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## **Viscosity, Thermal Conductivity and Thermal Diffusion Ratio of the Alkali Metal Vapours**

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### **ABSTRACT**

The Subcommittee of Transport Properties of IUPAC started in 1982 a project with the objective of correlating and predicting the transport properties of the alkali metal vapours, in the temperature and pressure zones that are useful to the scientific and industrial uses.

In a recent paper [1] the authors suggested a new approach to assess the available experimental data, based in the kinetic theory of gas mixtures, which is a modification of the method developed by Vargaftik and Yargin[2].

In the present communication, we present the surfaces for the viscosity and thermal conductivity, and thermal diffusion ratio which have been developed for lithium, sodium and potassium with average uncertainties of 1%, 0.5% and 0.5%, respectively, for temperature ranges 800-2000 K (lithium) and 700-1500 K (sodium and potassium).

For rubidium and cesium, the available data does not allow a similar development of the corresponding surfaces. It is interesting to note that no clear evidence for the presence of dimers was found for cesium within experimental uncertainty.

### **INTRODUCTION**

The need to have a reliable source of data for the transport properties of the alkali metal vapours has been explained in three previous papers. In Part I [3], we dealt with the theoretical calculation of the second virial, self-diffusion, viscosity and thermal conductivity coefficients of the monatomic alkali metal vapours, and in Part

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I.A [4] we actualised the data for the triplet ground state potentials and presented an analytical interpolation procedure for the calculation. In Part II [1] we have presented the treatment used to deal with the alkali metal vapours assuming that they behave as a reacting binary mixtures of monomers and dimers.

With the present paper, we have used the full theory previously presented [1,3-4] in order to generate plots for the viscosity, thermal conductivity and thermal diffusion ratio for the vapours of lithium ( $800 \leq T \leq 2000$ ,  $p \leq 0.8$  MPa), sodium ( $700 \leq T \leq 1500$ ,  $p \leq 1.0$  MPa) and potassium ( $700 \leq T \leq 1500$ ,  $p \leq 1.5$  MPa).

The average uncertainty of the plots are 1% for lithium, 0.5% for sodium and potassium. The tables generated will be presented elsewhere [5].

## THE MODEL

We assume that the alkali metal vapours consist of a binary mixture of monomers and dimers, with a temperature and pressure dependent composition.

The model has already been presented and discussed in detail in a previous paper [1]. We present here only the final expressions and the information needed to construct the surfaces presented. The theory uses the first order Chapman-Enskog solution of the Boltzmann equation for a gaseous binary mixture together with the Stogryn and Hirschfelder approximation for a reacting mixture.

### - Viscosity

$$\eta^*(y_D) = \frac{\eta(y_D, T)}{[\eta_M]_1} = \frac{1 + Z_\eta}{X_\eta^* + Y_\eta^*} \quad (1)$$

where,

$$Z_\eta = \frac{3}{5} A_{MD}^* \left\{ \frac{1}{2} y_M^2 + 2 y_M y_D \left[ \frac{3\sqrt{3}}{4} (\beta_{12}^{-2} + \frac{1}{\sqrt{2}} \beta_1^{-2}) - 1 \right] + 2 y_D^2 \right\}$$

$$X_\eta^* = X_\eta [\eta_M]_1 = y_M^2 + \sqrt{3} y_M y_D \beta_{12}^2 + \frac{1}{\sqrt{2}} y_D^2 \beta_2^2$$

$$Y_\eta^* = Y_\eta [\eta_M]_1 = \frac{3}{5} A_{MD}^* \left( \frac{1}{2} y_M^2 + \frac{3\sqrt{3}}{2\sqrt{2}} y_M y_D \beta_1^{-2} + \sqrt{2} y_D^2 \beta_2^2 \right).$$

- Thermal conductivity

$$\lambda^*(y_D, T) = \lambda_{tr}^*(y_D) + \lambda_{int}^*(y_D, T) + \lambda_r^*(y_D, T) \quad (2)$$

a) Translational: 
$$\lambda_{tr}^*(y_D) = \frac{\lambda(y_D, T)}{[\lambda_M]_I} = \frac{1 + Z_\lambda}{X_\lambda^* + Y_\lambda^*} \quad (3)$$

with

$$Z_\lambda = y_M^2 W^{(1)} + 2y_M y_D W^{(z)} + y_D^2 W^{(2)},$$

$$X_\lambda^* = X_\lambda [\lambda_M]_I = y_M^2 + \frac{4}{\sqrt{3}} y_M y_D \beta_{12}^2 + \sqrt{2} y_D^2 \beta_2^2,$$

$$Y_\lambda^* = Y_\lambda [\lambda_M]_I = y_M^2 W^{(1)} + \frac{4}{\sqrt{3}} y_M y_D W^{(y)} \beta_{12}^2 + \sqrt{2} y_D^2 W^{(2)} \beta_2^2,$$

$$W^{(1)} = \frac{4}{15} A_{MD}^* - \frac{1}{10} B_{MD}^* + \frac{5}{24},$$

$$W^{(2)} = \frac{4}{15} A_{MD}^* - \frac{2}{5} B_{MD}^* + \frac{1}{12},$$

$$W^{(y)} = \frac{9}{20\sqrt{2}} A_{MD}^* \beta_{12}^{-2} \beta_1^{-2} - \frac{1}{12} \left( \frac{12}{5} B_{MD}^* + 1 \right) - \frac{5}{64 A_{MD}^*} \left( \frac{12}{5} B_{MD}^* - 5 \right),$$

$$W^{(z)} = \frac{4}{15} A_{MD}^* \left[ \frac{9\sqrt{3}}{8\sqrt{2}} \left( \frac{1}{\sqrt{2}} \beta_{12}^{-2} + \beta_1^{-2} \right) - 1 \right] - \frac{1}{12} \left( \frac{12}{5} B_{MD}^* + 1 \right).$$

b) Internal: 
$$\lambda_{int}^* = \frac{\lambda_{int}}{[\lambda_M]_I} = \frac{2\sqrt{2}}{25R} \frac{A_D^* (C_{v,D}^{rot} + C_{v,D}^{vib})}{\beta_2^2 + \frac{\sqrt{2} A_D^* y_M}{\sqrt{3} A_{MD}^* y_D} \beta_{12}^2} \quad (4)$$

c) Chemical Reaction: 
$$\lambda_r^* = \frac{\lambda_r}{[\lambda_M]_I} = \frac{2\sqrt{3}}{25} A_{MD}^* \left( \frac{\Delta H^0(T)}{RT} \right)^2 \frac{y_M y_D}{(1 + y_D)^2} \beta_{12}^{-2} \quad (5)$$

- Thermal diffusion ratio

$$[k_T]_I = \frac{y_M y_D}{3\sqrt{3}} \beta_{MD}^2 \frac{S_1 y_M - S_2 y_D}{X_\lambda^* + Y_\lambda^*} (6C_{MD}^* - 5) \quad (6)$$

$$S_1 = \frac{3\sqrt{3}}{8} \beta_{12}^{-2} - \frac{15}{4A_{MD}^*} - 1 \quad (7)$$

$$S_2 = \frac{3\sqrt{3}}{2\sqrt{2}} \beta_1^{-2} + \frac{15}{8A_{MD}^*} - \frac{5}{2} \quad (8)$$

The variables of these calculations are: the molar composition of the mixture ( $y_M, y_D$  respectively, for monomer and dimer);  $A_j^*, B_j^*$  and  $C_j^*$  (where  $j=M, D, MD$ ) are the ratio of the collision integrals proposed by the kinetic theory [4,6] taken as independent of the type of interaction, i.e.,  $A_M^* = A_D^* = A_{MD}^*$ ,  $B_M^* = B_D^* = B_{MD}^*$  and  $C_M^* = C_D^* = C_{MD}^*$  [1] and  $\beta_1^2, \beta_2^2$  and  $\beta_{12}^2$  are given in table I.

$C_{v,D}^{rot}$  and  $C_{v,D}^{vib}$ , the rotational and vibrational contributions for the molar heat capacity of the dimers are given, respectively, by equations (9) and (10),

$$C_{v,D}^{rot} = R \quad (9)$$

$$C_{v,D}^{vib} = R \left( \frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2} \quad (10)$$

where  $\theta_v$  is the characteristic vibrational temperature given for each metal in table I;  $\Delta H^0(T)$ , the standard enthalpy of reaction is given by equation (11),

$$\Delta H^0(T) = \Delta H_0^0 + A T + B T^2 + C T^3 \quad (11)$$

with the parameters displayed in table II. The procedure used to obtain the parameters A, B and C is described in reference [6].

TABLE I - PARAMETERS NEEDED IN THE APPLICATION OF EQUATIONS (1) TO (10) [6].						
Metal	$\beta_1^2$	$\beta_2^2$	$\beta_{12}^2$	$\frac{\theta_v}{K}$		
Lithium	1.19	1.58	1.88	505.58		
Sodium	0.87	1.25	1.09	228.93		
Potassium	1.18	1.39	1.64	132.40		

TABLE II - PARAMETERS NECESSARY TO APPLY EQUATION (11) [6].

Metal	$\frac{\Delta H_0^0}{\text{kJ mol}^{-1}}$	$\frac{A}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{B \times 10^3}{\text{J K}^{-2} \text{mol}^{-1}}$	$\frac{C \times 10^6}{\text{J K}^{-3} \text{mol}^{-1}}$
Lithium	107.8	9.945835	-6.634476	1.864750
Sodium	71.38	7.711819	-5.631470	1.652149
Potassium	53.8	3.939518	-1.732501	1.804059

## CALCULATIONS

By applying equations (1) to (11) with the parameters defined in tables I and II the transport properties surfaces for lithium, sodium and potassium can be generated; the results obtained are shown in figures (1) to (9). For lithium the surface was calculated for  $800 \text{ K} < T < 2000 \text{ K}$  and pressures below  $0.8 \text{ MPa}$  with an average uncertainty of 1%. For sodium the temperature range used was between  $700 \text{ K}$  and  $1500 \text{ K}$  with the pressure being less than  $0.4 \text{ MPa}$ , resulting an uncertainty of 0.5%, while for potassium, the temperature range was between  $700 \text{ K}$  and  $1500 \text{ K}$  with pressures smaller than  $1.0 \text{ MPa}$  and the surface has an uncertainty of 0.5 %.

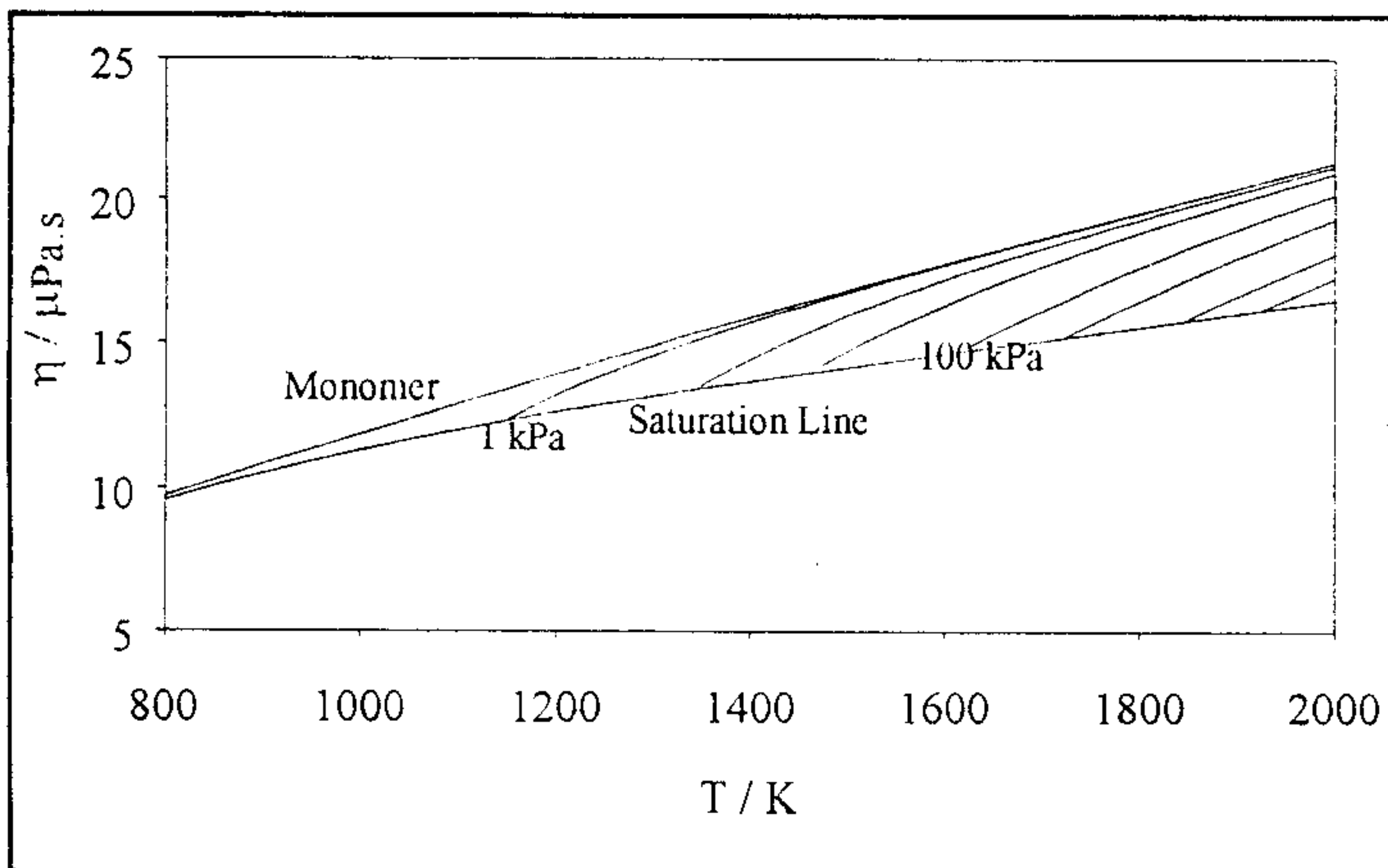


Figure 1 - Surface  $n_0T$  for the lithium vapour

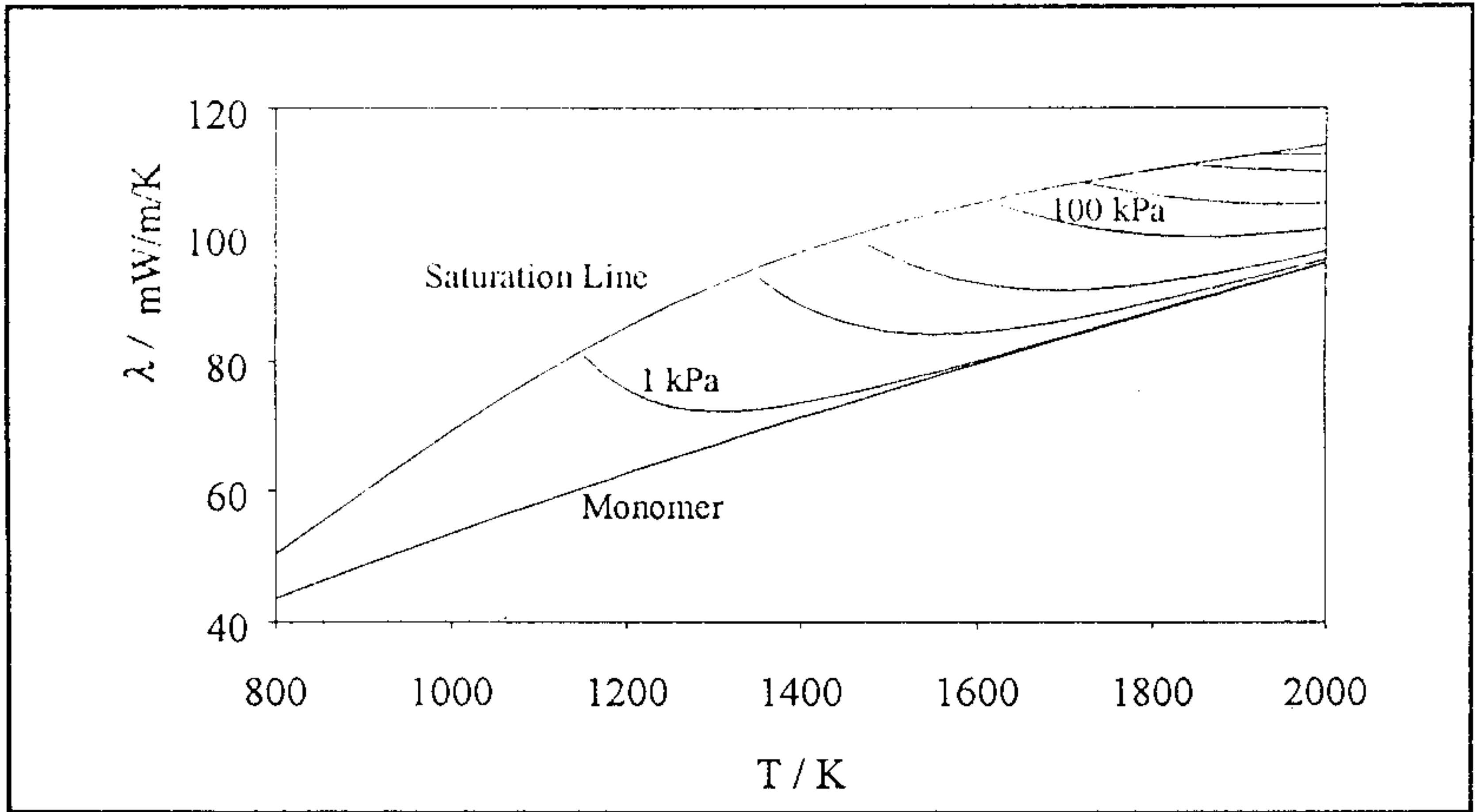


Figure 2 - Surface  $\lambda\rho T$  for the lithium vapour.

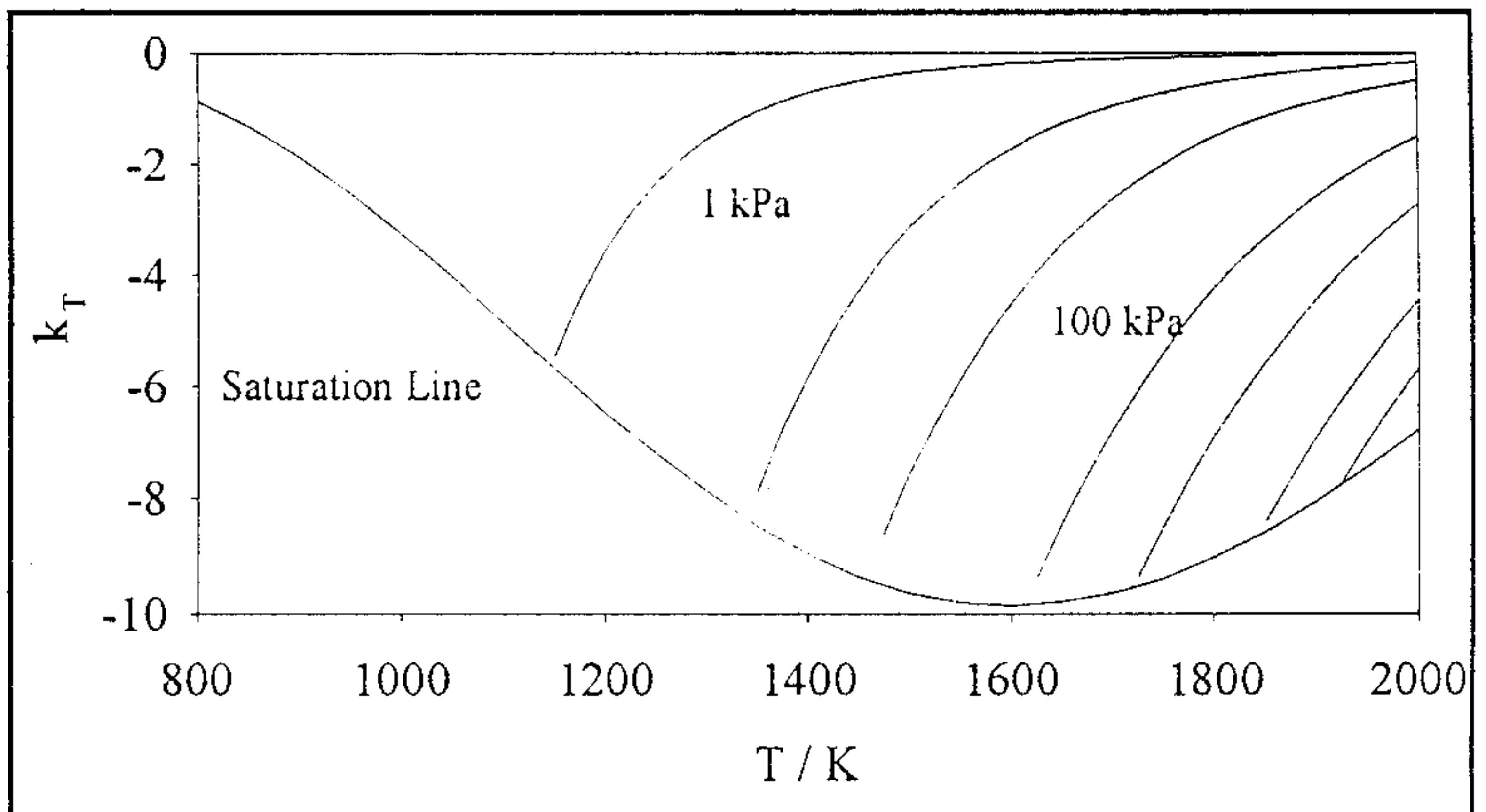


Figure 3 - Surface  $k_T\rho T$  for the lithium vapour.

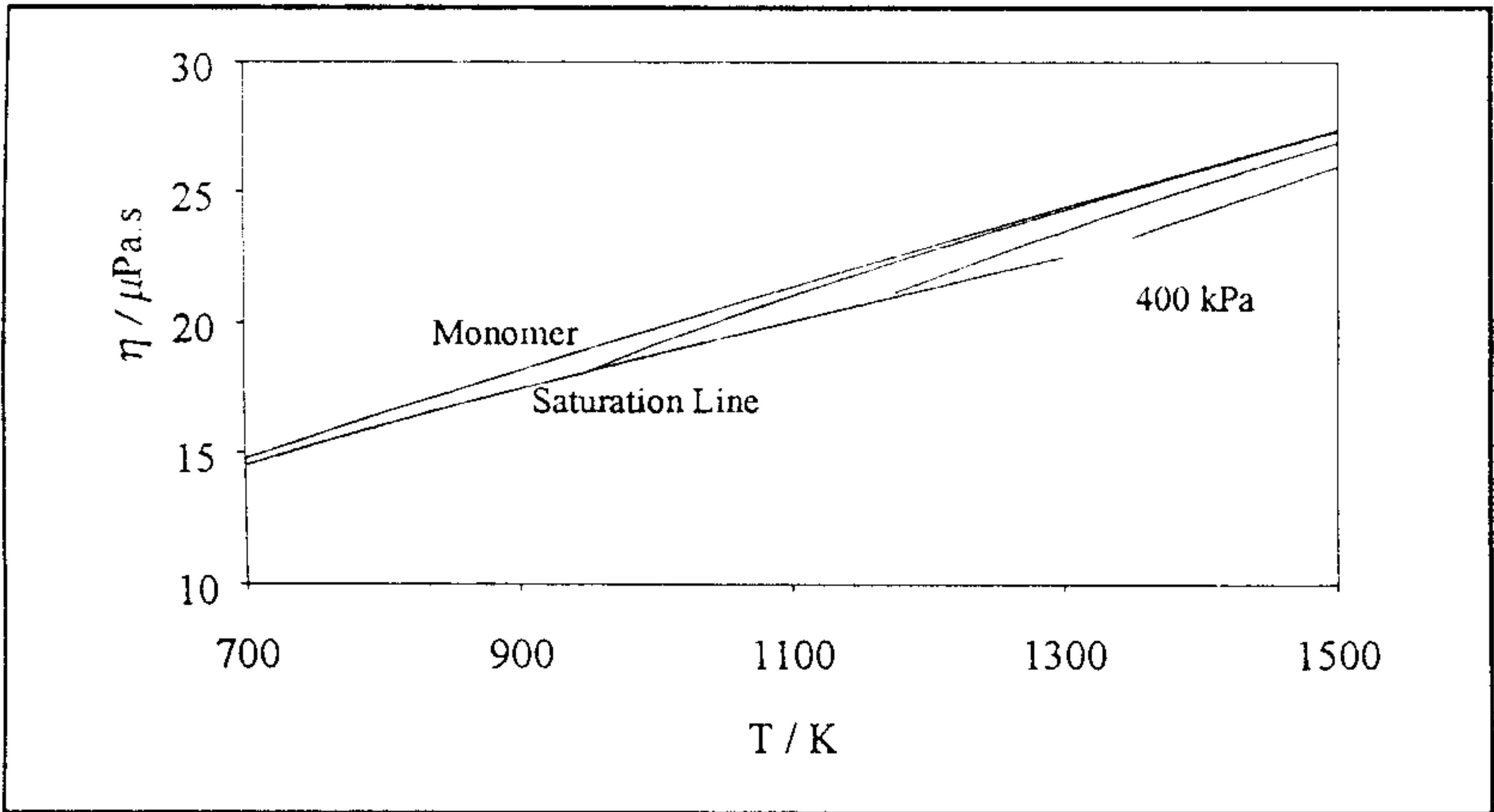


Figure 4 - Surface  $\eta\rho T$  for the sodium vapour.

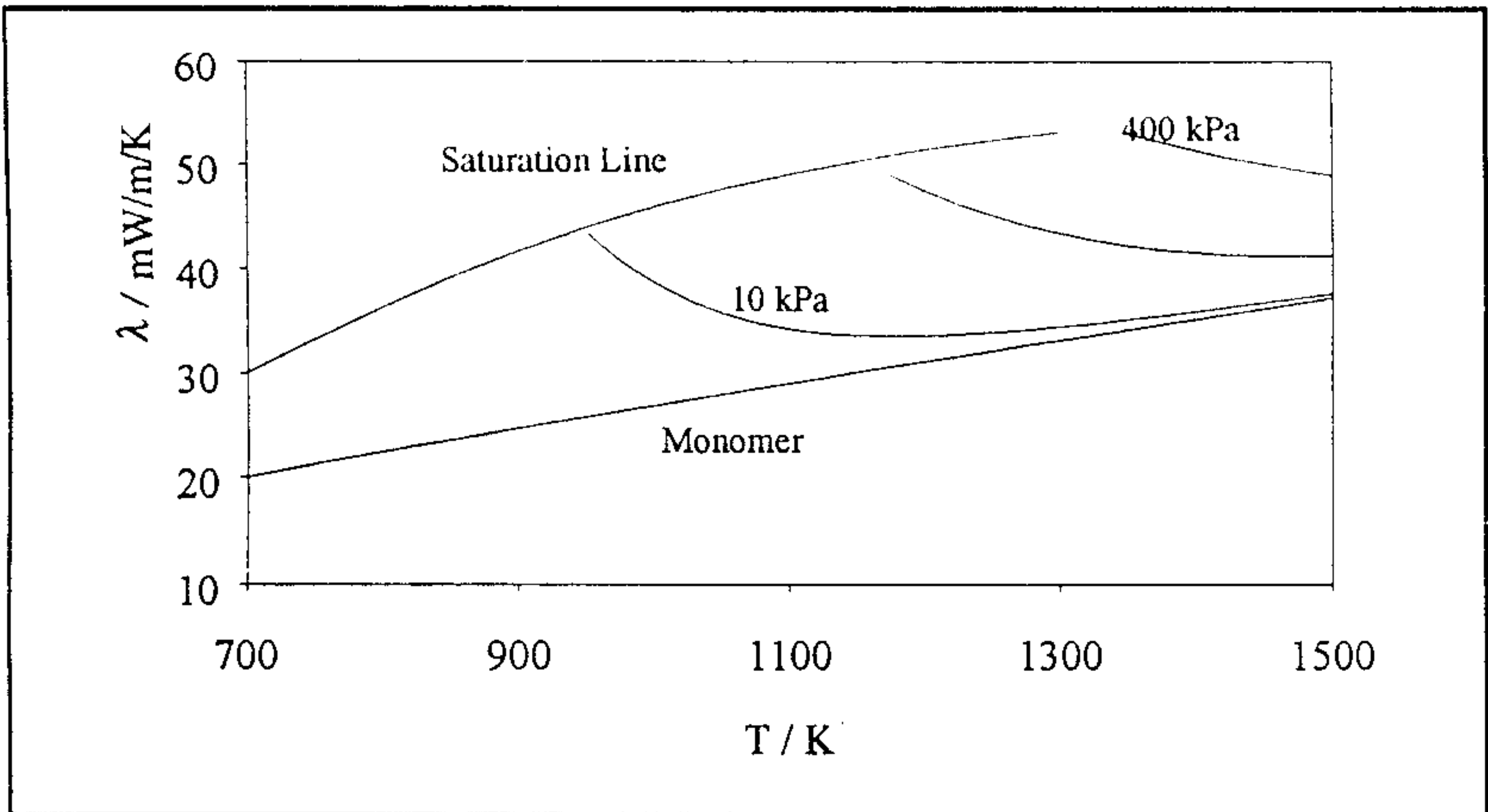


Figure 5 - Surface  $\lambda\rho T$  for the sodium vapour.

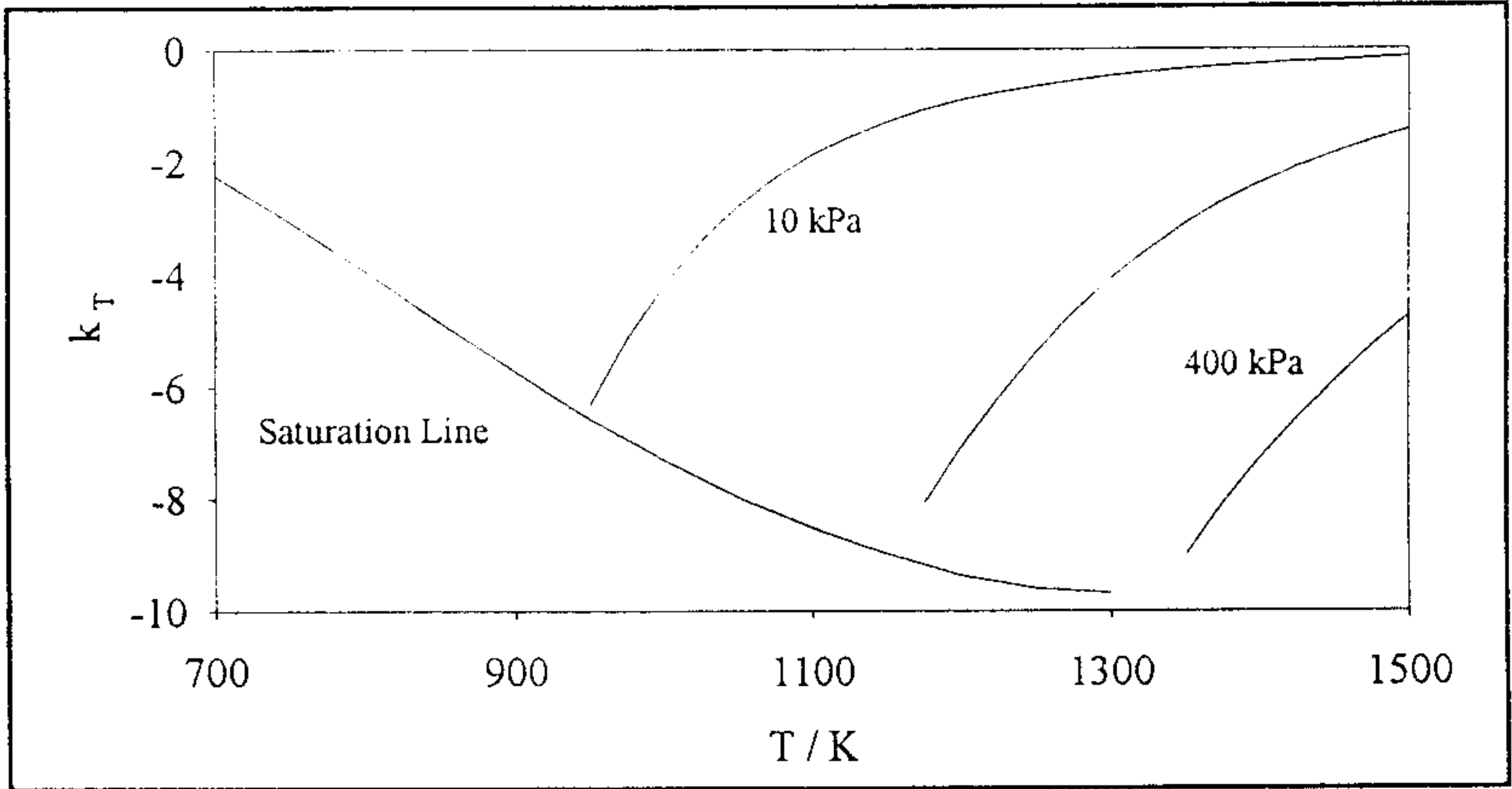


Figure 6 - Surface  $k_T\rho T$  for the sodium vapour.

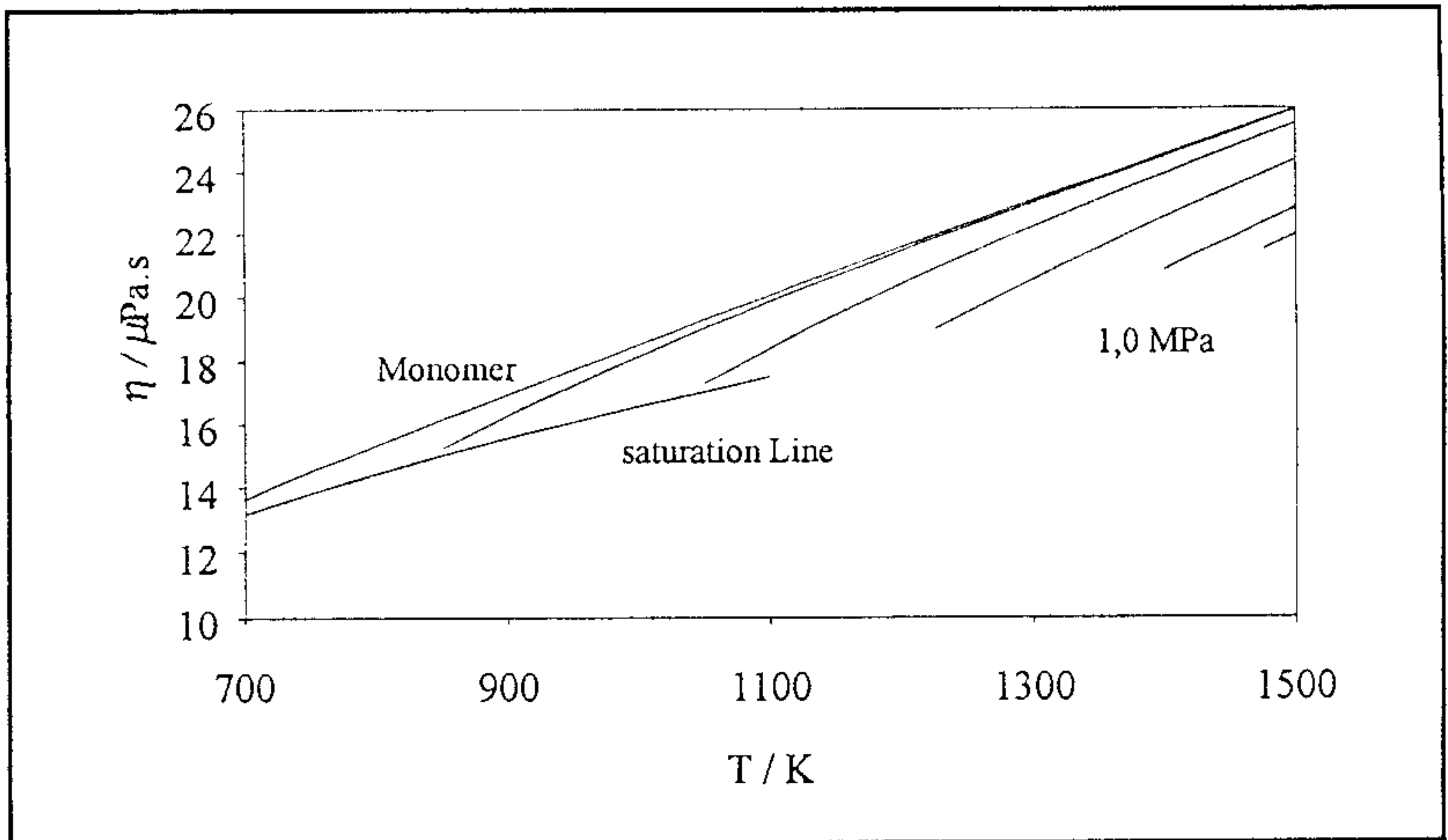


Figure 7 - Surface  $\eta\rho T$  for the potassium vapour.

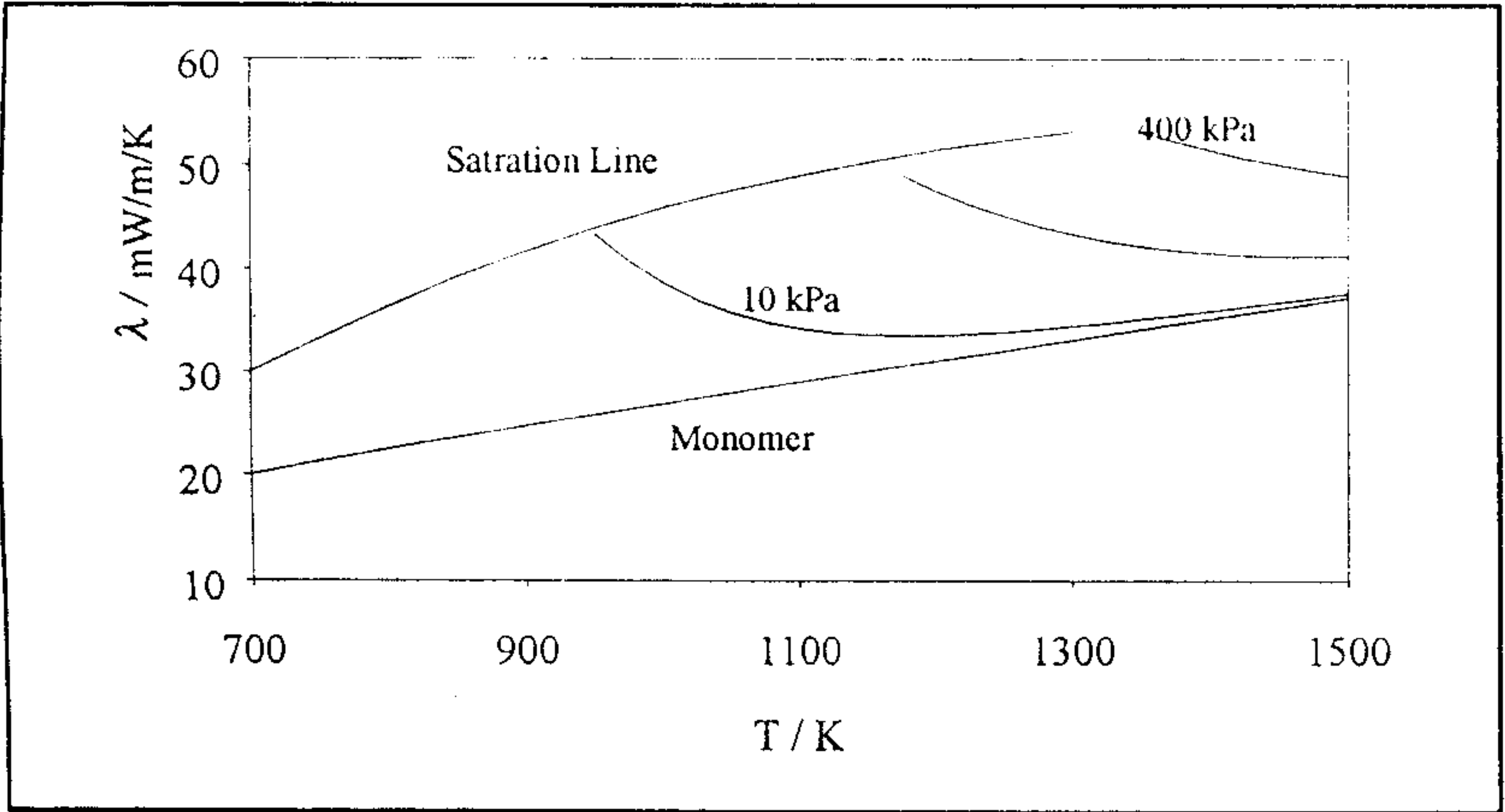


Figure 8 - Surface  $\lambda\rho T$  for the potassium vapour.

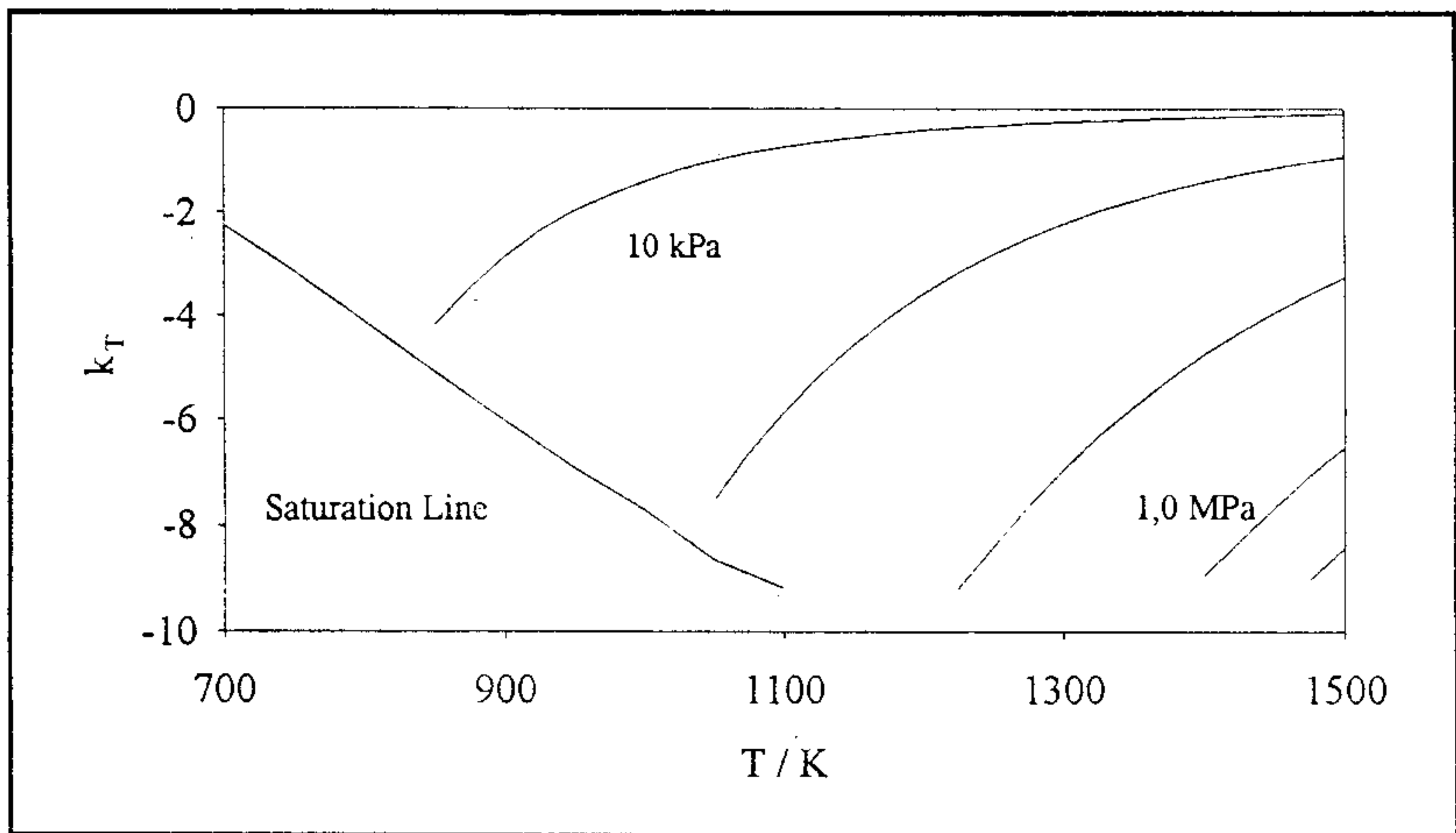


Figure 9 - Surface  $k_T\rho T$  for the potassium vapour.

## CONCLUSIONS

The surfaces herein presented are considered to be the best available representation of the transport properties of the alkali metal vapours. Their determination has been based on sound theoretical models, the only restriction being the present unavailability of the collision integrals for the monomer-dimer and dimer-dimer interactions. A complete discussion of the models can be found in reference [1].

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