.

When an isolated system of internal energy E is mechanically and heat coupled to another system, its energy becomes $G = E - (TS - PV) = E - U_\alpha$, where components $\mathbb{Q} = TS$ and $\mathbb{W} = PV$ are related to heat and mechanical energy, respectively. When energy due to heat transfer is equal to mechanical work associated with the system, we have $G = E$, that is, the internal energy of the system remains constant. It corresponds to the maximum possible mechanical work associated with systems. This also implies that $TS = PV \Rightarrow S = PV/T = S_\alpha^*$; entropy S is equal to S_α^* when the amount of heat and work exchange are equal for closed sys-

tems. For systems of ideal gases, this is equal to gas constant $S = S_\alpha^* = R$. Further, when $TS = PV$, $S_V^* = (TS - PV)/T = 0$.

Acknowledgements

PMA would like to express his gratitudes to Prof. T R S Prasanna for making thermodynamics so enjoyable. A graduate course on Metallurgical Thermodynamics taught by him was a major driving force behind this investigation.

References

- [1] Herbert B Callen, *Thermodynamics and an introduction to thermostatistics*, 2nd edn (Wiley, New York, 1985) p. 151
- [2] L Pogliani, *J. Chem. Educ.* **78**, 680 (2001), <https://doi.org/10.1021/ed078p680>
- [3] P G Debenedetti, *J. Chem. Phys.* **85**, 2132 (1986), <https://doi.org/10.1063/1.451105>
- [4] T Wada and A M Scarfone, *Phys. Lett. A* **335**, 351 (2005), <https://doi.org/10.1016/j.physleta.2004.12.054>
- [5] J A Scheilman, *Biophys. J.* **73**, 2960 (1997), [https://doi.org/10.1016/S0006-3495\(97\)78324-3](https://doi.org/10.1016/S0006-3495(97)78324-3)
- [6] A M Scarfone, H Matsuzoe and T Wada, *Entropy* **20**, 436 (2018)
- [7] R R Netz, *Phys. Rev. E* **101**, 022120 (2020)
- [8] Richard Courant and David Hilbert, *Methods of mathematical physics: Partial differential equations* (Wiley, New York, 2008) Vol 2, ISBN: 978-3-527-61724-1
- [9] J Dunkel and S Hilbert, *Nat. Phys.* **10**, 67 (2014), <https://doi.org/10.1038/nphys2815>
- [10] S Braun, J P Ronzheimer, M Schreiber, S S Hodgman, T Rom, I Bloch and U Schneider, *Science* **339**, 52 (2013), <https://doi.org/10.1126/science.1227831>
- [11] S Lokanathan and R S Gambhir, *Statistic and thermal physics: An introduction* (Prentice-Hall of India Pvt. Ltd., New Delhi, 1991) p. 61
- [12] David R Gaskell, *Introduction to metallurgical thermodynamics*, 2nd edn (Taylor & Francis Inc., London, 1981)
- [13] Erno Keszei, *ChemTexts* **2**, 14 (2016)
- [14] I M Klotz and R M Rosenber, *Chemical thermodynamics: Basic concepts and methods*, 7th edn (Wiley, New York, 2008)
- [15] S Nagata, *Chem. Phys.* **504**, 8 (2018), <https://doi.org/10.1016/j.chemphys.2018.02.001>
- [16] R H Swendsen, *Am. J. Phys.* **74**, 187 (2006), <https://doi.org/10.1119/1.2174962>
- [17] 2018 CODATA Value: Sackur-Tetrode constant, The NIST Reference on Constants, Units and Uncertainty, NIST <https://physics.nist.gov/cgi-bin/cuu/Value?s0sr>

- [18] Yaşar Demirel, *Nonequilibrium thermodynamics*, 2nd edn (Elsevier, Amsterdam, 2007) p. 22
- [19] http://www2.ucdsb.on.ca/tiss/stretton/database/van_der_waals_constants.html
- [20] O Redlich and J N S Kwong, *Chem. Rev.* **44**, 233 (1949), <https://doi.org/10.1021/cr60137a013>
- [21] J Wiebke, P Schwerdtfeger, G E Moyano and E Pahl, *Chem. Phys. Lett.* **514**, 164 (2011), <https://doi.org/10.1016/j.cplett.2011.08.024>
- [22] L E Strong and H F Halliwell, *J. Chem. Educ.* **47**, 347 (1970), <https://doi.org/10.1021/ed047p347>