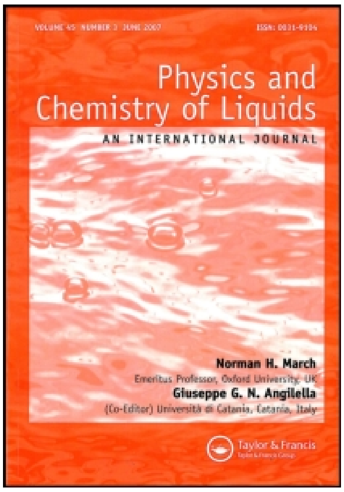

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VISCOSITY RELAXATION IN MOLTEN HgZnTe

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Rotating cup measurements of the viscosity of the pseudo-binary melt, HgZnTe have shown that the isothermal liquid with ZnTe mole fraction 0.16 requires tens of hours of equilibration time before a steady viscous state can be achieved. Over this relaxation period, the viscosity at 790°C increases by a factor of two, while the viscosity at 810°C increases by 40%. Noting that the Group VI elements tend to polymerize when molten, we suggest that the viscosity of the melt is enhanced by the slow formation of Te atom chains. To explain the build-up of linear Te n-mers, we propose a scheme, which contains formation reactions with second-order kinetics that increase the molecular weight, and decomposition reactions with first-order kinetics that inactivate the chains. The resulting rate equations can be solved for the time dependence of each molecular weight fraction. Using these molecular weight fractions, we calculate the time dependence of the average molecular weight. Using the standard semi-empirical relation between polymer average molecular weight and viscosity, we then calculate the viscosity relaxation curve. By curve fitting, we find that the data imply that the rate constant for n-mer formation is much smaller than the rate constant for n-mer deactivation, suggesting that Te atoms only weakly polymerize in molten HgZnTe. The steady-state toward which the melt relaxes occurs as the rate of formation of an n-mer becomes exactly balanced by the sum of the rate for its deactivation and the rate for its polymerization to form an $(n+1)$-mer.

Keywords: Pseudo-binary melt; Linear Te n-mers; Rate equations; Transport

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1. INTRODUCTION

Because of their narrow electronic band-gap, HgZnTe solid solutions have been proposed as effective detectors for infrared radiation [1]. To produce the best single crystals of these materials for this application, knowledge of the phase diagram that governs the freezing of the liquid is essential [2]. Besides the phase diagram, however, some information concerning the thermophysical properties of the melt, such as viscosity, density, specific heat, and enthalpy of mixing, can also be useful [3,4]. Of these thermophysical properties, the viscosity, is perhaps of the most interest scientifically. Measurements using the oscillating cup method [5,6] have shown that the isothermal melt requires tens of hours of equilibration time before a steady value of the viscosity can be achieved [3]. Over this equilibration time, which depends upon temperature, the viscosity can increase by as much as a factor of two before reaching a steady-state. We suggest that this relaxation phenomenon may be due to a slight polymerization of Te atoms in the melt.

The Group VI elements, S and Se, are famous for their many allomorphs [7]. Orthorhombic sulfur, which has the formula S_8, is the stable form at room temperature. This allomorph melts at 113°C to form a yellow red liquid [8]. Above 159°C, the viscosity of the liquid begins a rapid increase due to the conversion of S_8 rings into long chains, which may contain as many as 100,000 sulfur atoms [9]. Above 200°C, the chains begin to break up, however, and the viscosity of sulfur returns to a normal value [10]. Polymeric selenium can be prepared in a similar fashion, and both polymeric sulfur and polymeric selenium appear to form chains by a free radical mechanism [8].

By contrast, the viscosity of liquid Te is more like that of normal liquids [11], and the reality of polymeric Te in the liquid state has been the subject of some debate. The existence of a twofold coordinated chain structure in solid tellurium, on the other hand, is well documented [12]. Noting that the atomic coordination number of a Te atom in the melt lies between 2 and 3, Cabane and Friedel argued that the chain structure does not continue into the liquid [11]. Tsuzuki *et al.*, however, have recently studied the structure of the liquid near the freezing point using EXAFS and neutron inelastic scattering and report evidence for the existence of a twofold coordinated chain structure consisting of long and short covalent bonds [13]. They propose that a strong correlation between individual chains can account for a coordination number larger than 2. Electronic structure calculations also support their observations by suggesting that the chain structure of the solid is preserved upon melting [12,14].

To account for the time dependence of the viscosity in the HgZnTe melt, we propose that the liquid acts as a solvent that favors the formation of Te atom chains. We suggest that as the melt is cooled from a high temperature to the temperature for measurement of the viscosity, a free radical polymerization of Te atoms begins. As is the rule in the case of polymer solutions, the viscosity increases with increasing average molecular weight of the dissolved polymer [15].

Several molecular weight averages can be defined in the case of polymer solutions [16]. Colligative property measurements, for example, are sensitive to the number average molecular weight, while light scattering measurements depend upon the weight average molecular weight. The viscosity depends upon still another average molecular weight that is, nevertheless, close in numerical value to the weight average.

To estimate this average molecular weight, we use a simple free radical polymerization mechanism, including a depolymerization step, to calculate the time dependence to the concentration of each Te polymer molecular weight fraction. From these molecular weight fractions, we compute the weight average molecular weight of the distribution. Using the semi-empirical relation between average molecular weight and viscosity, we obtain a formula for the time dependence of the viscosity of the melt.

Upon examining this formula, we find that the viscosity achieves a steady value when a balance is achieved between the rate of formation of the chains and the rate of their depolymerization into species which do not affect the viscosity. This formula is fitted to the experimental viscosity measurements [3] carried out at temperatures 790 and 810°C, respectively, for the pseudo-binary HgZnTe melt with ZnTe mole fraction equal to 0.16. The comparison of the theory with experiment permits both the first-order rate coefficient for Te chain depolymerization and the pseudo first-order rate coefficient for Te atom chain formation to be evaluated as functions of temperature.

2. THEORY

We let η_0 be the Newtonian viscosity of the melt in the absence of Te atom chains. If $c\,\mathrm{g\,cm^{-3}}$ of Te polymer are created in the melt, the viscosity, η, is determined by the semi-empirical formula

$$\eta/\eta_0 = 1 + K\langle M\rangle^a c \tag{1}$$

where K is a constant, and "a" is an index that depends upon the shape of the dissolved macromolecules [15]. The value of "a" varies from $\frac{1}{2}$ for a random coil [15] to 2 for a rigid rod [17]. For a polymer that is not monodisperse, $\langle M\rangle$ is the "viscosity average" molecular weight [18] defined by

$$\langle M\rangle^a = \frac{\sum_{i=1}^{\infty} c_i M_i^{1+a}}{\sum_{i=1}^{\infty} c_i M_i} \tag{2}$$

In Eq. (2), M_i and c_i are the molar mass and concentration in mol cm^{-3} of the ith molecular weight fraction, respectively.

The elements, sulfur and selenium, polymerize to form helical chains, a structure intermediate between the random coil and the rigid rod. Without *a priori* knowledge of the structure of our proposed tellurium atom chains, we assume for mathematical convenience that $a = 1$. Making this assumption and noting that

$$c = \sum_{i=1}^{\infty} c_i M_i \tag{3}$$

we can substitute Eq. (2) into Eq. (1) to obtain

$$\eta/\eta_0 = 1 + K \sum_{j=1}^{\infty} c_i M_i^2 \tag{4}$$

Given a kinetic scheme for calculating the time dependence of the $\{c_i\}$, we can use Eq. (4) to evaluate the time dependence of the viscosity.

If M_1 is the atomic weight of a tellurium, the molar mass of a tellurium *j*-mer is $M_j = jM_1$. The lowest molecular weight polymer fraction is the dimer with $j = 2$; hence, Eq. (4) becomes

$$\eta/\eta_0 = 1 + KM_1^2 \sum_{j=2}^{\infty} j^2 c_j(t) \tag{5}$$

The next step is to compute $c_j(t)$ as a function of time.

Let symbol, (1), represent a single Te atom, (2) represent a dimer of Te atoms, and (*j*) a *j*-mer. We propose the following simple kinetic scheme for the polymerization of tellurium atoms:

$$\begin{array}{ccccccc} (1) & + & (1) & \rightarrow & (2) & \rightarrow & \text{inactive} \\ (1) & + & (2) & \rightarrow & (3) & \rightarrow & \text{inactive} \\ \vdots & & \vdots & & \vdots & & \vdots \\ (1) & + & (j-1) & \rightarrow & (j) & \rightarrow & \text{inactive} \end{array} \tag{6}$$

The second-order rate coefficient for the dimerization of two Te atoms is k''. Since the mechanism assumes the stepwise addition of single Te atoms, the rate coefficient for the formation of each succeeding *j*-mer is also k''. Once formed, however, we assume that each *j*-mer can also disappear into a form, which is inactive, so far as the viscosity is concerned. The first-order rate coefficient for this inactivation is k'. Since the HgZnTe melt is a pseudo-binary formed from the compounds HgTe and ZnTe [2], inactivation may result by the pseudo first-order reaction of a Te *j*-mer with metal atoms to reform the compounds, or in the case of the higher *j*-mers, by a first-order cyclization reaction to form Te rings. In any case, the essential role of the inactivation reaction is to prevent unbounded growth of the average molecular weight. To account for the time dependence of the viscosity, the average molecular weight should increase with time and approach a constant value asymptotically.

The concentration of tellurium (50 mol%) in the melt is so high that we can safely assume that little of the initial Te atom population is depleted as the *j*-mers form. For this reason, we can set $c_1(t) = c_1(0) = \text{constant}$. According to the kinetic scheme, the rate of formation of the dimer is thus the constant, $F = k''(c_1(0))^2$. The subsequent formation steps then become pseudo first-order with rate constant $k = k''c_1(0)$. Using this, notation, the rate equations governing the reactions in Eq. (6) are

$$\begin{aligned}
\frac{dc_2}{dt} &= F - (k + k')c_2 \\
\frac{dc_3}{dt} &= kc_2 - (k + k')c_3 \\
\vdots \qquad & \qquad \vdots \\
\frac{dc_j}{dt} &= kc_{j-1} - (k + k')c_j
\end{aligned} \tag{7}$$

We can reduce this system of differential equations to a system of algebraic equations by introducing Laplace transforms.

In the standard fashion [19] we define the Laplace transform, $\hat{c}_j(s)$, of the time function, $c_j(t)$, as

$$\hat{c}_j(s) = \int_0^\infty e^{-st} c_j(t)\, dt \tag{8}$$

Because it is the quenching of the melt that produces the conditions satisfactory for polymerization, we can assume that there is no j-mer present initially, and $c_j(0) = 0$ for all $j \geq 2$. After Laplace transformation, the system of Eq. (7) becomes

$$\begin{aligned}
(s + \lambda)\hat{c}_2(s) &= F/s \\
(s + \lambda)\hat{c}_3(s) &= k\hat{c}_2(s) \\
\vdots \qquad & \qquad \vdots \\
(s + \lambda)\hat{c}_j(s) &= k\hat{c}_{j-1}(s)
\end{aligned} \tag{9}$$

where we have defined

$$\lambda = k + k' \tag{10}$$

Equation (9) can be solved iteratively to obtain

$$\begin{aligned}\hat{c}_2(s) &= \frac{F}{s(s+\lambda)}\\ \hat{c}_3(s) &= \frac{kF}{s(s+\lambda)^2}\\ \vdots \qquad & \qquad \vdots\\ \hat{c}_j(s) &= \frac{k^{j-2}F}{s(s+\lambda)^{j-1}}\end{aligned} \tag{11}$$

Inverting these functions to the time domain [19], we find

$$c_j(t) = \frac{k^{j-2}F}{(j-2)!}\int_0^t d\tau\, \tau^{j-2} e^{-\lambda\tau}, \qquad j \geq 2 \tag{12}$$

For each value of j, the integral in Eq. (12) can be evaluated by parts. The results are summarized in Appendix A. A few examples of the functions that are obtained have been plotted in Fig. 1.

Closed forms for the functions, $c_j(t)$, are not required to evaluate the sum on the right hand side of Eq. (5), however. After substituting Eq. (12) into Eq. (5) and interchanging the integral and the sum, we obtain

$$\frac{\eta}{\eta_0} = 1 + KM_1^2F\left[\int_0^t d\tau\, e^{-\lambda\tau}\sum_{j=2}^{\infty}\frac{j^2}{(j-2)!}(k\tau)^{j-2}\right] \tag{13}$$

The integrand in Eq. (13) can be simplified as shown in Appendix B. The result is

$$\frac{\eta}{\eta_0} = 1 + KM_1^2F\int_0^t d\tau\big((k\tau)^2 + 5(k\tau) + 4\big)e^{-k'\tau} \tag{14}$$

The elementary integral that remains in Eq. (14) can be evaluated by parts to obtain

$$\begin{aligned}\eta/\eta_0 = 1 + \beta\big[(\alpha(2\alpha+5)+4) - (\alpha^2(k't)^2 + \alpha(2\alpha+5)(k't)\\ +\alpha(2\alpha+5)+4)e^{-k'\tau}\big]\end{aligned} \tag{15}$$

where we have set

$$\alpha = k/k' \tag{16}$$

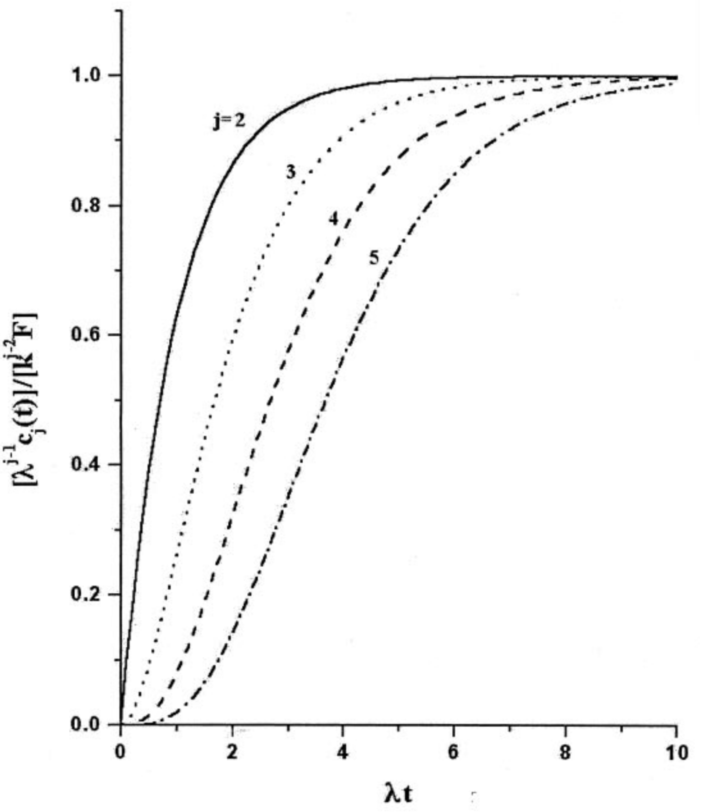

FIGURE 1 Plots of the functions defined by Eqs. (A.1)–(A.4).

and

$$\beta = FKM_1^2/k' \tag{17}$$

We define

$$\gamma = 2\alpha^2 + 5\alpha + 4 \tag{18}$$

Equation (15) can then be cast in the form

$$(\eta/\eta_0 - 1)/\beta\gamma = (1 - e^{-k't}) - (1/\gamma)(\alpha(2\alpha + 5) + \alpha^2(k't))(k't)e^{-k't} \tag{19}$$

According to Eq. (19), the viscosity relaxes with the specific rate, k', and reaches the limit $\eta_0(1+\beta\gamma)$ as t approaches infinity.

3. DISCUSSION

Figures 2 and 3 show Eq. (19) plotted for comparison with the experimental data. In making this comparison, we began by equating the viscosity of the unpolymerized melt, η_0, to the earliest (which was also the lowest) viscosity value in the data set. The numerical values of α, β, γ, and k' then were adjusted so as to obtain the best fit of

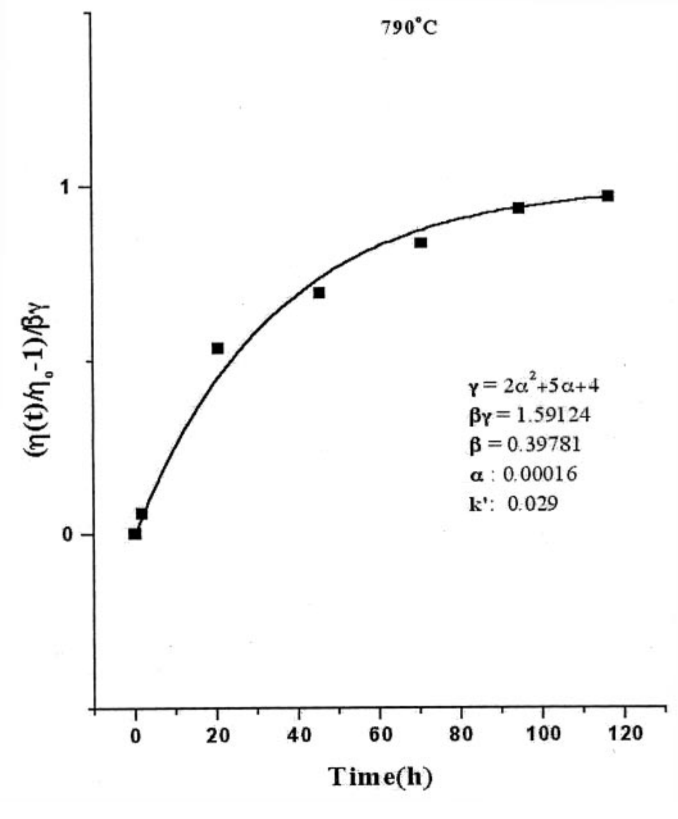

FIGURE 2 Curve fit of the function defined by Eq. (19) to the experimentally observed time dependence of the viscosity of molten HgZnTe at 790°C.

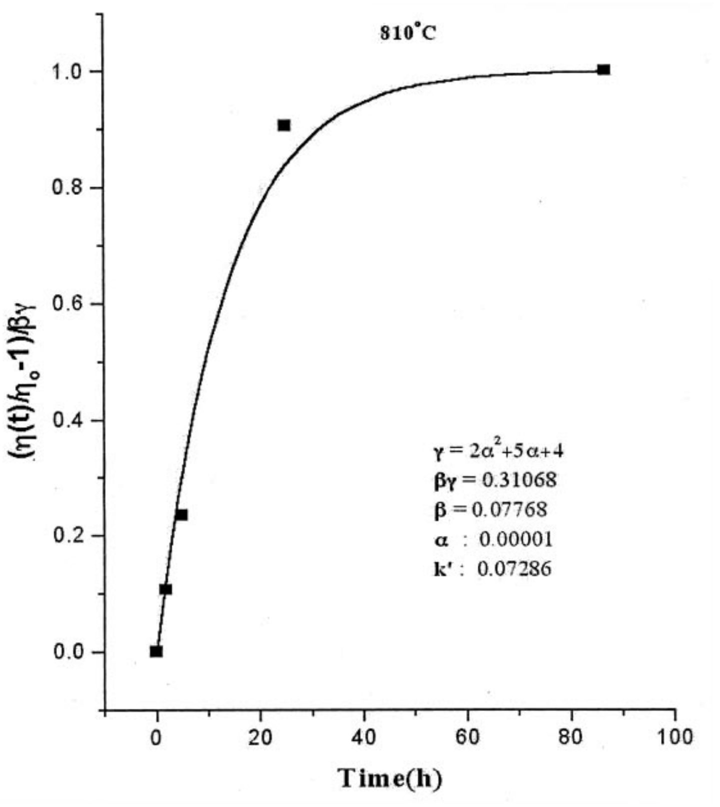

FIGURE 3 Curve fit of the function defined by Eq. (19) to the experimentally observed time dependence of the viscosity of molten HgZnTe at 810°C.

TABLE I Parameter values resulting from fitting Eq. (19) to HgZnTe viscosity data as shown in Figs. 2 and 3. The value of k was calculated using Eq. (16). The ZnTe mole fraction in the pseudo-binary melt was 0.16

T(K)	α (10^{-4})	β	($\gamma - 4$) (10^{-4})	k ($10^{-6}\,\mathrm{h}^{-1}$)	k' ($10^{-2}\,\mathrm{h}^{-1}$)
1063	1.6	0.40	8.2	4.6	2.9
1083	0.10	0.078	0.5	0.73	7.3

Eq. (19) to the time dependence of the data. The values of these parameters plus the derived parameter, k, are listed in Table I.

At both temperatures, the fit of Eq. (19) to the data dictated a very small value for α. This is because the existing data points form a curve which is everywhere concave down, whereas Eq. (19) evaluated for substantial values of α is slightly concave up at early times. Additional early time viscosity data need to be collected to search for the presence of this kind of curvature.

Every molecular weight fraction, $c_j(t)$, contributes to the final value of the viscosity. This follows as a consequence of the term, $1-\exp(-\lambda t)$, which approaches unity at long times and which appears in each of Eqs. (A.1)–(A.4). As the time approaches infinity, dc_j/dt goes to zero, and the rate of formation of a j-mer is just balanced by the sum of its rate of deactivation and its rate of polymerization to form a $(j+1)$-mer.

Since k is small, the values of k' and λ are nearly the same; hence, according to Eqs. (A.1)–(A.4), the ratio, $c_j(t)/c_2(t)$, becomes at long times equal to α^{j-2}. Because $\alpha \ll 1$, the steady-state concentration of the j-mer relative to that of the dimer decreases rapidly with j.

According to Table I, the value of k decreases with increasing temperature. Because k is only a *pseudo* first-order rate constant, however, it need not increase with increasing temperature, as otherwise would be expected for the rate constant for an elementary reaction. Indeed, since k is the product of an elementary rate constant, k'', and the Te atom concentration, $c_1(0)$, k can display a negative effective activation energy if $c_1(0)$ decreases for some reason with increasing temperature. This might occur, for example, if simultaneously, with polymerization, Te atoms were also involved in an endothermic equilibrium with Te atom rings. Ring structures are known, for example, in the case of sulfur and selenium [7]. Since Te is in Group VI, eight membered rings would be favored [20].

By contrast, k' is the rate coefficient for an elementary reaction. If we assume that k' satisfies the Arrhenius equation, $k' = A' \exp(-E'/RT)$, we can use the value of the gas law constant, R, and the two values of k' listed in the table to estimate the activation energy for destruction of a j-mer. We find $E' = 442\,\mathrm{kJ\,mol^{-1}}$. This value is somewhat larger than the double bond dissociation energy in gaseous Te [21]. Ignoring solvation effects, our estimate of E' may imply that deactivation step in Eq. (1) involves breaking of more than one bond joining Te atoms in the chain.

We note that the rotating cup method is directly sensitive to the kinematic viscosity, which is the ratio of the Newtonian viscosity to the mass density of the liquid [5,6]. In analyzing the data, we have used the ratio of the measured *kinematic* viscosities to represent the ratio of the *Newtonian* viscosities, which is required to evaluate the left hand side of Eq. (19). In doing so, we are assuming that the density of the melt is unaffected by the slight polymerization of the Te atoms.

These provisos not withstanding, the viscosity is one of the most sensitive measures of polymer molecular weight, and its determination is an accepted standard method for following the kinetics of polymerizing systems [22]. Thus a polymer kinetic explanation for the relaxation of viscosity in HgZnTe is not without plausibility.

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APPENDIX A

For the first few values of j, the integral in Eq. (12) can be evaluated by parts. The results are:

$$\frac{\lambda c_2(t)}{F} = 1 - e^{-\lambda t} \tag{A.1}$$

$$\frac{\lambda^2 c_3(t)}{kF} = \left(1 - e^{-\lambda t}\right) - (\lambda t)e^{-\lambda t} \tag{A.2}$$

$$\frac{\lambda^3 c_4(t)}{k^2 F} = \left(1 - e^{-\lambda t}\right) - \left(\frac{1}{2}(\lambda t) + 1\right)(\lambda t)e^{-\lambda t} \tag{A.3}$$

$$\frac{\lambda^4 c_5(t)}{k^5 F} = \left(1 - e^{-\lambda t}\right) - \left(\frac{1}{6}(\lambda t)^2 + \frac{1}{2}(\lambda t) + 1\right)(\lambda t)e^{-\lambda t} \tag{A.4}$$

APPENDIX B

In the sum in Eq. (13), we let $j = p + 2$. Upon expansion of the factor $(p+2)^2$,

$$\begin{aligned}&\int_0^t d\tau\, e^{-\lambda\tau} \sum_{p=0}^{\infty} (p+2)^2 \frac{(k\tau)^p}{p!} \\ &\quad = \int_0^t d\tau\, e^{-\lambda\tau} \left[\sum_{p=0}^{\infty} \frac{p^2 (k\tau)^p}{p!} + 4 \sum_{p=0}^{\infty} \frac{p (k\tau)^p}{p!} + 4 \sum_{p=0}^{\infty} \frac{(k\tau)^p}{p!} \right]\end{aligned} \tag{B.1}$$

The third sum within the bracket in Eq. (B.1) can be evaluated by recognizing the series expansion for the exponential function.

$$\sum_{p=0}^{\infty}\frac{(k\tau)^p}{p!}=e^{k\tau} \tag{B.2}$$

The second sum within the bracket can be evaluated by recognizing the exponential function and its first derivative. The computation is:

$$\sum_{p=0}^{\infty}\frac{p(k\tau)^p}{p!}=(k\tau)\sum_{p=0}^{\infty}\frac{p(k\tau)^{p-1}}{p!}=(k\tau)\frac{\partial}{\partial(k\tau)}e^{k\tau}=(k\tau)e^{k\tau} \tag{B.3}$$

Finally, the first sum within the bracket can be evaluated by recognizing the exponential function and its first two derivatives. The computation is:

$$\begin{aligned}\sum_{p=0}^{\infty}\frac{p^2(k\tau)^p}{p!}&=\sum_{p=0}^{\infty}\frac{p(p-1)(k\tau)^p}{p!}+\sum_{p=0}^{\infty}\frac{p(k\tau)^p}{p!}\\&=(k\tau)^2\frac{\partial^2}{\partial(k\tau)^2}e^{k\tau}+(k\tau)\frac{\partial}{\partial(k\tau)}e^{k\tau}\\&=(k\tau)^2e^{k\tau}+(k\tau)e^{k\tau}\end{aligned} \tag{B.4}$$

After substitution of Eqs. (B.2)–(B.4) into Eq. (B.1), we obtain the final result,

$$\int_0^t d\tau\, e^{-\lambda\tau}\sum_{p=0}^{\infty}(p+2)^2\frac{(k\tau)^p}{p!}=\int_0^t d\tau\big((k\tau)^2+5(k\tau)+4\big)e^{-k'\tau} \tag{B.5}$$

where we have used $\lambda=k+k'$.